determining the drift and the mass transfer.

For comparison with the present results, we reproduce the correlation suggested by Muenz and Marchello (8) giving the effective diffusivity $\mathcal{D}_w$ for unsteady state mass transfer to a deep liquid layer with traveling waves on the free surface:

$$\mathcal{D}_w/\mathcal{D} = 2.74\ (\nu/\mathcal{D})^{-1/6}\ (fh^2/\nu)^{1/3}$$

Owing to the differences in experimental conditions, namely, traveling waves vs. standing waves, deep liquid layers vs. thin films, and unsteady state transfer vs. steady state transfer, there is no obvious reason to expect the same dependence of the increase in mass transfer rate on the various parameters.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation through Grant GP2763. The authors wish to acknowledge R. Zane of the Lawrence Radiation Laboratory (Berkeley) for the design of the probe drive and its associated electrical circuity.

NOTATION

A = peak-to-peak probe amplitude, cm.
$\mathcal{D}$ = molecular diffusivity, sq.cm./sec.
f = wave frequency, sec.$^{-1}$
h = thickness of liquid layer, cm.
i = current density at limiting current, mamp./sq.cm.
i_0 = observed current density with no vibration, mamp./sq.cm.
i_{diff} = current density expected due to molecular diffusion only, mamp./sq.cm.
K = empirical constant, sec.$^{3/4}$/cm.
L = spacing between probe blades, cm.
$\overline{U}$ = drift velocity, cm./sec.
δ = boundary-layer thickness, cm.
λ = wavelength, cm.
ν = kinematic viscosity, sq.cm./sec.

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Manuscript received December 13, 1966; revision received May 1, 1967; paper accepted May 2, 1967.

A Kinetic Approach for Polymer Solution Data

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The phenomenological theory previously presented for describing the rheological properties of non-Newtonian materials was applied to two polymer solution systems. The basic shear diagram is needed over a wide range of shear rates and polymer concentrations, and such data are not readily available; however, what could be found supported the analysis. In order to confirm the theory further, ten solutions of polymethylmetacrylate in diethyphthalate with concentrations up to 55% were investigated at 40°C. The results indicated that the forward and reverse orders were 1 and 2 respectively and that the two parameters of the theory (a susceptibility to shear term and an equilibrium type of constant) were constant over the range of concentrations investigated. The flow data were reproduced to within a few percent for all solutions, although the errors were large for the very dilute concentration, where experimental difficulties precluded obtaining reliable data. The method allows correlation of polymer solution data over the range from lower to upper Newtonian viscosities and over a wide concentration range.

The rapid development of polymer science in the past twenty years has much to do with the present emphasis on the study of rheology. Most polymers known today behave as non-Newtonian fluids do, and a knowledge of their rheological behavior has become essential for good design such as in predicting the power input and the flow patterns in operations like mixing, extrusion, and molding. Many investigators have attempted to explain the basic reasons why these substances exhibit non-Newtonian flow behaviors. On a macroscopic scale these explanations may involve phenomena such as agglomeration or other particle interactions as a function of shear and time. On a microscopic basis, they may involve such molecular interactions as entanglement, dipole attraction, hydrogen bonding, or other forms of association. Furthermore, average molecular weight, molecular weight distribution, and structure of the material such as branching and the type of radicals in the branching will also contribute to this behavior. These effects and possibly others result in the

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observed non-Newtonian flow characteristics such as shear thinning or thickening and time dependency.

One of the major problems in the study of non-Newtonian materials has been the lack of adequate equations for the description of the flow characteristics. Equations with meaningful constants are needed to correlate the rheological properties with the fundamental structure of the material under consideration. The variation of the constants with molecular weight, molecular weight distribution, temperature, and structure would provide considerable insight into the mechanism of the flow and into the reasons for the nonlinear behavior. This paper, which presents an approach to this problem, results in an equation based upon the kinetic breakdown of the substance being considered. The basic approach and preliminary confirmation of the theory have been described by Denny and Brodkey (*4*). Brodkey, Denny, and Kim (*5*) presented some necessary modifications to the theory and offered further confirmation over a wider range of data. The present work extends the experimental confirmation much further as a result of having obtained a comprehensive set of data on one polymer solution over a very wide concentration range.

Denny and Brodkey (*4*) reviewed the previous literature on general nonempirical approaches to the description of non-Newtonian materials and this will not be repeated here. There have been several less general kinetic approaches (*10* to *12*, *28*) that have assumed some specific mechanism and then suggested a rate equation to describe the change; however, since these are specific to a particular suggested mechanism and are not designed to be a general approach and help establish the mechanism, they will not be discussed further. However, it might be well to put our approach into proper perspective with other means of treating rheological data. First, there are the empirical methods such as the power or Ostwald-deWaele (*22*, *23*), Ellis (*7*, *9*), Sisko (*27*), Reiner-Philippoff (*24*), Powell-Eyring (*25*), and Rodriguez (*29*) models. The semiempirical or phenomenological models form a second class of which the Eyring work is representative. It is in this class that the present effort resides. Finally, there are the microrheological approaches which assume a mechanism and are directed toward elucidating the basic reason why specific systems are non-Newtonian. In this class are such analyses as Rouse (*26*), Bueche (*3*), Michaels et al. (*19*-*21*), and Mason (*13* to *14*). In the empirical models, nothing is learned about the basic mechanism because little specific meaning can be given to the constants. In the phenomenological approaches as little is assumed about the specific mechanism as possible, and one hopes to gain some insight into this by evaluation of the constants and their variation with the parameters of the system (such as molecular weight, distribution, etc.). Finally, the microrheological analyses depend on a knowledge of the mechanism, and are only valid for systems that fulfill the basic assumptions and approximations of the theories. In general, a mechanism is suggested, and then one attempts to confirm the hypothesis by comparison to experimental data. Hopefully in time the latter two methods will complement each other, the former (phenomenological) providing the necessary insight to allow a more reasonable mechanism to be proposed than has heretofore been possible, and the latter (microrheological) allowing estimation and intelligent variation, at the investigator's will, of the characteristic parameters of materials.

