

June 24, 1966

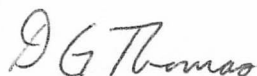
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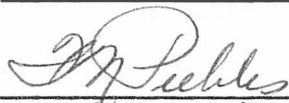
I am submitting herewith a dissertation written by Julian Orus Doughty entitled "An Experimental Study of Constitutive Equations for Viscoelastic Fluids." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Engineering Science.



Major Professor

We have read this dissertation
and recommend its acceptance:







Accepted for the Council:



Dean of the Graduate School

AN EXPERIMENTAL STUDY OF CONSTITUTIVE EQUATIONS
FOR VISCOELASTIC FLUIDS

A Dissertation
Presented to
the Graduate Council of
The University of Tennessee

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
Julian Orus Doughty
August 1966

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to many people who have made various contributions to this dissertation. A project such as this would be impossible without drawing on the skills of a great many people, some of whom made such significant contributions that the author would like to thank them formally in this section.

The most indispensable person was the author's advisor, Dr. D. C. Bogue, whose counsel and direction made the dissertation possible. His tireless efforts were a constant source of inspiration.

Appreciation is due to Mr. T. A. Long for help with the electrical equipment and to Mr. H. B. Thompson for assistance with the mechanical equipment.

Mrs. Dorothy Norton typed the final manuscript. Her cheerful willingness to try to decipher the author's handwriting is gratefully acknowledged.

Mr. Roger Schulken of Tennessee Eastman Corporation is thanked for his instruction on the use of the Weissenberg Rheogoniometer and for supplying normal stress data for comparison with the author's.

The research was primarily supported by the National Science Foundation under grant NSF GP-2005. Secondary support for the final stages of the work came from the National

Aeronautics and Space Administration under grant NSG 671.

Finally, the author wishes to express his deepest appreciation to his wife, Barbara Ann. For her acceptance of the inconveniences and hardships created by this project he is especially grateful.

ABSTRACT

Four viscoelastic constitutive equations are examined for their ability to correlate linear dynamic data with non-linear viscosity and first normal stress data. The theories examined are due to Oldroyd; Pao; Bogue; and Bernstein, Kearsley, and Zapas. The concepts and viscometric predictions of each theory are reviewed with more emphasis on the Pao theory due to a lack of discussion in the literature. A summary of classical linear theory is also presented.

Experimental data were obtained on a Weissenberg Rheogoniometer for two materials: solutions of 10 per cent polyisobutylene in Decalin and 12 per cent polystyrene in Aroclor. A limited amount of data were also obtained for a 3 per cent napalm solution. Where possible, viscometric data covered a shear rate range of five decades and dynamic data covered a frequency range of four decades. In some cases instrument or material limitations restricted the range. All data were taken at 25°C.

It was found that Oldroyd's three-constant theory and Pao's theory do not agree quantitatively with viscometric data. Bogue's theory and the Bernstein-Kearsley-Zapas theory do agree quantitatively with certain restrictions: (1) in the forms examined, these theories do not predict limiting viscosities at high shear rates; (2) an adjustable material

parameter is used (although it is possible that this parameter is constant for classes of materials); and (3) there are no data for the second normal stress difference.

Simplifications of some of the theories are presented and take the form of series truncations of discrete relaxation functions or of empirical representations of continuous relaxation functions. Also discussed is the problem of the minimum data required to represent a viscoelastic fluid, with suggestions concerning the range of data needed. Finally, dimensionless groups are extracted from a combination of a constitutive theory with a momentum balance and applications to complex problems are discussed.

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CHAPTER I

INTRODUCTION

Weissenberg performed a demonstration at the 1946 meeting of the British Rheology Club that has become classic in demonstrating viscoelastic behavior (37). He showed that viscoelastic fluids respond to the simple act of being stirred with a rod in an unexpected manner: they climb up the rod rather than being thrown away from it as one would expect for Newtonian fluids. This behavior (the development of stresses normal to the plane of shear) is interpreted as a result of molecular tangling. Shear dependent viscosity and history dependent flow are also phenomena that are associated with such fluids. The study of these diverse non-Newtonian effects is at the heart of the subject of viscoelasticity.

Viscoelastic behavior can be detected in several ways. Roberts (39) developed experimental methods based on normal stress measurements. It can also be detected by observing the phase angle between stress and strain during sinusoidal strain. Other methods depend upon the nature of the transient response of a material subjected to a step stress or strain, or to recoil following steady shear.

The study of viscoelasticity has been pursued from two different viewpoints. The molecular approach concerns itself

with the causal relationships between molecular behavior and viscoelastic properties. Efforts in this area are generally restricted to studies of linear deformations or low shear rates.

The other approach is the study of large deformations from a macroscopic continuum viewpoint. Equations to describe gross behavior are developed in the framework of continuum mechanics, guided by considerations of dimensional consistency and coordinate invariance, and contain parameters to be experimentally evaluated.

Various attempts have been made to develop continuum-type constitutive equations but, so far, none of them has been satisfactory for all purposes. It is desirable to have an equation that is coordinate invariant, simple enough for combination with the basis balances of mechanics, and capable of correlating observed data using easily determined parameters.

Most of the equations can be placed in one of two categories: those that have stress related to some integral of strain and those that involve time derivatives of stress. Four different constitutive equations are examined in this dissertation. One, due to Oldroyd (32,33), is of the stress derivative form and the others, due to Pao (34,36), Bogue (7), and Bernstein, Kearsley, and Zapas (2,3), are of the strain integral form.

Oldroyd's theory has historical importance in that it is generally considered to be the first constitutive equation to have the qualitative features necessary for description of viscoelastic behavior. It is a generalization of linear viscoelastic theory.

Pao's (34,36) theory is developed by generalizing an equation for rubber elasticity to a convected coordinate system. Somewhat similar theories have been proposed by Fredrickson (21) and Walters (46); however, their theories do not predict non-Newtonian viscosities.

Bogue's (7) theory is a development and modification of the general continuum theories of Coleman and Noll (13,14). By making reasonable definitions for unspecified functions in the Coleman-Noll equations, Bogue developed a constitutive equation in their general framework that makes explicit predictions for viscometric and "near viscometric" flows.

The Bernstein-Kearsley-Zapas (2,3) theory is a generalization of the strain energy approach to elastic solid theory. The strain energy function of solid theory is replaced by the integral of an unspecified scalar function. Zapas (52) presents an empirical function from which explicit results are obtained.

In this work the theories are evaluated for their ability to correlate viscometric data (a necessary but not sufficient condition for their correctness), and in some

cases attempts are made at simplification. A fundamental question discussed is whether a non-linear theory may be cast in terms of experimentally determined parameters that are completely specified by linear data.

In pursuance of these objectives, non-Newtonian viscosity and first normal stress data were gathered for two polymeric solutions. Linear dynamic data were also gathered for the same solutions over a range of frequencies that is approximately equivalent to the shear rate range covered. A Weissenberg Rheogoniometer was used to make the measurements.

CHAPTER II

REVIEW OF THEORIES

Linear theory has been successful in treating viscoelastic behavior in which small strains or low shear rates are involved. This theory is well documented (for example, 20,45,48). The equations can be developed from analog systems of springs (representing elasticity) and dashpots (representing viscosity). The systems are composed of two basic elements, the Voigt and Maxwell elements, the components of which define constants for viscoelastic representation. (See Figure 1.) Analyses are made by determining the

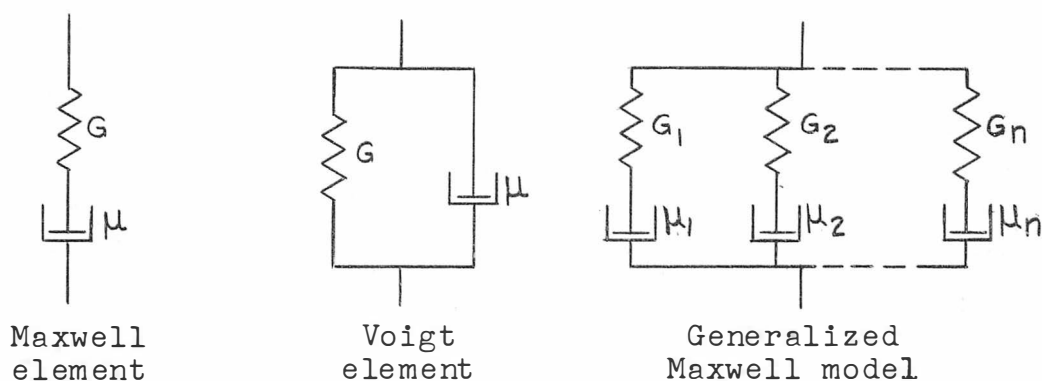


Figure 1. Illustration of Viscoelastic Models.

response of the system to a given linear (small) stress or strain input using non-convected time derivatives.

Linear viscoelastic data may be presented by a spectrum of paired values of λ_n and G_n , where the λ_n ,

relaxation times, are defined as μ_n/G_n . It is often convenient to define a continuous spectrum by allowing the number of elements in a model to become infinite. For instance, consider a generalized Maxwell model subjected to a step strain, γ_0 . The strain is identical for each element, and the total stress is the sum of the element stresses. Then the stress decay is given by (20)

$$\tau(t) = \gamma_0 \sum_n G_n e^{-t/\lambda_n}. \quad (\text{II-1})$$

Equation II-1 can be generalized to an infinite number of elements, giving

$$\tau(t) = \gamma_0 \int_0^{\infty} G(\lambda) e^{-t/\lambda} d\lambda, \quad (\text{II-2})$$

where $G(\lambda)$ is taken as a continuous function. Another quantity, $H(\lambda)$, is frequently used instead of $G(\lambda)$, where $H(\lambda) = \lambda G(\lambda)$. Then

$$\tau(t) = \gamma_0 \int_{-\infty}^{\infty} H(\lambda) e^{-t/\lambda} d \ln \lambda, \quad (\text{II-3})$$

where $H(\lambda)$ carries modulus units of stress. An equation similar to II-3 can be used to define $H(\lambda)$, the

relaxation spectrum, in preference to the use of mechanical models.

