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NOTATION

a = shape factor, cylinder = 1 and sphere = 2
C = heat capacity of solid
k = thermal conductivity of solid
L = latent heat of fusion
r = radial distance
R = interface position
t = time
T = temperature
U = overall heat transfer coefficient
ρ = density of solid or liquid, a constant

Superscript

$*$ = dimensionless variable

Subscripts

c = coolant
i = based on radius of inside wall
L = at melting point
m, n = number of radial and time increments
M = total number of radial increments

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A Generalized Differentiation Method for Interpreting Rheological Data of Time-Independent Fluids

J. A. LESCARBOURA, F. J. EICHSTADT, and G. W. SWIFT

University of Kansas, Lawrence, Kansas

A generalized differentiation method for analyzing rheological data of time-independent fluids is presented. The method is demonstrated to be valid and useful in analyzing rheological data and comparing such data obtained on the same time-independent fluid in rheometers of the capillary, annular, coaxial cylinder rotational, and falling cylinder types.

The interpretation of the rheological properties of time-independent fluids is most often approached in terms of the integration method, which requires that a particular ideal model be assumed a priori. Since the ideal models used for this purpose are empirical, one is limited in employing the integration method, since few real fluids are adequately represented by one ideal model over the entire range of shear rate that is of interest.

As pointed out by Savins et al. (*10*) the interpretation can be carried out in a more general manner by employing the differentiation method, which requires no a priori assumption regarding the appropriate rheological model. Instead, the relationship between shear stress and shear rate is expressed as

$$\dot{\gamma} = f(\tau) \tag{1}$$

In considering a particular rheometer, one obtains an integral equation that contains shear rate as expressed by Equation (1) and differentiates this equation with respect to one of the boundary conditions. The differential equation that results relates the kinematical and dynamical properties measured in the rheometer, for example, Q and ΔP in a capillary instrument, and the derivatives of these properties to the shear rate evaluated at the boundary $f(\tau_b)$. $f(\tau_b)$ can be computed from this expression after determining the derivatives from plots of experimental data and τ_b can be determined from a force balance. From the corresponding values of τ_b and $f(\tau_b)$ over the range of experimental data, one then determines the appropriate functional relationship. Apparently the differentiation method has not achieved widespread acceptance because of the difficulties experienced in determining the derivatives of the kinematical and dynamical properties measured in the rheometer. In addition to these difficulties, the formulation of the differentiation method for rheometers of complex geometry is somewhat obscure.

We present a generalized form of the differentiation method that utilizes the power law form proposed by Metzner and Reed (*7*) as an operator to systematize the method for determining the derivatives of the measured variables, and show that the generalized form is applicable to the capillary, rotational, annular, and falling cylinder rheometers.

DEVELOPMENT OF METHOD

The Capillary Rheometer

It has been demonstrated by several investigators (*8* to *10*) and summarized concisely by Wilkinson (*13*) that the differentiation method for interpreting rheological data in a capillary tube instrument of specified diameter requires only that: flow is laminar; there is no slip at the wall [Mooney (*8*) showed that this restriction can be eliminated if data from different capillary tubes are considered]; and the rate of shear at a point depends only on the shear stress, that is, Equation (1) applies. Then

$$Q/\pi R^3 = (1/\tau_R{}^3)\int_0^{\tau_R} \tau^2 f(\tau)\,d\tau \qquad (2)$$

The Rabinowitsch equation (*9*) is obtained by differentiating Equation (2) with respect to τ_R:

$$f(\tau_R) = 3Q/(\pi R^3) + \tau_R d[Q/(\pi R^3)]/d\tau_R \qquad (3)$$

where

$$\tau_R = R\Delta P/(2L) \qquad (4)$$

Metzner and Reed (*7*) rearranged the Rabinowitsch equation to obtain

$$\dot\gamma_R = f(\tau_R) = 3Q/(\pi R^3) + [Q/(\pi R^3)](d\{\ln[Q/(\pi R^3)]\}/d\{\ln[R\Delta P/(2L)]\}) \qquad (5)$$