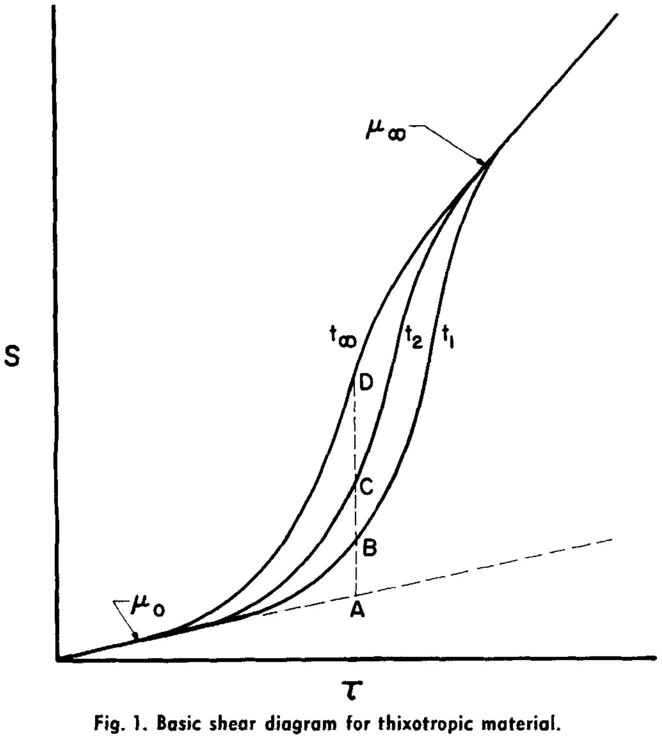

Fig. 1. Basic shear diagram for thixotropic material.

THEORY

Consider a thixotropic material with the flow characteristics (Oswald curve) shown in Figure 1. At low values of shear, the viscosity (defined as the ratio of shear stress to shear rate) remains constant. At high values of shear, the viscosity has a constant value but is smaller than the low shear value. The low shear and high shear viscosities have been designated as μ_0 and μ_∞, respectively. At any intermediate stress it is postulated that the viscosity will initially (zero time) have the value μ_0 (point A), but will decrease with time to a limiting value dictated by the t_∞ or steady state curve (point *D*). If the shear stress is increased to a value larger than that designed by line ABCD, it is easily seen that the viscosity will decrease by a larger amount in a given time or, in other words, the rate of decrease of viscosity with time is some function of the shear stress.

The system described has the ingredients which render it susceptible to analysis from a chemical kinetic standpoint. Namely: (1) A property of the system changes, indicating a change of state in the system. (2) This property changes as a function of time. (3) The rate of change of the property is a function of some externally controllable variable other than temperature. Possibly the following example will clarify our approach better, although the analogy should not be taken too literally. Take a reaction of species A going to B, and measure the reaction (or rate of change) by measuring the rate of change of pressure in the system, which in turn can be related to the fraction of material, A, converted. Parallel, in our case, is that A is some polymeric configuration (such as entangled molecules) and B is something less (less entangled, etc.). As will be seen, we propose to relate the rate of change of viscosity by an empirical relation to the conversion of species A, just as pressure is used in the kinetics case. We write a rate equation and then use various means to establish the value of the constants and the adequacy of the equation itself. Once all the constants have been determined and are consistent for the system under consideration, then and only then can we make a specific hypothesis about the detailed mechanism; that is, what basic mechanism of change will give the rate equation observed. This can be greatly different depending on the actual process. In reaction kinetics we often run into complex reactions involving both simultaneous and consecutive steps. What is important is that here we are suggesting a relatively general approach that can be used on any system to give meaningful constants and that hopefully can be used to establish a test for any given suggested mechanism.

Denny and Brodkey (*4*) hypothesized that some function involving a difference between μ_0 and μ is proportional to the amount of change, and that a similar function of μ and μ_∞ is proportional to the amount remaining unchanged. The reasoning is as follows: when the viscosity equals a constant, then no change in structure occurs (*11*). The viscosity at high rates of shear is constant at μ_∞, which is taken to mean no more change can occur no matter how high the shear rate. Therefore, the limiting indications of no change and maximum change at any shear rate are μ_0 and μ_∞, respectively. The viscosity μ falls somewhere between these two limiting values. Applying the inverse-lever principle to the function, the fraction unchanged is taken as

$$F = \frac{f(\mu) - f(\mu_\infty)}{f(\mu_0) - f(\mu_\infty)} \tag{1}$$

and the fraction changed would be $1 - F$. The function $f(\mu)$, which is linear with the concentration or amount of change, must be found as a function of the viscosity. Consequently, at this point some specific assumption must be made as to a form for $f(\mu)$. Denny and Brodkey took this as μ_θ, which in turn was defined as $d\tau/ds$; however, this does not now seem reasonable, and the following analysis was made for polymers and their solutions.