It is advantageous to have a non-linear theory that reduces to classical linear theory, since this provides a convenient special case and also enables one to make use of the available linear data. Except for Oldroyd's theory, the continuum theories considered here make explicit predictions for steady shear flow directly in terms of the relaxation spectrum, and Oldroyd's theory contains material constants that may be determined indirectly from linear data. Thus there is an important implication: non-linear results can be predicted with linear data (to within an adjustable constant in some theories). Continuum mechanics shows that there are no more than three independent material functions (the "viscometric functions" of Coleman and Noll, 11,31) for correlating viscometric flows, but it does not preclude the possibility of interdependence among the functions. In fact, several observed effects suggest such dependence: polymer solutions show a notable similarity between the frequency dependent linear dynamic viscosity and the non-linear shear dependent viscosity; in turbulent flow of concentrated polymer solutions, Meter (27) has supplied an "elastic" parameter by considering only the viscosity; and also large normal stress effects are usually associated with strongly non-Newtonian viscosities. Such suggestions of

interdependence of phenomenological functions are the motivation for considering the kinds of theories considered here.

It is usually difficult to make qualitative observations about a constitutive equation by inspection of its general form; however, insight can be gained by examining the special flows for which data are available. Since the supporting data for this dissertation are of simple shear or linear dynamic form, the constitutive equations will also be examined primarily for these flows. A discussion of the continuum theories considered here has already been presented by Bogue (7), and Bogue and Doughty (8).

I. LINEAR SINUSOIDAL STRAIN THEORY

Sinusoidal strain is a useful special case of linear strain. A viscoelastic fluid subjected to a small sinusoidal shear strain will exhibit a sinusoidal stress response with a phase angle shift, ϕ , in the range $0^\circ < \phi < 90^\circ$. (See Figure 2.) By comparison, an elastic solid will show zero

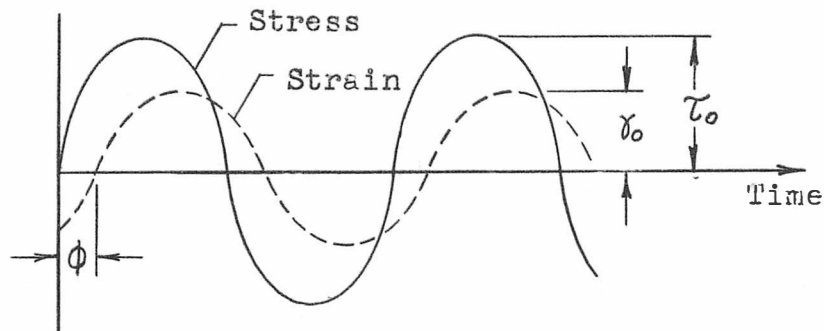


Figure 2. Linear Response to Sinusoidal Strain.

phase shift and an inelastic fluid will show a phase shift of 90° ; therefore, the phase angle shift can be taken as an indication of the elasticity at a given frequency. The elastic effect increases with frequency as the fluid has less time to relax.

The stress, strain, and shear rate (rate of strain) can be represented as complex functions:

$$\gamma^* = \gamma_0 e^{i\omega t}, \quad (\text{II-4})$$

$$\tau^* = \tau_0 e^{i(\omega t + \phi)}, \quad (\text{II-5})$$

$$K^* = \frac{d\gamma^*}{dt} = i\omega \gamma_0 e^{i\omega t}, \quad (\text{II-6})$$

where

- K = shear rate,
- t = time,
- γ = shear strain,
- ϕ = phase angle shift,
- τ = shear stress,
- ω = angular frequency,
- $()^*$ = a complex quantity,
- $()_0$ = an amplitude.

The complex modulus, G^* , is defined as τ^*/γ^* and the complex viscosity, η^* , as τ^*/K^* . These quantities are often resolved into components that are in-phase and

out-of-phase with the imposed strain. Thus:

$$G^* = G' + iG'' , \quad (\text{II-7})$$

and

$$\eta^* = \eta' + i\eta'' , \quad (\text{II-8})$$

where a prime denotes an in-phase component, and a double-prime denotes an out-of-phase component. Useful results from these equations are (20):

$$\frac{G''}{G'} = \frac{\eta'}{\eta''} = \tan \phi , \quad (\text{II-9})$$

$$G' = \frac{\tau_0}{\gamma_0} \cos \phi , \quad (\text{II-10})$$

$$G'' = \frac{\tau_0}{\gamma_0} \sin \phi , \quad (\text{II-11})$$

$$\eta' = \frac{\tau_0}{\omega \gamma_0} \sin \phi , \quad (\text{II-12})$$

$$\eta'' = \frac{\tau_0}{\omega \gamma_0} \cos \phi . \quad (\text{II-13})$$

The response can be expressed in terms of the visco-elastic constants, G_n and $\bar{\lambda}_n$, if some model is taken to represent the fluid. For instance, if the fluid is represented by the generalized Maxwell model, expressions for the complex viscosity and complex modulus become (20):

$$\eta' = \sum_n \frac{G_n \lambda_n}{1 + \omega^2 \lambda_n^2}, \quad (\text{II-14})$$

$$\eta'' = \sum_n \frac{\omega G_n \lambda_n^2}{1 + \omega^2 \lambda_n^2}, \quad (\text{II-15})$$

$$G' = \sum_n \frac{\omega^2 G_n \lambda_n^2}{1 + \omega^2 \lambda_n^2}, \quad (\text{II-16})$$

$$G'' = \sum_n \frac{\omega G_n \lambda_n}{1 + \omega^2 \lambda_n^2}. \quad (\text{II-17})$$

If the spectrum is taken to be continuous, the series expressions become integrals resulting in (20):

$$\eta' = \int_{-\infty}^{\infty} \frac{\lambda H(\lambda)}{1 + \omega^2 \lambda^2} d \ln \lambda, \quad (\text{II-18})$$

$$\eta'' = \int_{-\infty}^{\infty} \frac{\omega \lambda^2 H(\lambda)}{1 + \omega^2 \lambda^2} d \ln \lambda, \quad (\text{II-19})$$

$$G' = \int_{-\infty}^{\infty} \frac{\omega^2 \lambda^2 H(\lambda)}{1 + \omega^2 \lambda^2} d \ln \lambda, \quad (\text{II-20})$$

$$G'' = \int_{-\infty}^{\infty} \frac{\omega \lambda H(\lambda)}{1 + \omega^2 \lambda^2} d \ln \lambda. \quad (\text{II-21})$$

Since the function $H(\lambda)$ can be used to characterize linear viscoelastic behavior, one of the objectives of experimental work is its evaluation. Because of the integral form of the equations, however, approximation methods must be used to extract the function from experimental data. These methods are discussed in Chapter III.

II. OLDROYD'S THEORY

The first constitutive equations to be cast in tensor form were developed by Oldroyd (32,33). He was motivated by linear viscoelasticity and constructed his equations by replacing the time derivative of linear theory with convected time derivatives. His most general model contains eight material constants (32). A reduced model with three constants has been investigated by Williams and Bird (50,51) and is the form considered in this dissertation. Bird compares the role of Oldroyd's three-constant model with that of van der Waal's equation of state in non-ideal gas theories: both are simple and show the key qualitative features, although neither is accurate in detail (4).

The three-constant Oldroyd equation used by Williams and Bird is:

$$\tau_{ij} + \lambda_1 \left[\frac{\partial \tau'_{ij}}{\partial t} - \frac{1}{2} (\tau'_{ik} d_j^k + \tau'_{jk} d_i^k) + \frac{1}{3} \tau'_{kl} d^{lk} g_{ij} \right]$$

(continued on page 13)

$$= \eta_0 \left[d_{ij} + \lambda_2 \left\{ \frac{\partial d_{ij}}{\partial t} - \frac{1}{2} (d_{ik} d_j^k + d_{jk} d_i^k) + \frac{1}{3} d_{kl} d^{lk} g_{ij} \right\} \right]. \quad (\text{II-22})$$

In Equation II-22, the deviatoric stress, τ'_{ij} , is defined by

$$\tau_{ij} = -p g_{ij} + \tau'_{ij}, \quad (\text{II-23})$$

where τ_{ij} is the total stress and p is a scalar stress. It (p) will reduce to hydrostatic pressure in the static case if it is defined as

$$p = -\frac{1}{3} \tau^k_k. \quad (\text{II-24})$$

The convected derivative, $\partial \tau'_{ij} / \partial t$, is the Jaumann derivative, defined by

$$\frac{\partial \tau'_{ij}}{\partial t} = \frac{\partial \tau'_{ij}}{\partial t} + v^k \frac{\partial \tau'_{ij}}{\partial x^k} - \omega_i^k \tau'_{kj} - \omega_j^k \tau'_{ik}, \quad (\text{II-25})$$

where

$$\omega_i^k = \frac{1}{2} (g^{kj} v_{i|j} - v_{|i}^k) \quad (\text{II-26})$$

is the vorticity tensor. The quantities η_0 , λ_1 , and λ_2 are material constants.

In steady shear flow, Oldroyd's model yields the following relationships (26):

$$\frac{\tau_{12}}{K} = \eta = \eta_o \left(\frac{1+2/3 \lambda_1 \lambda_2 K^2}{1+2/3 \lambda_1^2 K^2} \right) , \quad (\text{II-27})$$

$$\frac{\tau_{11} - \tau_{22}}{K^2} = 2 \eta_o \left(\frac{\lambda_1 - \lambda_2}{1+2/3 \lambda_1^2 K^2} \right) , \quad (\text{II-28})$$

$$\tau_{22} - \tau_{33} = 0 . \quad (\text{II-29})$$

Linear sinusoidal results can also be expressed in terms of the same material constants. Results for the components of the complex viscosity are:

$$\eta' = \frac{\eta_o (1 + \lambda_1 \lambda_2 \omega^2)}{(1 + \lambda_1^2 \omega^2)} , \quad (\text{II-30})$$

and

$$\eta'' = \frac{\eta_o \omega (\lambda_1 - \lambda_2)}{(1 + \lambda_1^2 \omega^2)} . \quad (\text{II-31})$$

Thus, one predicts that the dynamic viscosity has the same general form and same asymptotic values as the apparent viscosity. The imaginary component approaches zero at both large and small frequencies and has a maximum value of

$$\left[\eta_o / 2 \right] \left[1 - \lambda_2 / \lambda_1 \right] \text{ at } \omega = 1 / \lambda_1 .$$

III. PAO'S THEORY

Pao's (34,36) continuum theory was developed by

extending an equation for rubber elasticity to a convected coordinate system and then defining transformations to relate the behavior back to laboratory coordinates. The equation which provides the starting point for the theory is:

$$\tau'_{ij} + p \delta_{ij} = G(C^{-1})_{ij} . \quad (\text{II-32})$$

This is a simplification of the Mooney relations (29) suggested by the experimental work of Rivlin and Saunders as discussed by Truesdell (44). The equation was given the ability to allow stress relaxation after an increment of strain by modifying it to

$$\Delta(\tau'_{ij} + p \delta_{ij}) = G e^{-\frac{t-\xi}{\lambda}} \Delta(C^{-1})_{ij}, \quad (\text{II-33})$$

where t is time, ξ is a past reference time, and λ is a relaxation time. Since polymeric behavior is dependent on a spectrum of relaxation times, the stress was expressed as the sum of the contribution of each relaxation time.