Equation (5) can be simplified by defining

$$n' = d\{\ln[R\Delta P/(2L)]\}/d\{\ln[Q/(\pi R^3)]\} = d[\ln(\Delta P)]/d[\ln(Q)] \qquad (6)$$

Then, Equation (5) becomes

$$\dot\gamma_R = [(3n' + 1)/n'][Q/(\pi R^3)] \qquad (7)$$

which is the generalized differentiation method expression for the rate of shear in capillary rheometers in terms of volume rate of flow, pressure drop, and derivatives thereof. The derivative function n' is the slope of a logarithmic plot of ΔP vs. Q. Metzner and Reed state that n' characterizes the degree of non-Newtonian behavior of a fluid, and that it is very nearly constant over a wide range of shear rate for many non-Newtonian fluids. Equation (7), however, is valid even if n' varies markedly over the shear rate range. Thus, $\dot\gamma_R$ values computed from Equation (7) and the corresponding τ_R values computed from Equation (4) can be used to construct the flow curve for a fluid from data taken in a capillary instrument, making no a priori assumption regarding the rheological model.

It is of value to discuss the derivative function n' in more detail. Since n' is a constant for given values of ΔP and Q (assuming that capillary dimensions, fluid, temperature, etc., are fixed), Equation (6) can be integrated to give

$$\tau_R = C_1\,[Q/(\pi R^3)]^{n'} \qquad (8)$$

Combining Equations (7) and (8), one obtains

$$\tau_R = C_1\,[n'\dot\gamma_R/(3n' + 1)]^{n'} \qquad (9)$$

or, since n' is constant at a point

$$\tau_R = C_2\,(\dot\gamma_R)^{n'} = m'(\dot\gamma_R)^{n'} \qquad (10)$$

Equation (10) is universally applicable to all time-independent fluids for given values of ΔP and Q. If $n' = n =$ constant for all values of ΔP, then $m' = m =$ constant and Equation (10) reduces, as a special case, to the well-known power law model. The analogy between Equation (10) and the power law model suggests that the differentiation method for the interpretation of rheological data could be developed without going through the classical Rabinowitsch development, provided the power law integration form is available for the rheometer in question. The power law model would be used as an operator where the values of the derivative function n' would be used, together with the corresponding point values of Q and ΔP, in the power law integration form to determine $\dot\gamma_R$. To show that this is possible, consider the integrated power law model form given by Wilkinson (*14*), where n' and m' indicate that these parameters are constants only at specified values of Q and ΔP:

$$Q/(\pi R^3) = [n'/(3n' + 1)][R\Delta P/(2Lm')]^{1/n'} \qquad (11)$$

Combining Equations (11) and (4), one obtains

$$\tau_R = m'\{[(3n' + 1)/n'][Q/(\pi R^3)]\}^{n'} \qquad (12)$$

τ_R can be eliminated from Equation (12) by using Equation (10):

$$\dot\gamma_R = [(3n' + 1)/n'][Q/(\pi R^3)] \qquad (13)$$

Equation (13) is the same as Equation (7), which was obtained from the Rabinowitsch development by Metzner and Reed.

The Coaxial Cylinder Rotational Rheometer

The method developed above can be applied to the coaxial cylinder rotational rheometer to obtain the shear rate at either wall in terms of torque, rotational velocity, and the derivative function thereof. In this case, the integrated power law model form (*15*), where n' and m' indicate that these parameters are constants only at specified values of Ω and T, is

$$\Omega = \{n'/[2(m')^{1/n'}]\}[T/(2\pi L)]^{1/n'}[(1/R_i{}^2)^{1/n'} - (1/R_o{}^2)^{1/n'}] \qquad (14)$$

or

$$\ln(T) = n'[\ln(\Omega)] + C_3 \qquad (15)$$

Then, the derivative function, n', is

$$n' = d[\ln(T)]/d[\ln(\Omega)] = d[\ln(\tau_i)]/d[\ln(\Omega)] = d[\ln(\tau_o)]/d[\ln(\Omega)] \qquad 16)$$