The change in μ can be attributed to some mechanism such as entanglement, association, or winding of polymer molecules. If a general empirical relation can be found which has been attributed to the same mechanism, it should be possible to relate the viscosity change to a concentration change. This expression must contain the viscosity. Such a general relationship does exist and is the basis for the Loshaek-Fox (*8*) equation

$$\mu_0 = AM_w{}^B$$

where M_w is the weight average molecular weight of the polymer under consideration, A is an empirical constant, and B is an empirical constant which has the value 3.5 for a wide variety of polymer melts and polymer solutions of chain length of about 600 carbon atoms or greater. The constant B is independent of the composition of the polymer and amount of branching, which indicates it is related only to the degree of mechanical interaction between the various molecules. The relation suggests that the change in structure is caused by a change in molecular weight which is linearly related to $[(1/A)\mu_0]^{1/3.5}$. For the flow system under consideration the change may be described as a decrease in the effective molecular weight and should be related linearly to $[(1/A)\mu]^{1/3.5}$. The preceding point may be clarified by referring to Figure 2. A material of a given molecular weight has, at low shear, a viscosity corresponding to point A. As the shear is increased, the viscosity is decreased (say to point B) due to the change in structure, and now the material behaves as one of lower molecular weight, that is, point D. It follows that in flow systems μ_0 indicates the maximum structure, and μ_∞ indicates the minimum structure that can be induced by shear. The desired function is $f(\mu) = A\mu^{1/3.5}$, which leads to

$$F = \frac{\mu^{0.286} - \mu_\infty{}^{0.286}}{\mu_0{}^{0.286} - \mu_\infty{}^{0.286}} \tag{2}$$

This suggestion is not meant to be final or even fixed for all systems. For example, for nonpolymeric or even dilute polymer solutions, a simple linear function, $f(\mu) = A\mu$, might suffice, which leads to

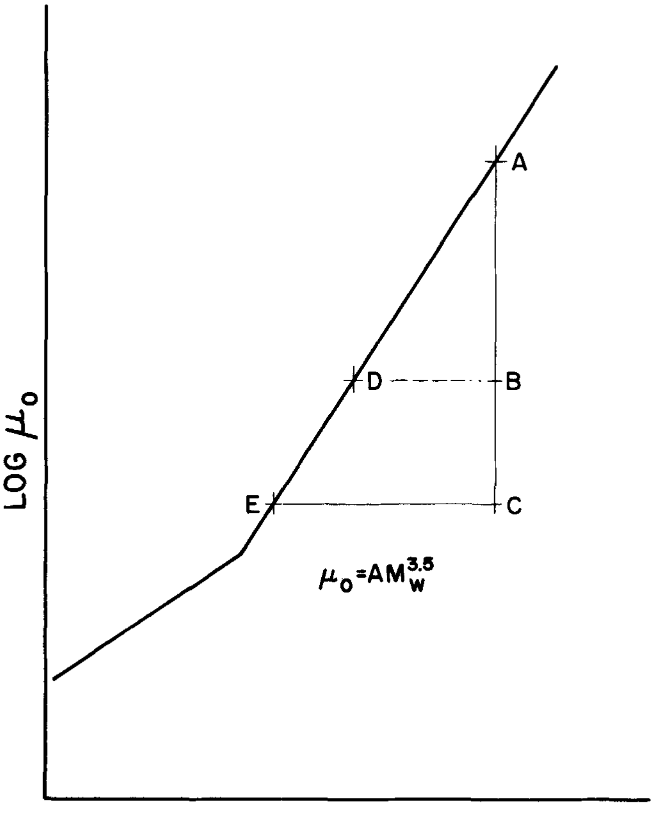

Fig. 2. Illustration of relation to relate viscosity to amount of change.

$$F = \frac{\mu - \mu_\infty}{\mu_0 - \mu_\infty} \tag{3}$$

Each suggestion must be tested against experimental data. Finally, it must be emphasized that reversibility of the change is proposed, that is, *molecular degradation is eliminated from consideration.*

The simplest equation which might describe the transient change from the zero to the infinite state is

$$\frac{-d(FC)}{dt} = k_1'(FC)^m - k_2'[(1-F)C]^n \tag{4}$$

where m and n are forward and reverse orders of reaction and k_1' and k_2' are the specific rate constants, and where C is the concentration of polymer. The concentration term comes into the fractions because the actual amount of non-Newtonian fluid is the fraction times the concentration, and only non-Newtonian fluid is assumed to be undergoing structural change. This is analogous to chemical reactions in solutions. As was observed previously, the rate of change of the viscosity is a function of the shear stress and the rate equation must reflect this. For generality, the effect is introduced into both the forward and reverse rate constants. As the exact function is not known, a power term (not power-law model) is employed:

$$k_1' = k_1\tau^{p_1} \text{ and } k_2' = k_2\tau^{p_2} \tag{5}$$

This is somewhat analogous to a catalyst effect in chemical kinetics; that is, at higher stresses a faster rate of change is obtained as compared to more catalyst giving a faster chemical reaction. Analysis of the data of Meissner

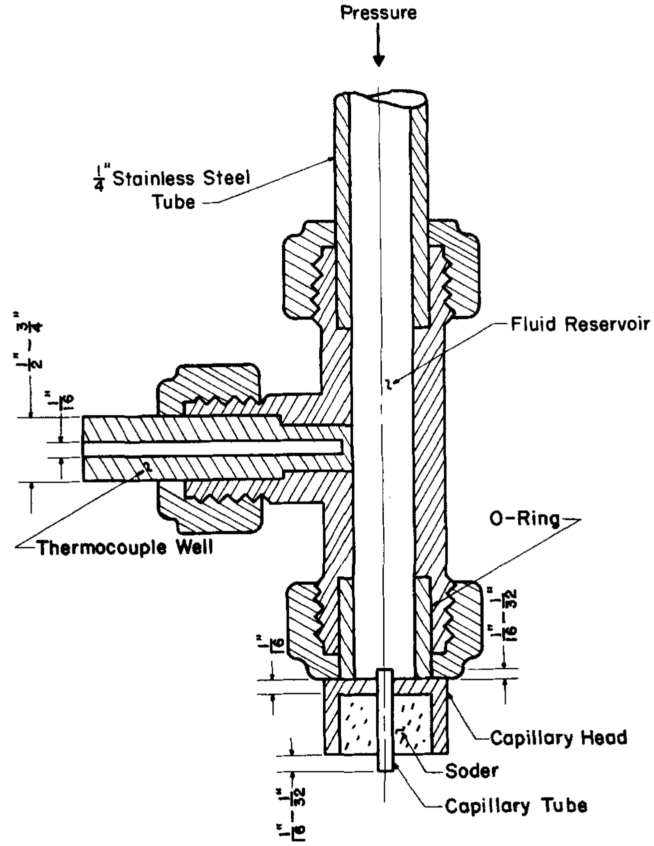

Fig. 3. Capillary viscometer and fluid reservoir.