Thus:

$$\Delta(\tau'_{ij} + p \delta_{ij}) = \sum_n G_n e^{-\frac{t-\xi}{\lambda_n}} \Delta(C^{-1})_{ij} . \quad (\text{II-34})$$

Finally, the equation was put into integral form by assuming that the increments in $(C^{-1})_{ij}$ are numerous and closely spaced. Then:

$$\tau'_{ij+p} \delta_{ij} = \int_{t_0}^t \sum_n G_n e^{-\frac{t-\xi}{\lambda_n}} \frac{d}{d\xi} (C^{-1})_{ij} d\xi . \quad (\text{II-35})$$

Equation II-35 is similar to one developed by Lodge (25) and does not predict non-Newtonian viscosities as it stands; however, it does have the capability of reducing to Newtonian fluid description for very short relaxation times and to rubber description for very long relaxation times.

Pao next introduced the concept of a natural state from which the strain must be measured in a relaxing fluid. $(r^{-1})_{ij}$ are the components of this strain, and Equation II-35 becomes:

$$\tau'_{ij+p} \delta_{ij} = \int_{t_0}^t \sum_n G_n e^{-\frac{t-\xi}{\lambda_n}} \frac{d}{d\xi} (r^{-1})_{ij} d\xi . \quad (\text{II-36})$$

To complete the theory, an equation of the form of Equation II-36 was written in a convected coordinate system:

$$\tau'_{ab+p} \delta_{ab} = \int_{t_0}^t \sum_n G_n e^{-\frac{t-\xi}{\lambda_n}} \frac{d}{d\xi} (r^{-1})_{ab} d\xi . \quad (\text{II-37})$$

In the present discussion, transformations between the components of the convected coordinates, denoted by indices a and b , and the laboratory coordinates, denoted by i and

j , are defined by

$$\begin{aligned} \frac{d}{dt}(r^{-1})_{ab} = & \frac{\partial}{\partial t} \left[(r^{-1})_{ij} \frac{\partial y^a}{\partial x^i} \frac{\partial y^b}{\partial x^j} \right] \\ & + \frac{\partial y^a}{\partial x^i} \frac{\partial y^b}{\partial x^j} \frac{\partial (r^{-1})_{ij}}{\partial x^k} \frac{dx^k}{dt} \end{aligned} \quad (\text{II-38})$$

and

$$\tau'_{ab} = \tau'_{ij} \frac{\partial y^a}{\partial x^i} \frac{\partial y^b}{\partial x^j} . \quad (\text{II-39})$$

The derivative defined by Equation II-38 is similar to the Jaumann derivative; the difference is that Pao's derivative tracks the fluid for a finite time rather than differentially.

Both Equations II-36 and II-37 are required for explicit prediction of flow results. Pao assumed that the stress components in both coordinate systems depend only on those strain components which carry the same subscripts as the stress components. (For instance, τ'_{12} depends only on $(r^{-1})_{12}$ and $d/d\xi (r^{-1})_{12}$, etc.) Unfortunately, Pao does not elaborate on this assumption, and its justification is not obvious. While one expects τ'_{12} to depend only on $(r^{-1})_{12}$ in the convected coordinate system (see Equation II-32), one does not necessarily expect this kind of relationship after transformation; however, it does enable the use of Equations II-36 and II-37 to eliminate the $(r^{-1})_{ij}$

components and predict explicit results for viscometric flows. For further discussion, see Appendix B.

The results predicted for steady viscometric flows are (36):

$$\frac{\tau'_{12}}{K} = \eta = P_1 + K^2 \frac{(P_2)^2}{P_1} \quad (\text{II-40})$$

and

$$\frac{\tau'_{11} - \tau'_{22}}{K^2} = 2 \left[P_2 + K^2 \frac{(P_2)^3}{(P_1)^2} \right], \quad (\text{II-41})$$

where the shear dependent variables P_1 and P_2 can be expressed either in terms of discrete spectra or continuous spectra:

$$P_1 = \sum_n \frac{G_n \lambda_n}{1 + K^2 \lambda_n^2} \equiv \int_{-\infty}^{\infty} \frac{\lambda H(\lambda) d \ln \lambda}{1 + K^2 \lambda^2} \quad (\text{II-42})$$

and

$$P_2 = \sum_n \frac{G_n \lambda_n^2}{1 + K^2 \lambda_n^2} \equiv \int_{-\infty}^{\infty} \frac{\lambda^2 H(\lambda) d \ln \lambda}{1 + K^2 \lambda^2} . \quad (\text{II-43})$$

Thus, Pao's theory makes explicit non-Newtonian predictions directly from linear viscoelastic data. In principle, an equation for $\tau'_{22} - \tau'_{33}$ can be obtained, but it is not presently available.

IV. THE BERNSTEIN-KEARSLEY-ZAPAS THEORY

A viscoelastic fluid theory has been developed by Bernstein, Kearsley, and Zapas (2,3) that is motivated by the form of the strain energy equation for purely elastic solids. For incompressible, isothermal flows their theory can be written as:

$$\tau'_{ij} = -p g_{ij} + 2 \int_{-\infty}^t \left\{ \frac{\partial U}{\partial I} c_{ij}^{-1}(t, t') - \frac{\partial U}{\partial II} c_{ij}(t, t') \right\} dt' , \quad (\text{II-44})$$

where

$$\left. \begin{aligned} c_{ij}^{-1} &= g^{ab} g_{ki} g_{lj} \frac{\partial x^k}{\partial X^a} \frac{\partial x^l}{\partial X^b} \\ (c^{-1})^{kl} &= g^{ab} \frac{\partial x^k}{\partial X^a} \frac{\partial x^l}{\partial X^b} \end{aligned} \right\} \begin{array}{l} \text{relative Finger} \\ \text{strain tensor} \end{array} ,$$

$$c_{ij} = g_{ab} \frac{\partial X^a}{\partial x^i} \frac{\partial X^b}{\partial x^j} \quad \begin{array}{l} \text{relative Cauchy} \\ \text{strain tensor} \end{array} ,$$

x^i = coordinates of points at time t ,

X^i = coordinates of points at earlier time t' ,

t' = a dummy time index,

$U = U(I, II, t-t')$, an unspecified scalar function.

The motivation for the form of Equation II-44 can be seen by comparing it with purely elastic theory (38):

$$\tau'_{ij} = -pg_{ij} + \frac{\partial W}{\partial I} c_{ij}^{-1} - 2 \frac{\partial W}{\partial II} c_{ij} . \quad (\text{II-45})$$

The connection between W and U is expressed by

$$\frac{\partial U(I, II, t-t')}{\partial I} = \frac{\partial^2 W(I, II, t-t')}{\partial I \partial t'} \quad (\text{II-46})$$

and

$$\frac{\partial U(I, II, t-t')}{\partial II} = \frac{\partial^2 W(I, II, t-t')}{\partial II \partial t'} . \quad (\text{II-47})$$

The W in Equations II-46 and II-47, however, does not have the same functional dependence as the W in Equation II-45; nor does it have the same physical interpretation. In Equation II-45, W is the strain energy function which is independent of time; in Equations II-46 and II-47, W is a decaying function of time and has no direct physical association. In an important application of this theory, Zapas and Craft (54) have shown that any uniaxial strain history can be predicted from the results of a single step stress-relaxation experiment (covering the same range of extension and time) without any assumption as to the form of the function W , showing that the form of Equation II-44 is reasonable, though not necessarily unique. For most

problems involving fluid polymer behavior, however, it is necessary to choose an empirical form for the function to fit data. Zapas (53) has advanced such a function (not published yet) which he developed from elastic rubber behavior. The reasonableness of the function is enhanced by the fact that the same form can be used for fluid behavior by allowing the material parameters to become functions of time. The function is

$$\begin{aligned}
 W(I, II, s) = & \frac{\alpha(s)}{2}(I-3)^2 + \frac{3}{4}m(s) \ln\left(\frac{I+II-3}{3}\right) \\
 & + 7 \left[\frac{3}{4}m(s) - c(s) \right] \ln\left(\frac{I+6}{II+6}\right) + c(s)(I-3) , \\
 & \text{(II-48)}
 \end{aligned}$$

where $m(s)$, $c(s)$, and $\alpha(s)$ are decaying functions of time, and $s=t-t'$ is a backward running time. Then, from Equation II-48,

$$\begin{aligned}
 - \frac{\partial U}{\partial I} = - \frac{\partial^2 W}{\partial I \partial t'} = & \alpha'(s)(I-3) + \frac{3}{4}m'(s)\left(\frac{1}{I+II-3}\right) \\
 & + 7 \left[\frac{3}{4}m'(s) - c'(s) \right] \frac{c'(s)}{I+6} + c'(s) \\
 & \text{(II-49)}
 \end{aligned}$$

and

$$\begin{aligned}
 - \frac{\partial U}{\partial II} = - \frac{\partial^2 W}{\partial II \partial t'} = & \frac{3}{4}m'(s) - \frac{7 \left[\frac{3}{4}m'(s) - c'(s) \right]}{II+6} . \\
 & \text{(II-50)}
 \end{aligned}$$

A variety of viscosity functions can be predicted depending on the form of the functions α , m , and c . Zapas states (53) that the function α is necessary only for shear-thickening behavior, and that c is unimportant for polyisobutylene and similar solutions at low or moderate shear rates. The function must be included, however, to predict the high shear rate plateau observed for polymer systems.