since the shear stress at the inner and outer walls is given by

$$\tau_i = T/(2\pi LR_i{}^2) \qquad (17)$$

and

$$\tau_o = T/(2\pi LR_o{}^2) \qquad (18)$$

respectively. Combining Equations (10), (14), and (17) one gets

$$\dot\gamma_i = 2\Omega/[n'\,(1 - \kappa^{2/n'})] \qquad (19)$$

Combining Equations (10), (14), and (18), one obtains

$$\dot\gamma_o = 2\Omega/[n'\{(1/\kappa)^{2/n'} - 1\}] \qquad (20)$$

where, in Equations (19) and (20), $\kappa = R_i/R_o$. Equations (19) and (20) are the expressions for the shear rate at the inner and outer walls, respectively, of a coaxial cylinder rotational rheometer in terms of torque, rotational velocity, and their derivative function n'. As indicated by Equation (16), n' is the slope of a logarithmic plot of T

TABLE 1. THE RHEOLOGICAL PARAMETERS FOR THE BINGHAM PLASTIC AND ELLIS MODEL FLUIDS, THE DIMENSIONS OF THE RHEOMETERS, AND THE SOURCES FOR THE EQUATIONS USED TO GENERATE THE ARTIFICIAL DATA

Fluid model		Rheometer type: Capillary	Annular*	Falling cylinder	Coaxial cyl. rotational*
	Dimensions	$R = 0.0204$ cm. $L = 18.5$ cm.	$R = 1.270$ cm. $\kappa = 0.800$	$R = 1.269$ cm. $\kappa = 0.9501$	$R_o = 1.270$ cm. $\kappa = 0.800$
Bingham plastic	Rheological constants	$\mu_p = 8$ poise; $\tau_y = 26$ dyne/sq. cm.			
	Equation source	(14)	(3)	(2)	(15)
Ellis	Rheological constants	$\alpha = 1.7$; $\eta_o = 0.29$ poise; $\tau_{1/2} = 45.2$ dyne/sq. cm.			
	Equation source	(6)	(6)	(1)	(6)

* Unit length used.

vs. Ω. The expressions developed cannot be compared directly with those of Mooney (*8*) and others (*4, 11*), because their expressions are not in closed form. However, it can be shown that Equation (19) minus Equation (20) gives the equation Mooney used as a starting point for his differentiation method development:

$$\dot{\gamma}_i - \dot{\gamma}_o = (2\Omega/n')\{1/(1-\kappa^{2/n'}) - 1/[(1/\kappa)^{2/n'}-1]\} = 2\Omega/n' \quad (21)$$

Replacement of n' in Equation (21) by its value from Equation (16) gives

$$\dot{\gamma}_i - \dot{\gamma}_o = 2\Omega d[\ln(\Omega)]/d[\ln(\tau_i)] = 2\tau_i d\Omega/d\tau_i \quad (22)$$

or

$$d\Omega/d\tau_i = (\dot{\gamma}_i - \dot{\gamma}_o)/(2\tau_i) \quad (23)$$

which is the equation developed by Mooney for the coaxial cylinder rotational rheometer as a starting point for the development of the differentiation method. Thus, by using the proper operator, Equation (10), the Rabinowitsch equation for capillary rheometers and the Mooney equation for coaxial cylinder rotational rheometers can be obtained from the integrated power law model forms for the rheometers. Furthermore, the expressions for shear rate in the coaxial cylinder rotational viscometer, Equations (19) and (20), are in closed form and involve no assumptions beyond those specified in the first paragraph of the capillary development.