(*15*) shows that for isothermal conditions the change of viscosity may be expressed as a function of shear stress only and therefore the choice of τ^p as opposed to s^p, as used by Denny and Brodkey. The rate equation now becomes

$$\frac{-d(FC)}{dt} = k_1\tau^{p_1}(FC)^m - k_2\tau^{p_2}\left[(1-F)C\right]^n \quad (6)$$

EVALUATION OF CONSTANTS

This is a phenomenological theory and the constants of Equation (6) are to be evaluated from experimental data. The means for doing this parallels the methods used for homogeneous kinetics (*5*, *6*); however, rate data are most difficult to obtain (*6*) and a really successful evaluation by the rate method has yet to be accomplished (*6*). Furthermore, Equation (6) is a very simple form and may well be inadequate for the complete time-rate-of-change data. Nevertheless, it has been found satisfactory for the equilibrium or steady state data (data taken under conditions where the rate term disappears; that is, what is normally called the Oswald curve as given by the t_∞ curve of Figure 1). One might conclude from this that Equation (6) is a reasonable representation for the rate controlling step near equilibrium. For dilute solutions, one has to rely entirely on the steady state data method except for a few highly thixotropic materials. In most cases the thixotropic or time effect is so negligible in dilute solutions that it is impossible to obtain rate data with instruments that exist today.

Under steady state condition, Equation (6) becomes

$$k_1\tau^{p_1}(FC)^m - k_2\tau^{p_2}\left[(1-F)C\right]^n = 0 \quad (7)$$

or

$$K\tau^p = \frac{k_1}{k_2}\tau^{p_1-p_2} = \frac{(1-F)^n}{F^m}C^{n-m} \quad (8)$$

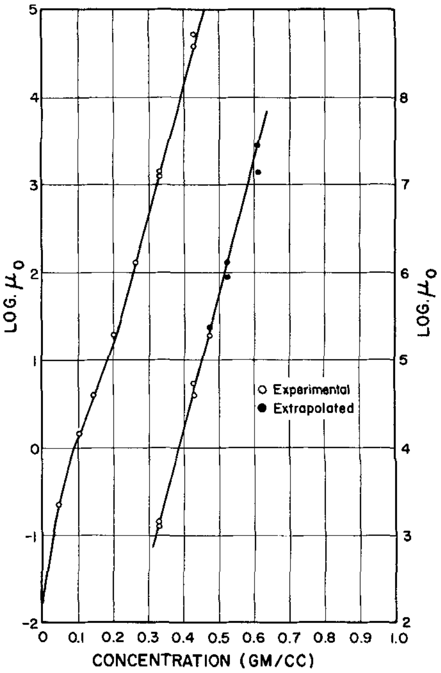

Fig. 4. Lower Newtonian viscosity as a function of concentration.

where K is an equilibrium constant. If one plots τ vs. $\frac{(1-F)^n}{F^m}C^{n-m}$ on a log-log scale for various combinations of m and n, ideally only the right combination of m and n would give a straight line, and those are the forward and reverse orders of reaction, respectively. The values of p and K can be evaluated from the slope and intercept of the straight line. With this method, the individual values of p_1, p_2, k_1, and k_2 cannot be obtained and only $p = p_1 - p_2$ and $K = k_1/k_2$ are evaluated. However, p and K are enough for the full characterization of the system, if one is not concerned with thixotropic effects. In homogeneous kinetics it is often observed that reaction orders are integers. In every case to be discussed here excellent correlations were obtained with m and n as integers. It was felt that little would be gained by allowing them to be completely arbitrary; therefore, they were greatly restricted.

In the limit of a Newtonian fluid the equation becomes indeterminate. The singularity is a result of applying the rate concept to the Newtonian material in which no rate change occurs. What is really implied in this limit is that no matter what the value of τ, the viscosity is constant and F is indeterminate or simply meaningless.

EXPERIMENTAL PROCEDURES

We chose polymethylmethacrylate, one of the typical random coiling macromolecules, for this study; such systems in the bulk state and in nonelectrolytic solvents behave as Ostwald fluid (*16*). The upper Newtonian regime of these materials is not always reached for other than dilute solutions because fracture or turbulence occurs first. The lower Newtonian vicosities follow the 3.5 power law at or about a chain length of about 600 carbon atoms.

Ten different solutions of polymethylmethacrylate in diethylphthalate were used (Table 1). The polymeric material is a commercial grade, Plexiglass V-100 colorless polymer of medium range molecular weigth (~ 100,000). The solutions were prepared by a combination of agitation and heating until they appeared homogeneous. The more dilute solutions were filtered under vacuum to remove any small particles of gel that might have existed. For higher concentra-

TABLE 1. CONCENTRATIONS OF SOLUTIONS INVESTIGATED

Solution	Concentration g./cc.	Wt. %
C-0-0	0.04	3.6
C-0-1	0.105	9.6
C-0-2	0.145	13.0
C-0-3	0.200	18.0
C-1	0.264	23.0
C-2	0.33	30.0
C-4	*0.427	38.5
C-5	*0.470	42.5
C-7	*0.524	47.4
C-06	*0.61	55.0

* Extrapolated values.

tions, additional polymer was added to the dilute solutions, and by kneading and heating a uniform mixture was obtained.