Setting α equal to zero produces the following results for viscometric flows:

$$\frac{\tau'_{12}}{K} = \eta = \int_0^{\infty} \left[\frac{-m'(s)}{1 + \frac{2}{3}K^2s^2} - 2c'(s) \right] s ds, \quad (\text{II-51})$$

$$\frac{\tau'_{11} - \tau'_{22}}{K^2} = \int_0^{\infty} \left[\frac{-m'(s)}{1 + \frac{2}{3}K^2s^2} - 2c'(s) \right] s^2 ds, \quad (\text{II-52})$$

$$\frac{\tau'_{22} - \tau'_{33}}{K^2} = \int_0^{\infty} \left[\frac{\frac{3}{2}m'(s)}{3 + 2K^2s^2} - \frac{14 \left[\frac{3}{4}m'(s) - c'(s) \right]}{9 + K^2s^2} \right] s^2 ds. \quad (\text{II-53})$$

Although Zapas does not choose an explicit form for $m(s)$, a series of exponentials is convenient and reasonable in that the theory will then reduce to the classical spectrum

of Maxwell elements in linear viscoelastic deformations.

Thus,

$$m(s) = \sum_n G_n e^{-s/\lambda_n} \equiv \int_{-\infty}^{\infty} H(\lambda) e^{-s/\lambda} d \ln \lambda, \quad (\text{II-54})$$

and

$$m'(s) = \sum_n \frac{G_n}{\lambda_n} e^{-s/\lambda_n} \equiv \int_{-\infty}^{\infty} \frac{H(\lambda)}{\lambda} e^{-s/\lambda} d \ln \lambda. \quad (\text{II-55})$$

For this assumed form for $m(s)$, the Bernstein-Kearsley-Zapas theory makes the following predictions for simple shear flow with $c=0$:

$$\frac{\tau'_{12}}{K} = \eta = \int_0^{\infty} \int_{-\infty}^{\infty} \frac{H(\lambda) e^{-s/\lambda} s}{\lambda(1+\frac{2}{3}K^2 s^2)} d \ln \lambda ds, \quad (\text{II-56})$$

$$\frac{\tau'_{11} - \tau'_{22}}{K^2} = \int_0^{\infty} \int_{-\infty}^{\infty} \frac{H(\lambda) e^{-s/\lambda} s^2}{\lambda(1+\frac{2}{3}K^2 s^2)} d \ln \lambda ds, \quad (\text{II-57})$$

$$\frac{\tau'_{22} - \tau'_{33}}{K^2} = -\frac{3}{2} \int_0^{\infty} \int_{-\infty}^{\infty} \frac{H(\lambda) e^{-s/\lambda} (12+13K^2 s^2) s^2}{\lambda(3+2K^2 s^2)(9+K^2 s^2)} \cdot d \ln \lambda ds. \quad (\text{II-58})$$

Equations II-56, II-57, and II-58 must be integrated numerically except for low shear rates.

V. BOGUE'S THEORY

Viscoelastic constitutive equations have been developed by Bogue (7) by empirically modifying an equation from the general continuum theories of Coleman and Noll (13,14). The modification starts with the second order theory of Coleman and Noll:

$$\begin{aligned} \tau'_{ij} = & -p g_{ij} + \int_0^\infty m(s) J_{ij}(s) ds \\ & + \int_0^\infty \int_0^\infty \left[b(S_a, S_b) J_{ik}(S_a) J_j^k(S_b) \right. \\ & \left. + c(S_a, S_b) J_k^k(S_a) J_{ij}(S_b) \right] dS_a dS_b . \quad (\text{II-59}) \end{aligned}$$

In Equation II-29, $J_{ij}(s) = g_{kl}(\partial X^k / \partial x^i)(\partial X^l / \partial x^j)$ is the deformation history tensor; $m(s)$, $b(S_a, S_b)$, and $c(S_a, S_b)$ are unspecified decay functions; s , S_a , and S_b are backward running time indices.

The theory represented is incompressible, finite, and second order: finite in that it is not restricted to small deformations, and second order in that it weighs fluid history to some second order extent. As a consequence of

the latter condition, one would not expect it to be valid for flows that change rapidly with time or in which the flow varies rapidly along a streamline. It is valid for viscometric and "near viscometric" flows. It is the least general simple fluid theory that reduces to classical linear viscoelasticity, predicts normal stresses and stress relaxation. It does not, however, predict non-Newtonian viscosities without including a triple integral term with additional unspecified functions. This important characteristic was added to Bogue's theory by adjusting the memory function using qualitative concepts from Pao's theory.

Bogue's general equation has the form:

$$\begin{aligned} \tau'_{ij} = & -p g_{ij} + \int_0^\infty \frac{dm_k(s)}{ds} J_{ij}(s) ds \\ & + \int_0^\infty \int_0^\infty \left[\frac{d^2 b_k(s_a)}{ds_a ds_b} J_{ik}(s_a) J_j^k(s_b) \right. \\ & \left. + \frac{d^2 c_k}{ds_a ds_b} J_k^k(s_a) J_{ij}(s_b) \right] ds_a ds_b, \quad (\text{II-60}) \end{aligned}$$

where

$$\begin{aligned} m_k(s) &= \sum_n G_n e^{-\alpha'_n(s)}, \\ b_k(s_a, s_b) &= 2 \sum_n G_n e^{-\alpha'_n(s_a) - \alpha'_n(s_b)}, \end{aligned}$$

c_k = an unspecified function of the same
magnitude as $b_k(S_a, S_b)$,

$$\left. \begin{aligned} \alpha_n(s) &= \frac{s}{\lambda_n} + a |II_J|^{1/2} \\ \alpha'_n(S_a) &= \frac{S_a}{\lambda_n} + a' |II_J(S_a)|^{1/2} \end{aligned} \right\} a' \gg a .$$

Bogue's memory function, $m_k(s)$, is seen to be a function of the second invariant, II_J , as well as a function of time. The physical motivation for this is the idea that a fluid is influenced less by its history if it is being strained rapidly.

The deformation history tensor for smooth flows may be written (30)

$$J_{ij}(s) = -d_{ij}s + \frac{1}{2}A_{ij}^{(2)}s^2 + \dots , \quad (II-61)$$

where

$$A_{ij}^{(2)} = \frac{\partial d_{ij}}{\partial t} + v^k_d{}_{ji|k} + d_{ik}v^k_{|j} + d_{kj}v^k_{|i} \quad (II-62)$$

is the second Rivlin-Ericksen tensor. Neglecting the higher order terms in Equation II-61 and approximating the second invariant by

$$II_J = II_d s^2 , \quad (II-63)$$

the theory can be combined with the continuity equation to develop equations that predict explicit results for "near

viscometric" flows and reduce to classical linear viscoelastic equations. (The terms neglected in Equations II-61 and II-63 are identically zero for viscometric flows.)

For viscometric flows, Bogue's theory makes the following predictions:

$$\frac{\tau'_{12}}{K} = \eta, \quad (\text{II-64})$$

$$\frac{\tau'_{11} - \tau'_{22}}{K^2} = -2\gamma, \quad (\text{II-65})$$

$$\frac{\tau'_{22} - \tau'_{33}}{K^2} = \beta + 2\gamma, \quad (\text{II-66})$$

where

$$\eta(K) = \sum_n \frac{G_n \lambda_n}{1+a|K|\lambda_n} \equiv \int_{-\infty}^{\infty} \frac{H(\lambda) d \ln \lambda}{1+a|K|\lambda}, \quad (\text{II-67})$$

$$\gamma(K) = - \sum_n \frac{G_n \lambda_n^2}{(1+a|K|\lambda_n)^2} \equiv - \int_{-\infty}^{\infty} \frac{\lambda H(\lambda) d \ln \lambda}{(1+a|K|\lambda)^2}, \quad (\text{II-68})$$

and

$$\beta(K) = 2 \sum_n \frac{G_n \lambda_n^2}{(1+a'|K|\lambda_n)^2} \equiv 2 \int_{-\infty}^{\infty} \frac{\lambda H(\lambda) d \ln \lambda}{(1+a'|K|\lambda)^2}. \quad (\text{II-69})$$

Bogue's theory may also be used to obtain solutions to other flows of interest such as finite strain relaxation

following steady shear (recoil), finite stress relaxation following cessation of steady shear, and stress growth at commencement of steady shear (7). In the latter flow it has the capability of predicting a peak stress that is higher than the steady state stress, a commonly observed phenomena known as overshoot.

CHAPTER III

EXPERIMENTAL APPARATUS AND METHODS

To evaluate the theories presented, both linear dynamic and non-linear shear data were needed for the same fluids covering a wide range of frequencies and shear rates. A literature survey failed to reveal any work in which linear dynamic data, non-Newtonian viscosity data, and normal stress data were displayed for the same polymer solution. In one report, Bogue (7) used the dynamic data of DeWitt, Markovitz, Padden, and Zapas (18) with the viscosity data of Brodnyan, Gaskins, and Philippoff (10). However, he was forced to compare non-linear data from a 5 per cent weight solution with linear data from an interpolated 6.6 per cent solution in order to have the dynamic data predict the correct zero shear viscosity. Because of the sensitivity of the solutions to concentration, mixing techniques, and possibly to aging, it is more desirable to obtain all data from samples of one batch over as short a time period as possible.

The solutions tested were 10 per cent weight polyisobutylene in Decalin and 12 per cent polystyrene in Aroclor. The solutes are identified in Table I. All tests were conducted at 25°C.

A concurrent birefringent study of the polystyrene

TABLE I
IDENTIFICATION OF POLYMER SOLUTES

Solute	Identification	Approximate Molecular Weight	Formula
Polystyrene	Styron 666 K27-71 Lot PHC93 Dow Chem. Co.	170,000	$\left[\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{C}_6\text{H}_5 \end{array} \right]_n$
Polyisobutylene	Vistanex L-100 Enjay	90,000	$\left[\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}-\text{CH}_2- \\ \\ \text{CH}_3 \end{array} \right]_n$

solution in two-dimensional flow was made by Adams (1), and capillary studies were made by LaNieve (24) of both solutions. Measurements were also attempted on a napalm solution in conjunction with recoil studies by Cox (15); unfortunately, equipment sensitivity did not allow linear dynamic data and difficulties in obtaining steady state shear also restricted the range on viscosity and normal stress data (see Appendix D).

I. THE WEISSENBERG RHEOGONIOMETER

All data were taken on a Weissenberg Rheogoniometer (45), manufactured by Farol Research Ltd., Bognor Regis, Sussex, England. It is capable of making all the measurements needed (dynamic, viscous, and normal stress).