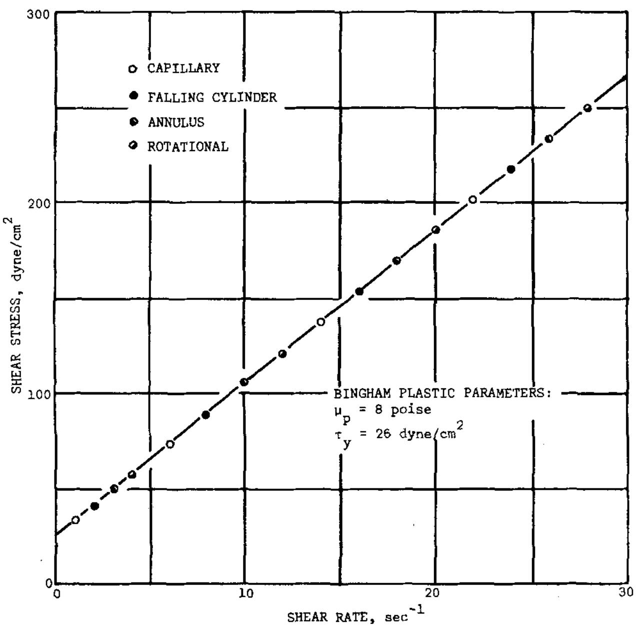

Fig. 1. The flow curve obtained for a Bingham plastic fluid by applying the generalized differentiation method to artificially generated data for four types of rheometers.

The Concentric Annulus Rheometer

Attempts to apply the differentiation method to flow in concentric annuli have been for the most part unsuccessful. Savins et al. (*10*) presented an equation for $f(\tau_R)$ that is based on the assumption that a narrow annulus can be approximated by parallel plates. Vaughn and Bergman (*12*) developed a method to relate capillary and concentric annulus flow data that has some of the characteristics of the differentiation method. Both methods are of limited application. The method we have developed can be applied to the concentric annulus to obtain the shear rate at either wall in terms of volume rate of flow, pressure drop, and the derivative function thereof. In this case, the integrated power law model form of Fredrickson and Bird (*3*), where $s' = 1/n'$ and m' indicate that these parameters are constants only at specified values of Q and ΔP, is

$$Q/(\pi R^3) = (1-\kappa)^{s'+2}[R\Delta P/(2Lm')]^{s'} [\Upsilon(s',\kappa)]/(s'+2) \quad (24)$$

where κ is the ratio of the outer radius of the inner cylinder to the inner radius of the outer cylinder and $\Upsilon(s',\kappa)$ is a tabulated function in the Fredrickson and Bird paper. The shear stress at the outer wall is

$$\tau_R = (1-\lambda^2)\, R\Delta P/(2L) \quad (25)$$

where $\lambda(s',\kappa)$ has also been tabulated by Fredrickson and Bird. Equation (24) can be written as

$$\ln(\Delta P) = n'[\ln(Q)] + C_4 \quad (26)$$

so that the derivative function n′ is defined by

$$n' = d[\ln(\Delta P)]/d[\ln(Q)] \quad (27)$$

Combining Equations (10), (24), and (25) one gets

$$\dot{\gamma}_R = (1-\lambda^2)^{s'}(s'+2)[Q/(\pi R^3)]/[(1-\kappa)^{s'+2}\Upsilon(s',\kappa)] \quad (28)$$

which is the generalized differentiation method expression for the shear rate in the concentric annulus rheometer in terms of volume rate of flow, pressure drop, and the derivative function $n' = 1/s'$. Again, the derivative function is just the slope of a logarithmic plot of ΔP vs. Q, and the flow curve for a fluid can be obtained from flow data taken in a concentric annulus by constructing the plot to determine the derivative function, and using Equations (25) and (28) together with tabulated values of $\lambda(s',\kappa)$ and $\Upsilon(s',\kappa)$.