For the measurement of low shear, steady state flow data, the Weissenberg Rheogoniometer was used. This unit, a plate and cone type, is manufactured by Farol Research Engineers, Ltd., Bognor Regis, Sussex, England. The shear range is 10^{-4} to 10^4 sec.$^{-1}$. For high shear flow data, a capillary viscometer of our own construction was used (Figure 3). This unit uses capillaries of two different inside diameters with L/D values ranging from 30 to 117 (Table 2). Capillary data were first corrected for Couette (*22*) and Hagenbach (*1*) effects by the method of Bagley (*1*) and Metzger and Brodkey (*17*), before correcting for the non-Newtonian effect (*18*). The flow curves for the various concentrations of solutions at 40°C. are given in Figure 10. In Figure 10 various curves in each solution indicate runs that were made on different dates. Successive downward shifts in the flow curves with time suggested that there was a slight increase in concentration due to evaporation of solvent during storage.

Since the lower Newtonian viscosity range of samples C-7 and C-06 were below the measurable shear limit of the viscometer, they were extrapolated from a plot of $1/\mu$ vs. shear rate. Some runs were made on other solutions where data were not obtained at the lower Newtonian range; for these, the same extrapolation technique was used to evaluate the lower Newtonian viscosity. Figure 4 shows the effect of concentration on the lower Newtonian viscosity. At concentrations above 10-to 15%, the semilogarithmic plot of μ_0 vs. C gives a straight line with a slope of 15.2. As the concentration is reduced below this value, there is a slight deviation from the line. The straight line was drawn through points whose μ_0 values were experimentally determined and whose flow curves were measured right after their concentration determination. The result is in good accord with the polyacrylic acid data of Brodnyan and Kelley (*2*) where the same type plot gave a slope of 11.0..

Turbulent flow appeared at the shear rate of about 5 sec.$^{-1}$ in C-7, C-5, and C-4 solutions. Data above these levels were, of course, not used.

TABLE 2. DIMENSIONS OF CAPILLARIES USED

Capillary No.	Diameter (inches)	(L/D)	Material of Construction
1	0.009	117	Steel
2	0.00886	82	Steel
3	0.00895	57	Steel
4	0.00536	67.2	Brass
5	0.00529	47	Brass
6	0.00521	30.1	Brass
7	0.00528	34.8	Brass
8	0.0089	82.5	Steel

INTERPRETATION OF DATA AND DISCUSSION

There are several questions that can be answered only

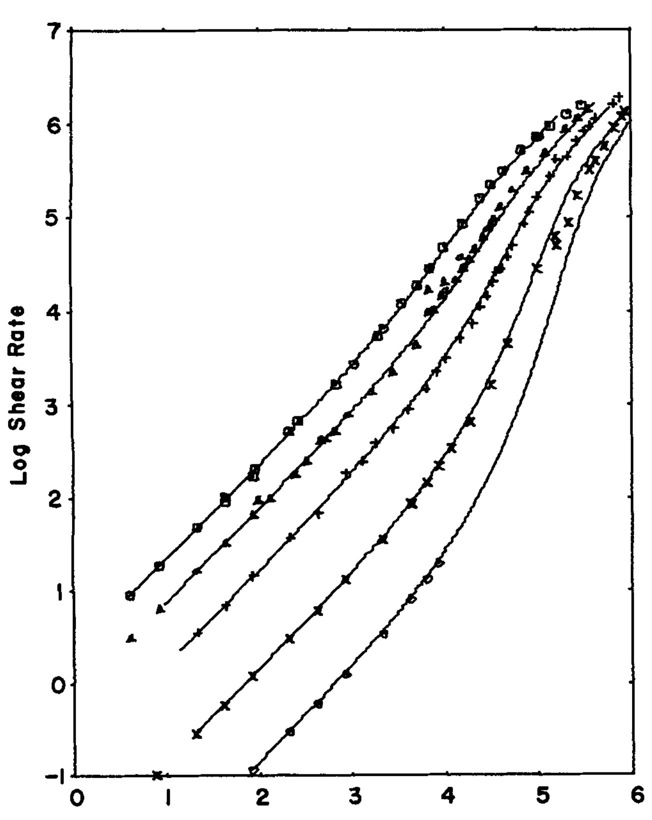

Fig. 5. Basic shear diagram for polyacrylic acid–F defined by Equation (2), *m* = 1, and *n* = 3.

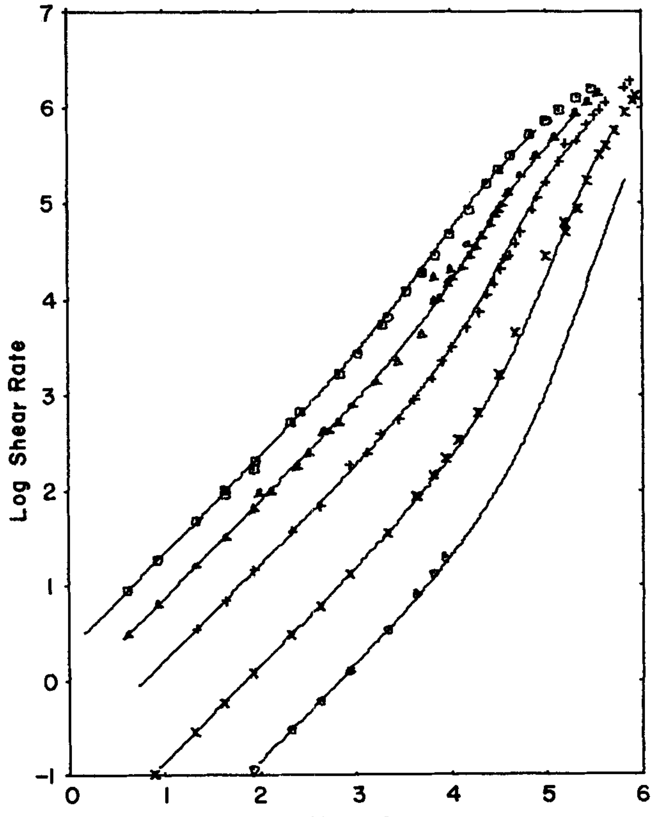

Fig. 6. Basic shear diagram for polyacrylic acid–F defined by Equation (3), *m* = 1, and *n* = 3.