The instrument is basically a cone and plate rheometer (although other configurations can be used). It is driven by two synchronous motors each of which drives through a gear box with 60 ratios from 1:1 to a reduction ratio of $10^{5.9}:1$ in logarithmic steps. One motor-gear system provides a constant angular velocity drive for the cone and plate, and the other provides the sinusoidal drive through a cam and worm gear mechanism. The torque on the upper member of the cone and plate combination (the undriven member) is transmitted through an air bearing to a calibrated torsion rod, and the rotation of one end of the torsion rod is

measured by an electric transducer. This provides a measure of the torque transmitted through the sample from which the shear stress can be determined. The lower member of the cone and plate is fastened to a shaft which rests near the center of a calibrated leaf spring. A servo system adjusts one end of the spring to maintain a constant gap between the cone and plate system as it is influenced by normal stresses. The net normal thrust is determined by the amount of end adjustment required to hold the gap constant. All readings are transduced to electrical impulses. The environment temperature around the sample is controlled by a temperature housing with constant temperature water circulating through it. Sample temperature was indicated by a thermocouple mounted in the upper member of the cone and plate. A control of about $\pm 1/4^{\circ}\text{C}$. was indicated by the thermocouple. (The viscous heating effect is discussed later in this chapter.)

The rheogoniometer used is capable of producing steady shear rates in the range from about 5,500 to 0.001 sec.^{-1} , and sinusoidal strain frequencies from 60 c.p.s. to 7.5×10^{-5} c.p.s. Possible shear stress measurements range from 0.8 to 3.6×10^6 dynes/sq.cm., and normal stress measurements from 1.3 to 6.3×10^4 dynes/sq.cm. (45). The ranges given vary somewhat according to the auxiliary equipment available and, in the case of the stress limits, according to the precision required for the measurement. Also,

the lower limits on the frequency and shear rate range are misleading because the strain input is affected by mechanical "noise" from the drive system.

Measurements on the Weissenberg Rheogoniometer do not require calibration with fluids of known properties; however, comparisons were made with independent data from other sources to be certain that no instrument constants had been miscalculated. Data for the polyisobutylene solution were compared with viscosity data by LaNieve (24) (see Figure 3); normal stress data provided by Tennessee Eastman Co., of Kingsport, Tennessee (see Figure 4); and dynamic data by DeWitt, Markovitz, Padden, and Zapas (18) (see Figure 5).

The torsion rods were calibrated by the manufacturer; however, the leaf springs for normal force measurement had to be calibrated in place. This was done by the author by placing standard weights directly on the plate with everything except the cone in the operating condition. Of all measurements made, the normal force measurements were the least reproducible. A data scatter of ± 10 per cent was found in calibrating the springs; however, the maximum scatter occurred for the smallest measurable values of normal force (about 10,000 dynes). The data scatter was about ± 1.5 per cent for the largest forces used in the calibration (4.9×10^5 dynes).

All steady-state measurements were read directly from

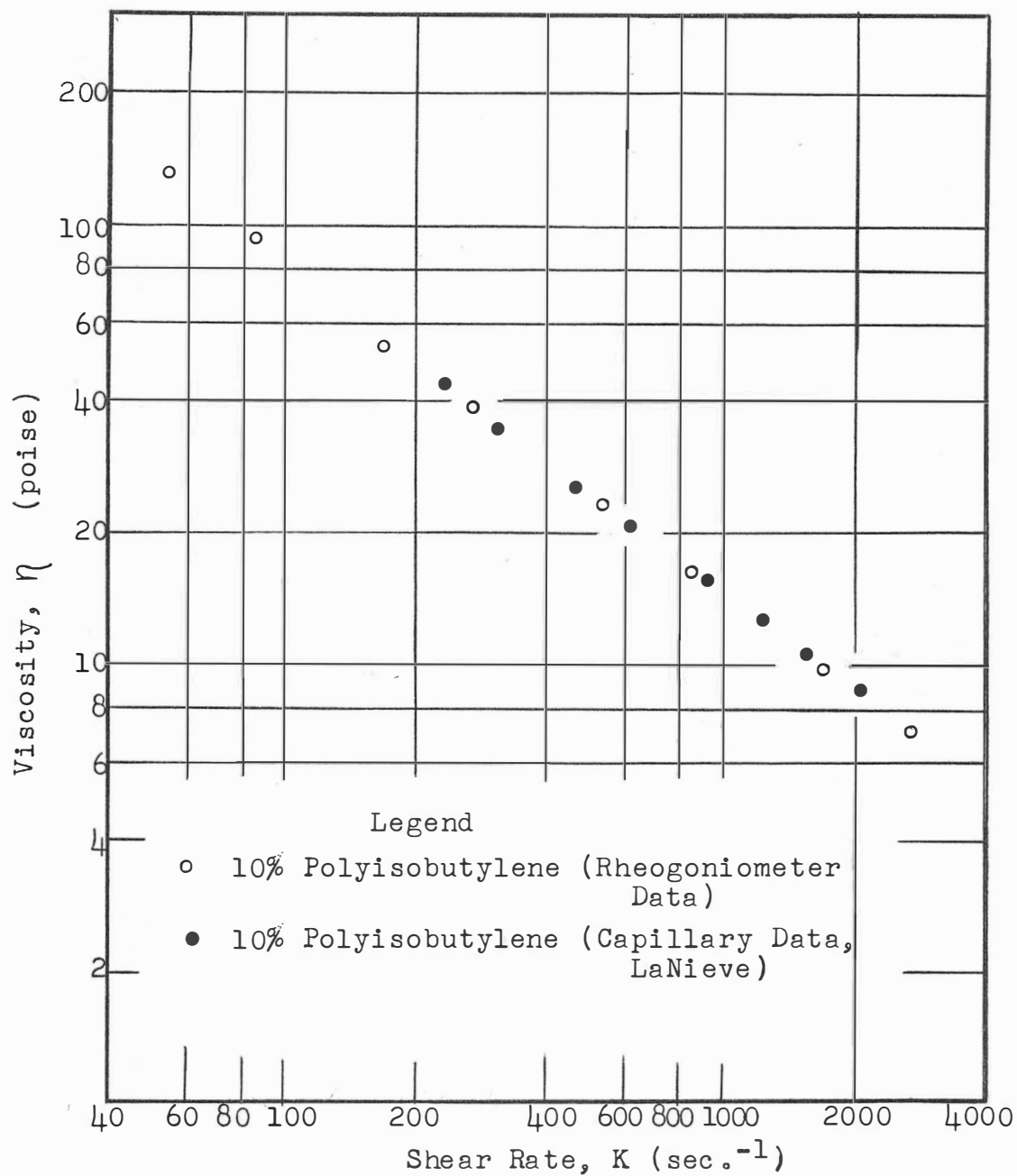


Figure 3. Comparison of Rheogoniometer Viscosity Data with Capillary Data.

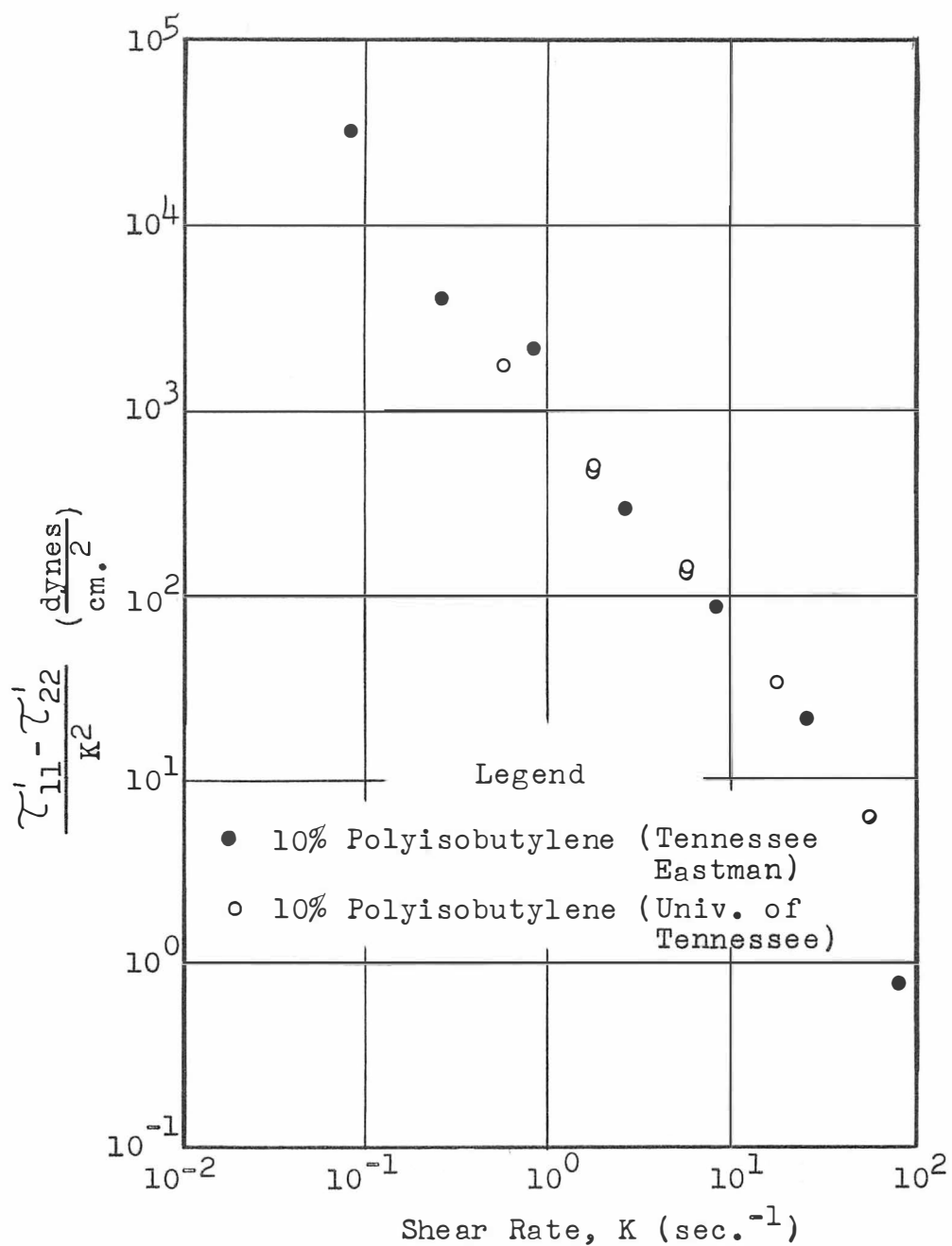


Figure 4. Comparison of Normal Stress Data with Data from Tennessee Eastman Corporation.