The Falling Cylinder Rheometer

The falling cylinder instrument represents another form of the concentric annulus rheometer and has been treated approximately by Ashare et al. (*1*) and rigorously by Eichstadt and Swift (*2*). By applying our method to this case and using the integrated power law model form of Eichstadt and Swift, where $s' = 1/n'$ and m' indicate that these parameters are constants only at specified values of

v_t and $(\sigma - \rho)$, give

$$v_t = \phi_t R[(\kappa/\lambda)^2 gR(\sigma-\rho)/(2m')]^{s'} \qquad (29)$$

where ϕ_t and λ are each functions of s' and κ and are presented in tabular form by Eichstadt and Swift (2). The shear stress at the outer wall of the flow channel (the inner wall of the fall tube) is

$$\tau_R = gR(\sigma-\rho)(\kappa/\lambda)^2(1-\lambda^2)/2 \qquad (30)$$

Equation (29) can be written as

$$\ln(\sigma-\rho) = n'[\ln(v_t)] + C_5 \qquad (31)$$

so that the derivative function $n' = 1/s'$ is defined by

$$n' = d[\ln(\sigma-\rho)]/d[\ln(v_t)] \qquad (32)$$

Combining Equations (10), (29), and (30) one gets

$$\dot{\gamma}_R = (1-\lambda^2)^{s'}[v_t/(\phi_t R)] \qquad (33)$$

which is the generalized differential method expression for the shear rate in the falling cylinder rheometer in terms of the density difference, the terminal velocity of fall, and the derivative function $n' = 1/s'$. The derivative function is the slope of a logarithmic plot of $(\sigma-\rho)$ vs. v_t, and the flow curve for a fluid can be obtained from data taken in a falling cylinder rheometer by constructing the plot to determine the derivative function and by using Equations (30) and (33) together with tabulated values for $\lambda(s', \kappa)$ and $\phi_t(s', \kappa)$.

DISCUSSION

The shear rate for a time-independent fluid that has no wall effect is a unique function of shear stress [Equation (1)] regardless of the geometry of flow. Thus, data taken on a given time-independent fluid in a capillary rheometer will fall on the same flow curve (τ vs. $\dot{\gamma}$) as those data taken on the same fluid in an annular, a falling cylinder, or a coaxial cylinder rotational instrument, if the reduction of the dynamical and kinematical data from each instrument is treated in accordance with the generalized differentiation method. As experimental data for the same non-Newtonian fluid were not available from all of the four types of rheometers, artificial data were generated for Bingham plastic and Ellis model fluids in each of the rheometers for the purpose of demonstrating the utility of the method. Table 1 gives the rheological parameters of the Bingham plastic and Ellis model fluids, the dimensions of the rheometers, and the sources for the equations used to generate the artificial data. The artificial data were generated for each fluid in each rheometer by solving for the kinematical variable at specified values of the dynamical variable using the appropriate equation, rheological constants, and dimensions. For example, for the Bingham plastic model fluid in the capillary rheometer, Q was computed at specified values of ΔP by using the equation cited by Wilkinson (14) where $\mu_p = 8$ poise, $\tau_y = 26$ dyne/sq.cm., $R = 0.0204$ cm., and $L = 18.5$ cm. These artificially generated data for each fluid in each of the rheometers were used to construct plots of the logarithm of the dynamical variable vs. the logarithm of the kinematical variable. The values of the derivative functions were then determined from these plots by using graphical methods. The derivative functions obtained, together with their corresponding values of kinematical and dynamical variables, were then treated in accordance with the generalized differentiation method to compute $\dot{\gamma}_R$ and τ_R values. The results are presented in Figure 1 for the Bingham plastic model fluid, and in Figure 2 for the Ellis model fluid. In both cases, the procedure gives back the

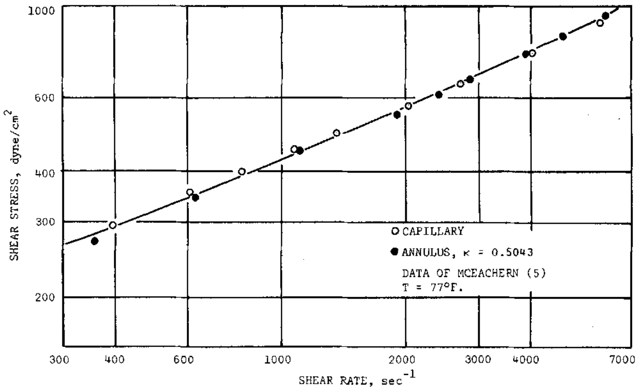

Fig. 3. The flow curve obtained by applying the generalized differentiation method to the data of McEachern (5) for 0.7% Natrosol-H in a capillary rheometer and an annular flow loop.