by comparison of the theory with experimental data; for example, the proper form for Equation (1), or the validity of the shear stress dependency suggested in Equation (5). To answer these, the equilibrium Equation (8) was applied to the data of Brodnyan and Kelley (2) on five solutions of polyacrylic acid in water at concentrations from 0.037 to 0.31 g./ml. By plotting the appropriate terms as previously suggested, the best values of m, n, p, and K were determined for the entire set of data. The orders of reaction, m and n, were allowed to vary from 0 to 3; that is, 16 combinations were tested. However, in all cases only $m = 1$ and $n = 2$ or 3 were at all satisfactory and only these are discussed in the sequel. These data also served as a preliminary verification of the concentration effect, which could be further established later by the wide concentration range covered in the experimental study. All comparisons were made by machine calculation and plotting in order to reduce labor and allow a range of conditions to be investigated. The basic shear diagram is easily reconstructed from the known values of the concentration and the best values of m, n, p, and K. To do this F is calculated from Equation (8) for a given τ. From F and known values of μ_0 and μ_∞, μ can be calculated from the appropriate relation (2) or (3). The stress, τ, and viscosity, μ, define s, which allows construction of the basic shear diagram.

The first test was to determine whether shear stress or shear rate should be raised to the power p [Equation (5)]. This was done with the conversion term, F, defined by both Equations (2) and (3), and for m equal to 1 and n equal to 2 and 3. In each case when shear rate was used the results were totally unsatisfactory, but satisfactory with shear stress; therefore the plot suggested by Equation (8)

$$(1 - F)^n C^{n-m}/F^m \text{ vs. } \tau \qquad (9)$$

was used in all subsequent calculations. The second test was to attempt to determine if the linear Equation (3) or the nonlinear Equation (2) was better. The basic shear diagrams with the experimental data are shown in Figures 5 and 6 for one pair of combinations tested. The standard deviations for all the data from their respective curves were 11.5% and 9.7% for the two figures. This includes all the data shown, some of which is clearly in error, and some of which is affected by turbulence. The estimated experimental error for all the data is somewhere between 6 and 8%; it should be remembered that the above reported standard deviations cannot be reduced below this inherent scatter of the data. It is realized that this is hard on the correlator because the standard deviation also contains the experimental error. However, it is reproducible by anyone and does provide a feel for the reliability of the correlation (that is, by looking at the difference between the standard deviation and the estimated experimental error). In previous work by others the standard deviation of the data from the smoothed data curve and the standard deviation of the smoothed data curve from the correlating equation were not reported because of the uncertainty in establishing the smoothed curve. The values reported here alleviate that problem and can serve as a basis for comparison. The linear case is better as we can see by a careful look at the figures. For this set (Figure 6) the average value for p is 2.01 and for log K is -10.3 which is determined by weighing the individual p's and log K's according to the number of points. A standard deviation on these is meaningless. The important number is the final comparison with data, which as previously noted was 9.7%. The final test in this series was to compare $m = 1$, $n = 2$ vs. $m = 1$, $n = 3$. The first of these is given as Figure 7 and the second was already presented as Figure 6. A careful investigation of the figures shows that there is little difference, with the actual deviations being 9.6% and 9.7%, respectively. To provide

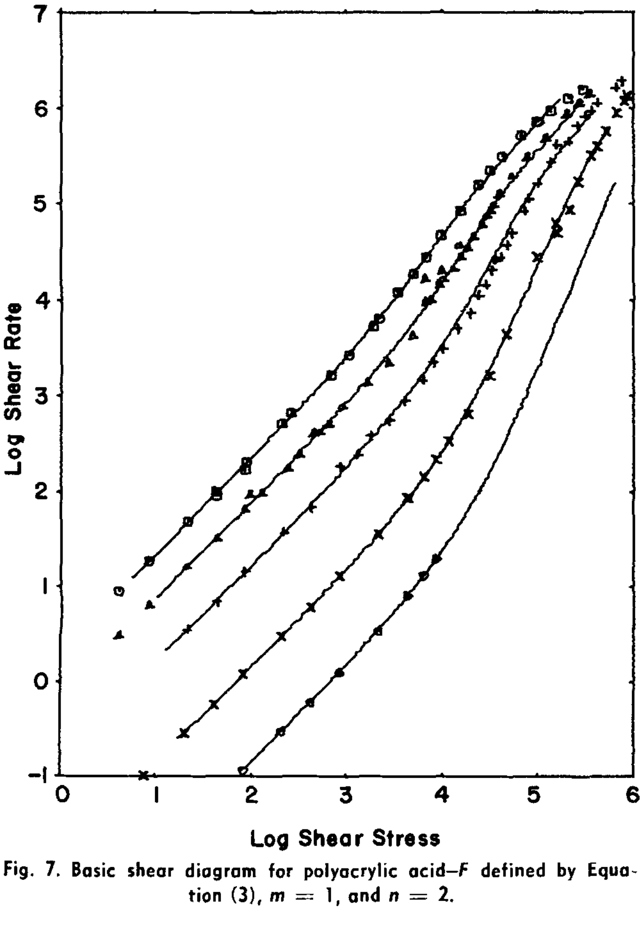

Fig. 7. Basic shear diagram for polyacrylic acid—F defined by Equation (3), $m = 1$, and $n = 2$.