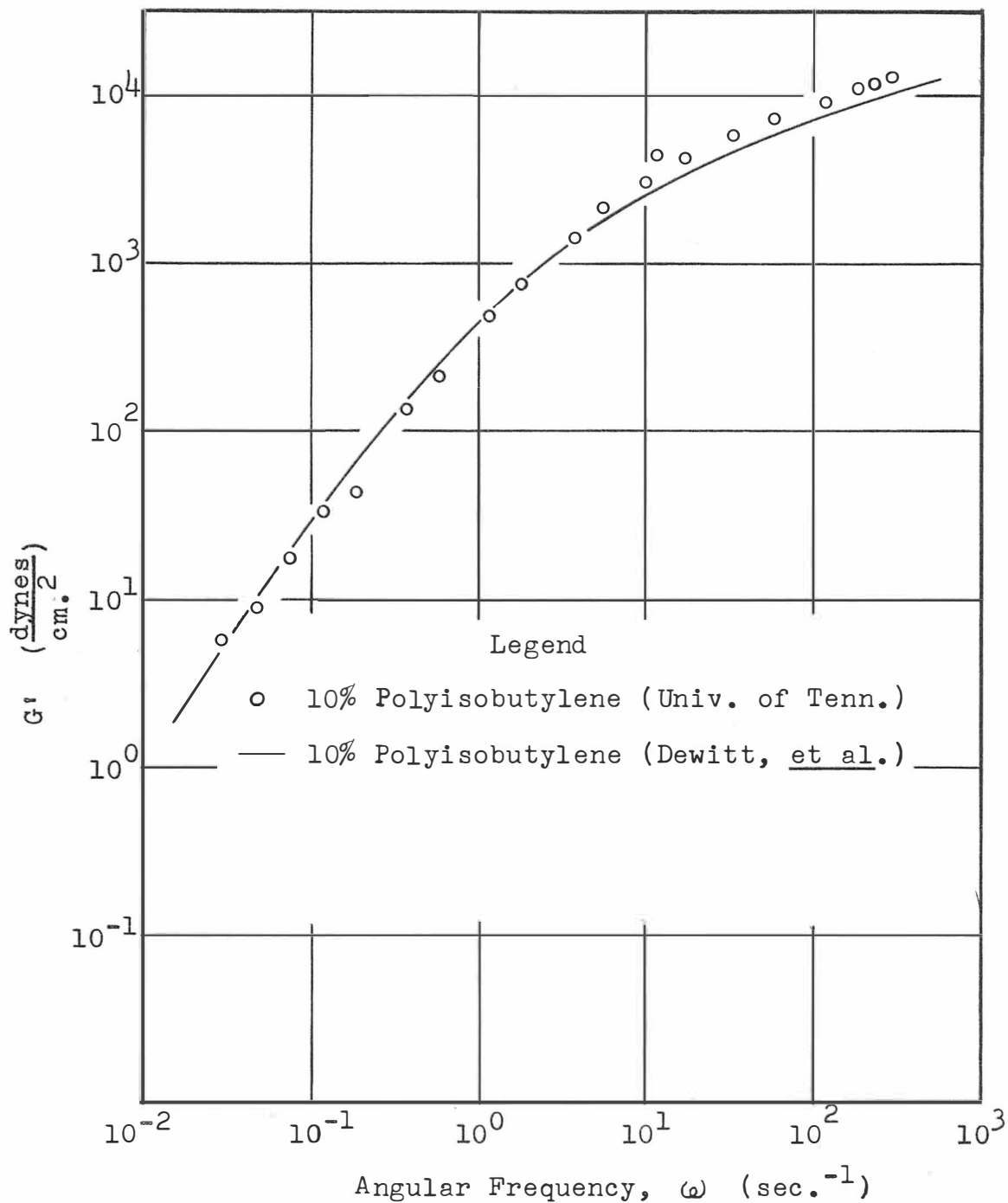


Figure 5. Comparison of Dynamic Data with Data by Dewitt, et al.

instruments in the package supplied by the manufacturer. The oscillation measurements were made by feeding the transduced stress and strain signals into a dual channel Tektronix 502 oscilloscope for high frequency measurements and into a dual channel Sanborn 150 chart recorder for low frequency measurements.

II. CONE AND PLATE THEORY

A development of rheological equations for the cone and plate is given in Appendix B. Some of the more important results will be presented here, along with a discussion of inherent inaccuracies in the instrument.

The cone and plate geometry makes an ideal configuration for non-Newtonian viscometric measurements because, except for certain negligible effects, the sample experiences the same shear rate throughout.

The shear rate is given by

$$K = \frac{\omega}{\alpha} , \quad (\text{III-1})$$

where ω is the rotational speed of the cone and α is the angle between the cone and plate. The shear stress is related to the torque by

$$\tau_{12} = \frac{3T}{2\pi R^3} , \quad (\text{III-2})$$

where T is the torque and R is the radius of the cone and plate.

The normal stress difference, $\tau'_{11} - \tau'_{22}$, can be related to the total thrust against the cone without any assumptions about relationships existing among the normal stresses. The expression is

$$\tau'_{11} - \tau'_{22} = \frac{2F}{\pi R^2}, \quad (\text{III-3})$$

where F is the total thrust. In deriving this equation, one finds that the normal stress varies logarithmically with radius as was shown experimentally by Roberts (39) in his first use of the cone and plate as a rheogoniometer. That is,

$$-\frac{\partial \tau_{11}}{\partial (\ln r)} = \tau'_{11} + \tau'_{22} - 2\tau'_{33}, \quad (\text{III-4})$$

where the right side of the equation is independent of r .

Some of the major causes of inexactness in the cone and plate are:

1. It is physically impractical to use cone angles of less than $1/2$ degree.
2. The vertex of the cone is truncated to prevent mechanical contact with the plate.
3. There is an edge effect at the free surface of the sample. (The surface may be concave or

convex.)

4. Inertial effects can cause a radial pressure gradient and also secondary flow.
5. There will be a temperature gradient through the sample because of viscous heating.

For most tests the errors resulting from the conditions stated above can be made negligible by the geometry of the cone and plate. Use of a small cone angle minimizes the error involved for conditions 1, 3, 4, and 5. Use of a small radius minimizes 4 and 5, and the effect of condition 2 is minimized by making the vertex truncation as small as possible.

In making normal stress measurements, Ginn and Metzner (22,23) found it necessary to make corrections for centrifugal and edge effects. This was accomplished by making measurements on Newtonian fluids under conditions similar to those for which the viscoelastic data were taken and correcting the viscoelastic data according to the inelastic readings (i.e., assuming any normal force reading on a Newtonian fluid to be a measure of the error involved). However, in the present work, normal force measurements were made on NBS Oil M and a normal stress of only 455 dynes per square centimeter was observed for the most adverse conditions (i.e., a large radius cone operating at a large angular velocity). Since the fluids tested for this

dissertation showed a normal stress difference on the order of 10^5 dynes/sq.cm. at similar shear rates, the error was considered to be insignificant.

The effect of viscous heating was approximated by an equation given by Bird and Turian (6) for a cone and plate geometry:

$$\Delta T_{MAX} = \frac{3T\omega\alpha}{16\pi kR} . \quad (III-5)$$

High shear rate measurements were taken on a 2.5 cm.-diameter cone and plate with a cone angle of $1/2^\circ$. The highest shear rate tested was $5,410 \text{ sec.}^{-1}$ and the largest viscosity observed at that condition was 24.1 poise. Using an estimated thermal conductivity of 0.08 B.T.U./hr.-ft.- $^\circ\text{F.}$, an estimated maximum temperature difference of 0.7°C. existed in the sample.

III. EXPERIMENTAL METHODS

All steady state data were taken as prescribed by the manufacturer of the rheogoniometer (19). The major difficulty was that of maintaining the correct sample temperature. All data were taken at an indicated temperature of $25^\circ\text{C.} \pm 1/4^\circ$. Unfortunately, room temperature control was not within the limits desired. Sample temperature control was accomplished by enclosing the cone and plate in the

temperature control housing and allowing them to stabilize at operating temperature while the sample was immersed in a temperature bath. The sample was then loaded as quickly as possible and measurements were taken. This technique was essential with the polyisobutylene-Decalin solution because the solvent showed evidence of evaporation within an hour after loading. The evaporation of the Aroclor in the polystyrene-Aroclor system was slower.

Oscillation stress and strain data were recorded on the Sanborn 150 dual channel chart recorder for frequencies below about 1 c.p.s. Amplitude measurements were made directly from the chart. Phase angle shifts were measured from the chart by projecting the stress intercepts on the time axis laterally to the strain time axis and comparing the intercept shift with a measured cycle for the strain wave. This technique could not be used for higher frequencies because the maximum paper feed on the recorder was 100 mm./sec., and a minimum cycle distance of about 100 mm. is required to make reliable phase shift measurements.

For frequencies above 1 c.p.s., the oscillation output was fed into a dual channel oscilloscope. Measurements were taken by superimposing the stress and strain waves on the same time axis. It was necessary to filter the signals before they could be measured because the signal carrier frequency of 1,000 c.p.s. could be followed by the

oscilloscope. This caused considerable attenuation in the signals, but that was of no concern since both signals were attenuated by the same ratio, and only the ratio of the amplitudes is significant.

IV. DATA REDUCTION METHODS

Calculation of steady-state shear rates, viscosities and normal stress differences was made directly from Equations III-1, III-2, and III-3, using the instrument calibration constants discussed earlier. Components of the complex viscosity and complex modulus were also made directly using Equations II-9 through II-13; however, approximate methods had to be used to determine the relaxation spectrum (see Chapter II). Several methods are listed by Ferry (20) for approximating the spectrum from components of the complex modulus or complex viscosity. The method of Swarzl and Staverman (42) was rather arbitrarily selected for calculating a first approximation for the spectrum. Their equation is

$$H(\lambda) = \frac{2}{\pi} \left[G'' - \frac{d^2 G''}{d(\ln \omega)^2} \right] \frac{1}{\omega} = \lambda \quad (III-6)$$

A Fortran computer program was developed to facilitate the use of Equation III-6 with dynamic data (see Appendix C). Fundamentally, the program operates by fitting a parabola

to data points $n-2$, n , and $n+2$ (where the points are numbered successively for increasing ω) and evaluating $H(\lambda = \frac{1}{\omega})$ for the ω corresponding to point n . It then moves to point $n+1$ and utilizes points $n-1$, $n+1$, and $n+3$ to calculate $H(\lambda = \frac{1}{\omega})$ for the ω corresponding to point $n+1$. This process is continued to point $m-2$, where there are m data points. It was necessary to fit the parabola to points separated by one intervening point in order to keep the derivatives in Equation III-6 from being too greatly affected by data scatter. Thus, the technique had a "smoothing" effect on the data which was found by experience to be necessary.