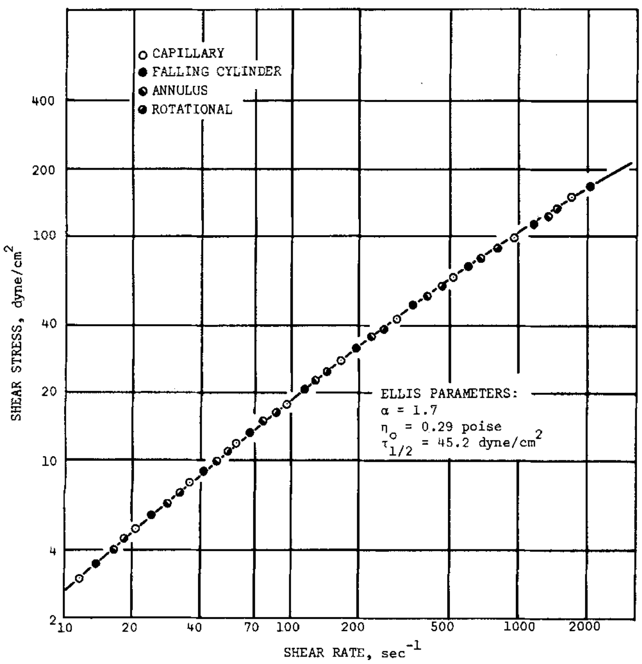

Fig. 2. The flow curve obtained for an Ellis fluid by applying the generalized differentiation method to artificially generated data for four types of rheometers.

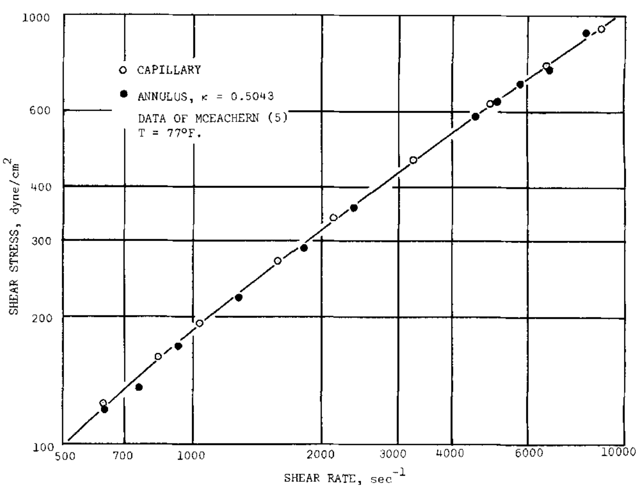

Fig. 4. The flow curve obtained by applying the generalized differentiation method to the data of McEachern (5) for 1% Natrosol-G in a capillary rheometer and an annular flow loop.

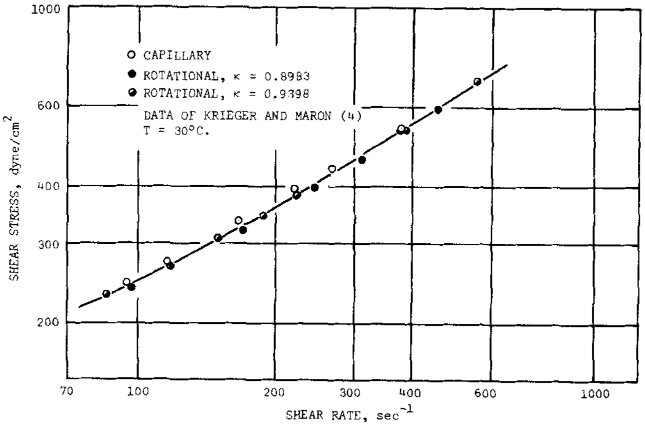

Fig. 5. The flow curve obtained by applying the generalized differentiation method to the data of Krieger and Maron (4) for GR-S latex (62.2% solids) taken in a capillary rheometer and two coaxial cylinder rotational rheometers with different radius ratios.

model parameters used for artificial data generation, indicating that the determination of the derivative function by graphical methods is satisfactory. The agreement of the plotted points for the four different rheometers by using the Bingham plastic fluid is of particular significance, since in this case the derivative function varies over a significant range with changes of the dynamical variable.