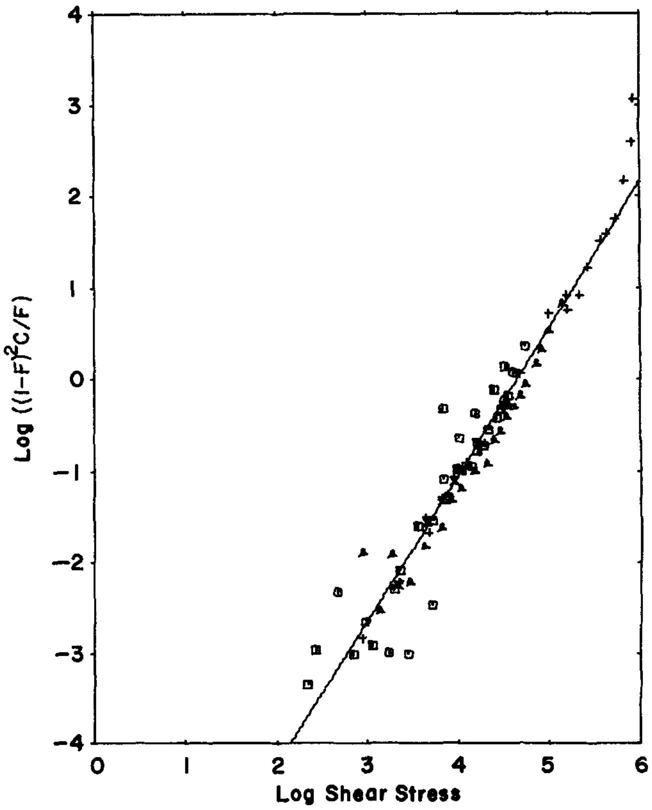

Fig. 8. Correlation curve for polyacrylic acid corresponding to Figure 7—$p = 1.60$ and log $K = -7.42$.

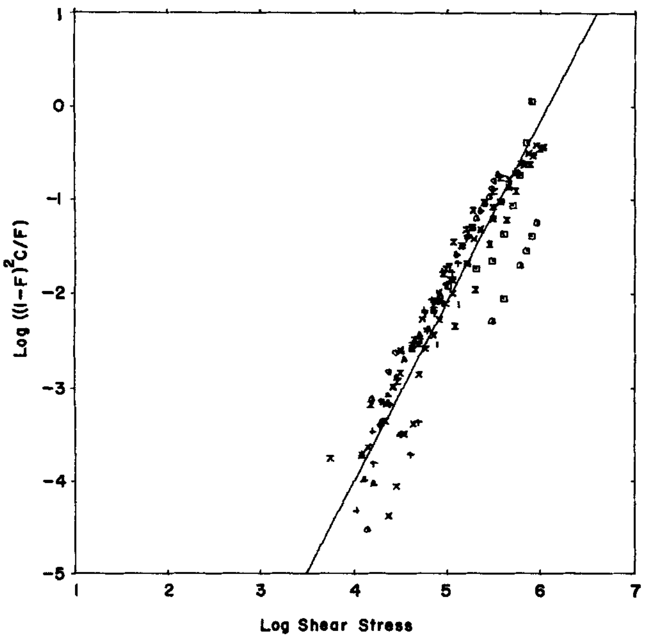

Fig. 9. Correlation curve for polymethylmethacrylate in diethylphthalate—$p = 1.90$ and $\log K = -11.6$.

a basis for the reader, the correlation plot of the best case discussed above is shown in Figure 8. The line is a weighted least squares, where the weighing is toward the higher points, since the more scattered lower points involve the differences of large numbers and thus are less reliable. Finally, since the difference between using Equation (2) or (3) and n equal to 2 or 3, did not cause a gross change, these tests were repeated with the new solution data; however, the wide range of shear rates was not available with the latter.

For the concentrated solutions of our data, μ_∞ could not be obtained and a value of $\mu_\infty/\mu_{\text{solvent}}$ of 1 was used. For these solutions this always involves a difference from a large number and no error is introduced. The best correlation of the data was obtained using Equation (2) and the value of m and n as 1 and 2, respectively. The average values of p and $\log K$ are 1.90 and −11.6, respectively. The overall deviation was 10.4%, with the lowest possible error, owing to the inherent scatter of the data being between 5 and 10%. Included in these deviations are some poor data due to turbulence, etc. The correlation curve is shown as Figure 9 and the basic shear diagram as Figure 10.

The data, which we used even though we considered it poor, had some scatter in the points, notably at either end. The effects that were considered to be the cause of the scatter are

1. In the low shear range near the lower Newtonian regime, the movement of the upper cone is so small that even when the most sensitive meter scale is used, errors were introduced in reading the torque since the magnitude of noise in the electronics of the system was almost as high as the torque level. Furthermore, in this range the difference of large numbers is used; that is, in determining $(1 - F)$, since F is close to 1.

2. In the high shear range, some of the sample between the cone and the plate tended to come out of the gap because of high centrifugal forces caused by the higher rotational speeds of the bottom plate and because of normal force effects. This resulted in false torque readings. At the highest levels, the material tends to ball up and these extreme points were, of course, discarded.

3. Viscous heating can effect the high shear regime. The C-0-1 through C-0-3 solution data were not used. Since μ_∞ was only crudely known for the C-0-1 data and not at all for the C-0-2 and C-0-3 solutions, even a slight error in this region gave gross errors in the p and K values. This stems from the use of differences of large numbers in this region; that is, μ_0 and μ_∞ are of the same order. Extrapolated values of μ_∞ were tried, but a good method of extrapolation is not known. The one known μ_∞ is that for the C-0-1 solution. However, we think that viscous heating was important to this. Above 10^5 sec.$^{-1}$, we were able to use only one capillary and the heating effect could not be investigated. Potentially, the heating effect is great. Brodnyan and Kelley used a water solution system which is less susceptible to viscous heating because of the high heat capacity of the fluid as contrasted to the organic system we used. Our idea was to obtain as wide a concentration range as possible and we made up solutions over an extreme range, so extreme that we were unable to obtain reliable data for the more dilute solutions and for the high shear concentrated data.