From the initial approximation of the relaxation spectrum a corrected spectrum was obtained by successive numerical adjustments that were continued until the final spectrum produced the G'' versus ω curve using Equation II-17. The adjustments were made by simply changing the relaxation spectrum by the amount of the difference in points on the curve obtained from integrating the spectrum being corrected and corresponding points on the measured G'' curve. This technique is logical because the denominator in the integral of Equation II-17 acts to "weigh" values of $H(\lambda)$ in the neighborhood of $\lambda = \frac{1}{\omega}$ much more than other values. In fact, a rough approximation to the relaxation spectrum can be obtained from (20):

$$H(\lambda) \approx G''(\omega) \Big|_{\omega = \frac{1}{\lambda}} \quad (III-7)$$

Thus, the process causes rapid convergence to a spectrum that will reproduce the G'' curve.

A program is also given in Appendix C to calculate G' , G'' , and η' from the relaxation spectrum. Dynamic data and relaxation spectra are shown in Figures 6 and 7.

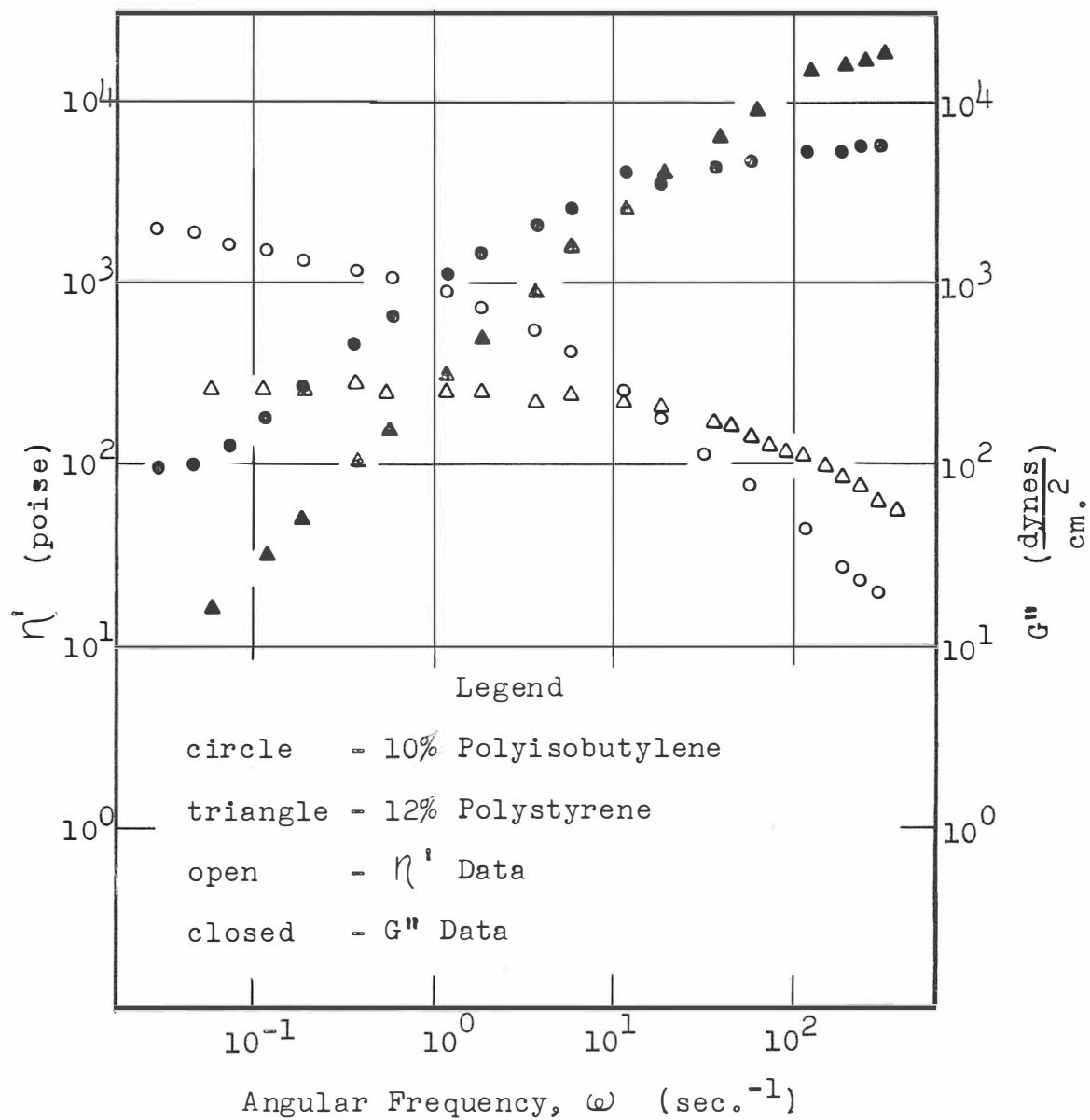


Figure 6. Linear Dynamic Data for Polystyrene and Polyisobutylene Solutions.

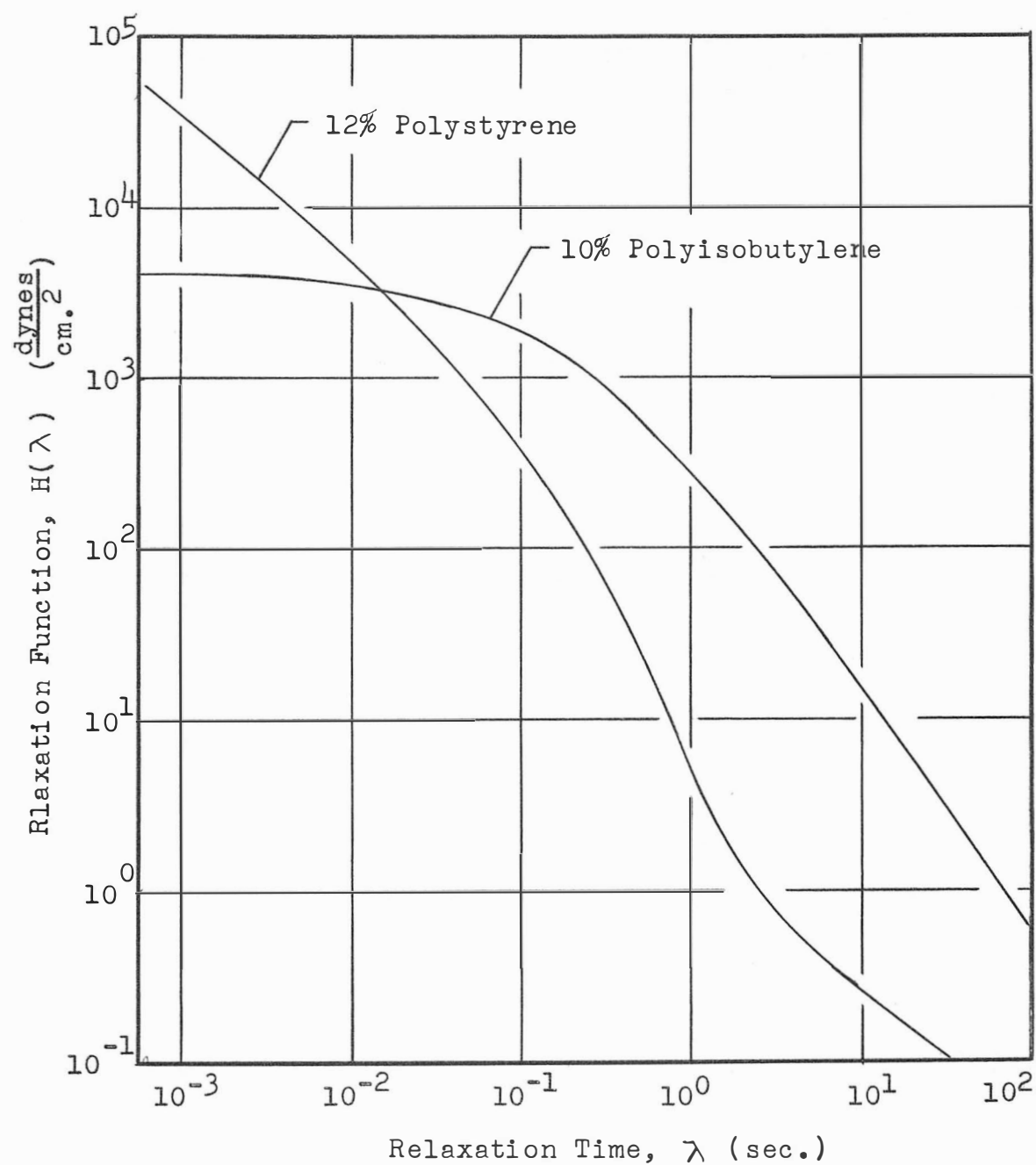


Figure 7. Relaxation Spectra for Polystyrene and Polyisobutylene Solutions.

CHAPTER IV

APPLICATION OF THE THEORIES TO VISCOMETRIC FLOWS

The validity of a constitutive equation can be tested by determining its ability to correlate data from widely different experiments (i.e., linear, transient, non-linear, etc.). The theories are quantitatively examined here for their ability to predict non-linear viscosities and normal stresses from linear dynamic data. It is felt that any theory capable of doing this is certainly worthy of further attention.

Oldroyd's three-constant theory is considered separately from the others because of the form it yields for dynamic data. Whereas the other theories produce non-linear equations directly in terms of the relaxation spectrum and will accept any spectrum that is single-valued in $H(\lambda)$, Oldroyd's equations yield three-constant predictions for dynamic data that must be fitted to the data.