To illustrate further the utility of the generalized differentiation method, and to show the effect of experimental error, the experimental data of McEachern (5) and those of Krieger and Maron (4) were treated. McEachern obtained data for 0.7% Natrosol-H and for 1% Natrosol-G in both a capillary viscometer and an annular flow loop. The flow curves for these two fluids, with the data from the capillary and annular rheometers used, are shown in Figure 3 for 0.7% Natrosol-H and in Figure 4 for 1% Natrosol-G. The experimental data for GR-S latex containing 62.2% solids obtained by Krieger and Maron in a capillary rheometer and in two concentric cylinder rotational instruments of different radius ratio, treated in accordance with the generalized differentiation method, are presented in Figure 5. The agreement of the data obtained with different instruments for the same fluid in the presence of random experimental error is excellent.

CONCLUSIONS

The generalized differentiation method presented in this paper has been demonstrated to be valid and useful in analyzing rheometric data and comparing such data obtained on the same fluid in rheometers of the capillary, annular, coaxial cylinder rotational, and falling cylinder types, provided the fluid is time-independent. The method can undoubtedly be applied to other rheometers, provided the integrated power law model form for the rheometer in question is available for applying the derivative function to the computation of the shear rate at the rheometer boundary.

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NOTATION

C_i = constants defined in text; $i = 1, 2, 3, 4, 5$
$f(\ )$ = function of ( )
g = local acceleration due to gravity, cm./sec.^{2}
L = length of tube; height of cylinder, cm.
m = power law model parameter, (dyne) (sec.^{n})/sq.cm.
m' = point value consistency parameter, (dyne) (sec.^{n})/sq.cm.
n = power law model parameter, dimensionless
n' = derivative function, dimensionless
Q = volume rate of flow, cc./sec.
R = radius of tube, cm.
R_i = radius of inner cylinder in coaxial cylinder rotational rheometer, cm.
R_o = radius of outer cylinder in coaxial cylinder rotational rheometer, cm.
s' = reciprocal of derivative function, dimensionless
T = torque, dyne/cm.
v_t = terminal velocity of falling cylinder, cm./sec.

Greek Letters

α = Ellis model parameter, dimensionless
$\dot{\gamma}$ = rate of shear, 1/sec.
$\dot{\gamma}_i$ = rate of shear at R_i, 1/sec.
$\dot{\gamma}_o$ = rate of shear at R_o, 1/sec.
γ_R = rate of shear at R, 1/sec.
ΔP = pressure drop, dyne/sq.cm.
η_o = Ellis model parameter, g./(cm.)(sec.)
κ = ratio of inner radius to outer radius, dimensionless
λ = dimensionless radius of maximum velocity, defined by Fredrickson and Bird (3) for concentric annuli and by Eichstadt and Swift (2) for falling cylinder rheometers
μ_p = plastic viscosity, g./(cm.)(sec.)
ρ = fluid density, g./cc.
σ = density of the falling body, g./cc.
τ = shear stress, dyne/sq.cm.
τ_i = shear stress at R_i, dyne/sq.cm.
τ_o = shear stress at R_o, dyne/sq.cm.
τ_R = shear stress at R, dyne/sq.cm.
τ_y = yield stress, dyne/sq.cm.
$\tau_{1/2}$ = Ellis model parameter, dyne/sq.cm.
T = dimensionless function as defined by Fredrickson and Bird (3)
ϕ_t = dimensionless function as defined by Eichstadt and Swift (2)
Ω = rotational velocity, 1/sec.

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