Our discussion would not be complete without some comparison to other methods commonly used to represent rheological data. But first it should be emphasized that the power p is not the same as the power-law model, which empirically relates shear stress to shear rate. For the solution data, the power for the power-law would vary from unity at the lower Newtonian range down to less than 0.5 and back to unity at the upper Newtonian range, whereas p is approximately 2.0 over the entire range. Therefore, it is clear that p is not the same as what is normally considered the non-Newtonian index of the power-law model.

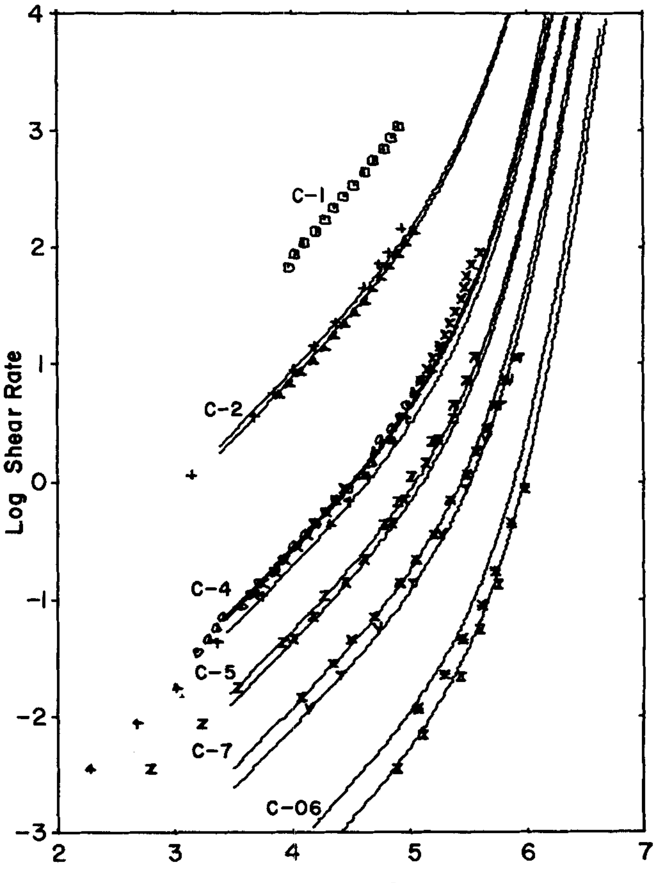

Fig. 10. Basic shear diagram for polymethylmethacrylate corresponding to Figure 9—F defined by Equation (2), $m = 1$, and $n = 2$.

A number of alternate models were cited in the introduction. The empirical models (2 constants, usually one besides μ_0 or μ_∞) by Ellis (*7, 9*), Sisko (*27*) and others cannot represent the full range of data from the lower Newtonian to the upper Newtonian ranges. Furthermore, they are not designed to simply incorporate concentration effects except by observing the changes in the empirical constants with concentration. Rodriguez (*29*) has shown that similar models based on microrheological theories are also inadequate although they often do incorporate the concentration in a unique manner. Rodriguez has presented an empirical model like the above, but with the advantage that while not fitting the data of Figure 8 perfectly nor as well as the present model, it does reflect correctly the changes in shape that are observed with concentration. Rodriguez's model fails at the high shear range where the shape of the curve is incorrect and the predicted viscosity is too low. More complex models (3 constants, usually one besides μ_0 and μ_∞) of Powell-Eyring (*25*) and Reiner-Philippoff (*24*) also provide the proper shape for comparison over the entire range, but since there is only one empirical constant (other than μ_0 and μ_∞), the fit as in the case of Rodriguez's model is not quite good enough. In addition concentration in these models is not simply incorporated and one can only observe changes in the constants with concentration. One hopes they are indeed constant as in the case of Rodriguez's model. The kinetic interpretation model does better than any of the above. It incorporates concentration change in an expected and unique manner, and hopefully the parameters of the theory will in time be shown to have specific meaning with regard to the flow mechanism rather than being just empirical constants. But it should be noted that this approach has a number of constants besides μ_0 and μ_∞ fixed by the data (p, K, m, and n as integers and quite limited).

CONCLUSIONS

The results of this investigation have shown that the rate equation concept can be used to describe the flow behavior of Ostwald type non-Newtonian fluids. The results have shown that this equation, which can take into account such effects as concentration, temperature, and structure, can be used as an excellent means of correlating flow data. With this equation and properly evaluated constants, the flow curve of a given material can be reproduced to within a couple of percent of the experimental error.

For ten solutions of polymethylmetacrylate in diethylphthalate with concentrations up to 55%, the results indicated that the forward and reverse orders were 1 and 2 respectively and that the two parameters of the theory (a susceptibility to shear term and an equilibrium type constant) were constant over the range of concentrations investigated. The flow data were reproduced to within a few percent of the experimental error for all solutions, although the errors were large for very dilute solutions, where experimental difficulties precluded obtaining reliable data. It should be emphasized that the method allows correlation of polymer solution data over the range from lower to upper Newtonian viscosities and over a wide concentration range.

ACKNOWLEDGMENT

The authors wish to thank the National Science Foundation for their early support of our work (GP-573) and the National Aeronautics and Space Administration for their support (NsG591). The Rohm and Haas Company kindly supplied the polymer, and Uniform Tubes, Inc., the fine capillaries for the viscometer. W. E. Lewis provided considerable help in the final programming and evaluation.

NOTATION

a, A, B = constants
C = concentration
E = energy
f = function
F = fraction conversion
k_1 = specific forward rate constant
k_2 = specific reverse rate constant
K = equilibrium constant
m, n = orders of reaction
p = susceptibility to stress parameter
s = shear rate
t = time
τ = shear stress
μ = viscosity

Subscripts

0 = initial
∞ = final
1 = forward
2 = reverse

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Manuscript received April 28, 1967; revision received August 9, 1967; paper accepted October 20, 1967. Paper presented at AIChE Salt Lake City meeting.