I. OLDROYD'S THEORY

The most direct method of determining Oldroyd's constants from dynamic data is to fit directly by forcing one of the theoretical curves to pass through three points of the corresponding curve from experimental data (i.e., using

Equation II-30 or II-31). If the theory were exact, it would not matter which data points were selected for the fit. A fit to the η' curve is facilitated by the fact that one of the constants can be obtained by inspection of Equation II-30 for zero frequency:

$$\eta(0) = \eta'(0) . \quad (\text{IV-1})$$

It was found that the values obtained for λ_1 and λ_2 varied according to which points were selected for the fit. This is shown for the polystyrene solution in Table II. A fit for the polyisobutylene solution was further complicated by the fact that the dynamic viscosity did not show an asymptotic value over the frequency range tested. Therefore, because of the difficulties encountered in fitting through three points, a least squares fit by a computer program by Merriman (26) was taken as the best fit available. This fit produced the following Oldroyd constants for the polyisobutylene solution:

$$\begin{aligned} \eta_0 &= 1,083 \text{ poise,} \\ \lambda_1 &= 0.0585 \text{ sec.,} \\ \lambda_2 &= 0.000914 \text{ sec.;} \end{aligned}$$

and for the polystyrene solution:

$$\eta_0 = 237 \text{ poise,}$$

TABLE II
VALUES OBTAINED FOR OLDROYD'S CONSTANTS ACCORDING
TO POINTS FITTED ON THE POLYSTYRENE
DYNAMIC VISCOSITY CURVE

Points Fitted log ω	η_0 poise	λ_1 sec.	λ_2 sec.
$-\infty$	257	0.016	0.00347
2.0			
2.5			
$-\infty$	257	0.075	0.0460
1.0			
1.5			
$-\infty$	257	0.0272	0.00662
1.5			
2.5			

$$\lambda_1 = 0.0108 \text{ sec.},$$

$$\lambda_2 = 0.00223 \text{ sec.}$$

The inability to fit the experimental dynamic data with Equation II-30 is illustrated in Figure 8. Also, the resulting predictions for viscosities and normal stresses are shown and compared with data in Figures 9 and 10.

Whereas Oldroyd's theory produces curves with the correct general shape, quantitative agreement with non-linear data is poor. The equations predicted for the dynamic quantities are apparently not flexible enough, and the equations for non-linear behavior are tied explicitly to the dynamic equations (i.e., there are no material constants in the non-linear theory that do not appear in the linear theory). Some characteristics of the results predicted by Oldroyd's theory can be seen quite easily by examining Equations II-27 through II-31. Both the non-Newtonian viscosity and dynamic viscosity are predicted to approach η_0 at values of low shear and low frequency. Both viscosities are predicted to approach $\eta_0(\lambda_1 \lambda_2 / \lambda_1^2)$ for high shear rate and high frequency. The normal stress difference, $(\tau'_{11} - \tau'_{22})/K^2$, is given a low shear asymptote of $2\eta_0(\lambda_1 - \lambda_2)$ and ever-decreasing values for high shear rate. The normal stress difference, $\tau'_{22} - \tau'_{33}$, is predicted to be zero (Weissenberg's assumption), a condition contrary to the

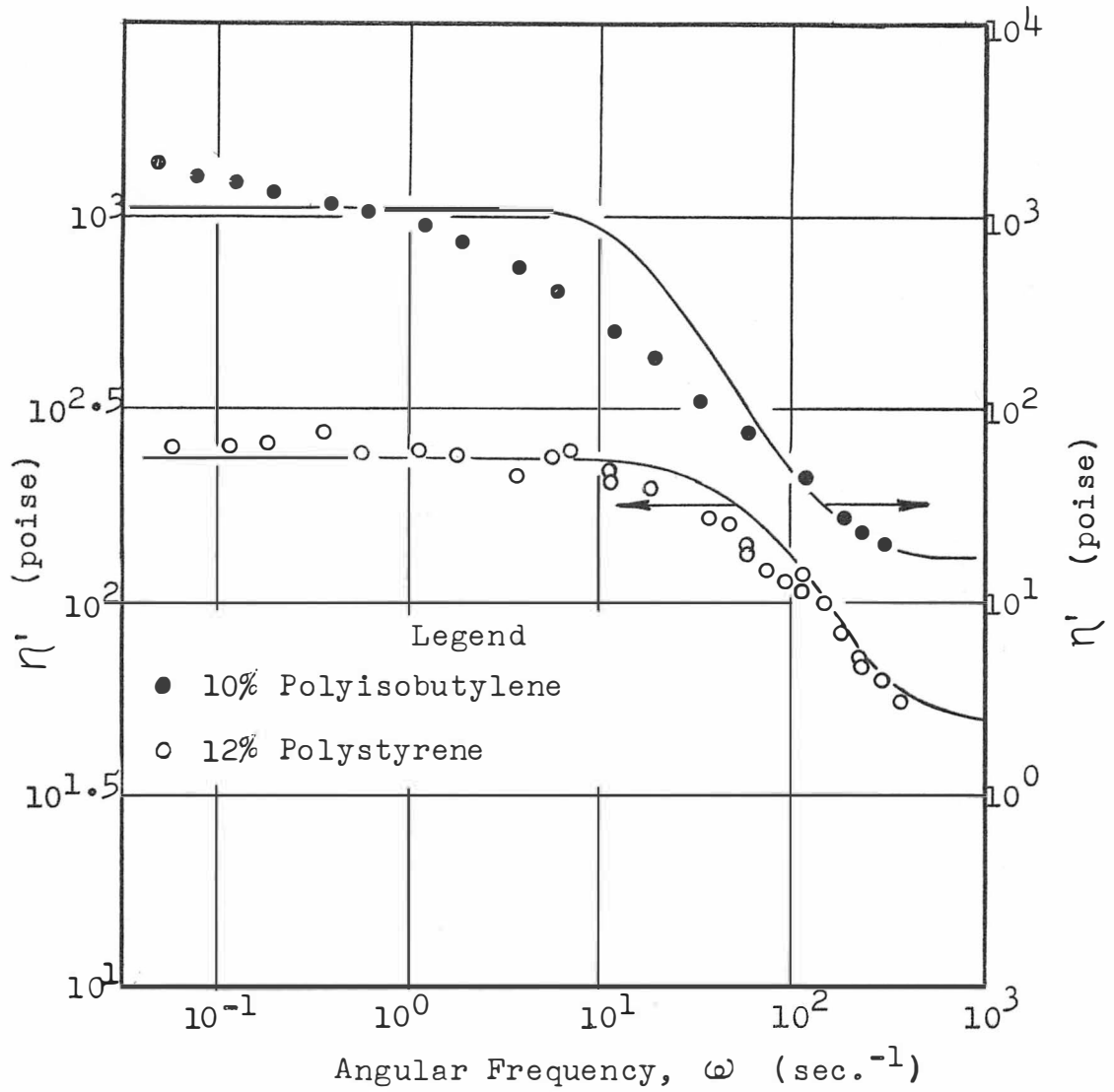


Figure 8. A Least Squares Fit of Oldroyd's Theory to Dynamic Viscosity Data.

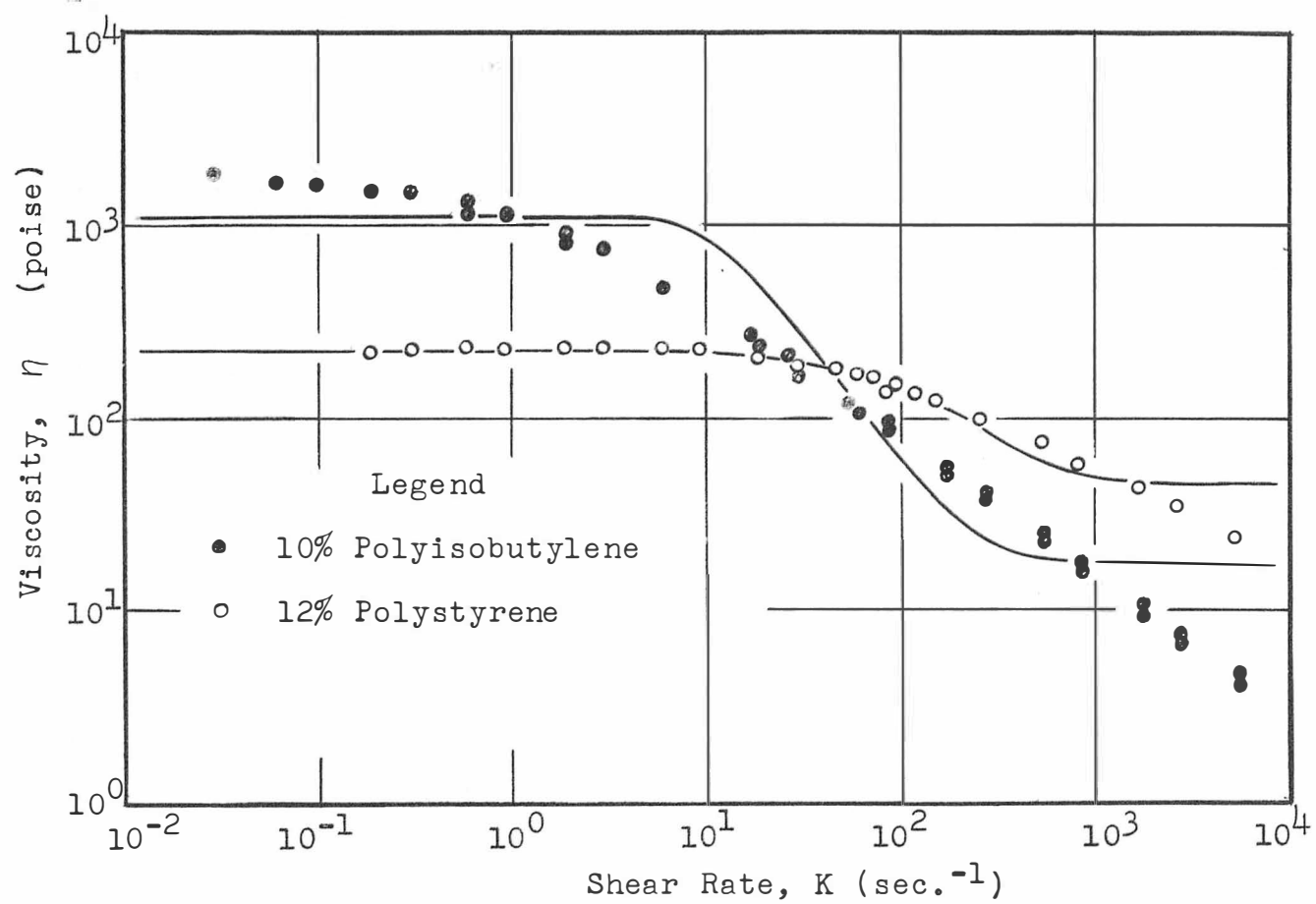


Figure 9. Comparison of Oldroyd's Theory with Viscosity Data.

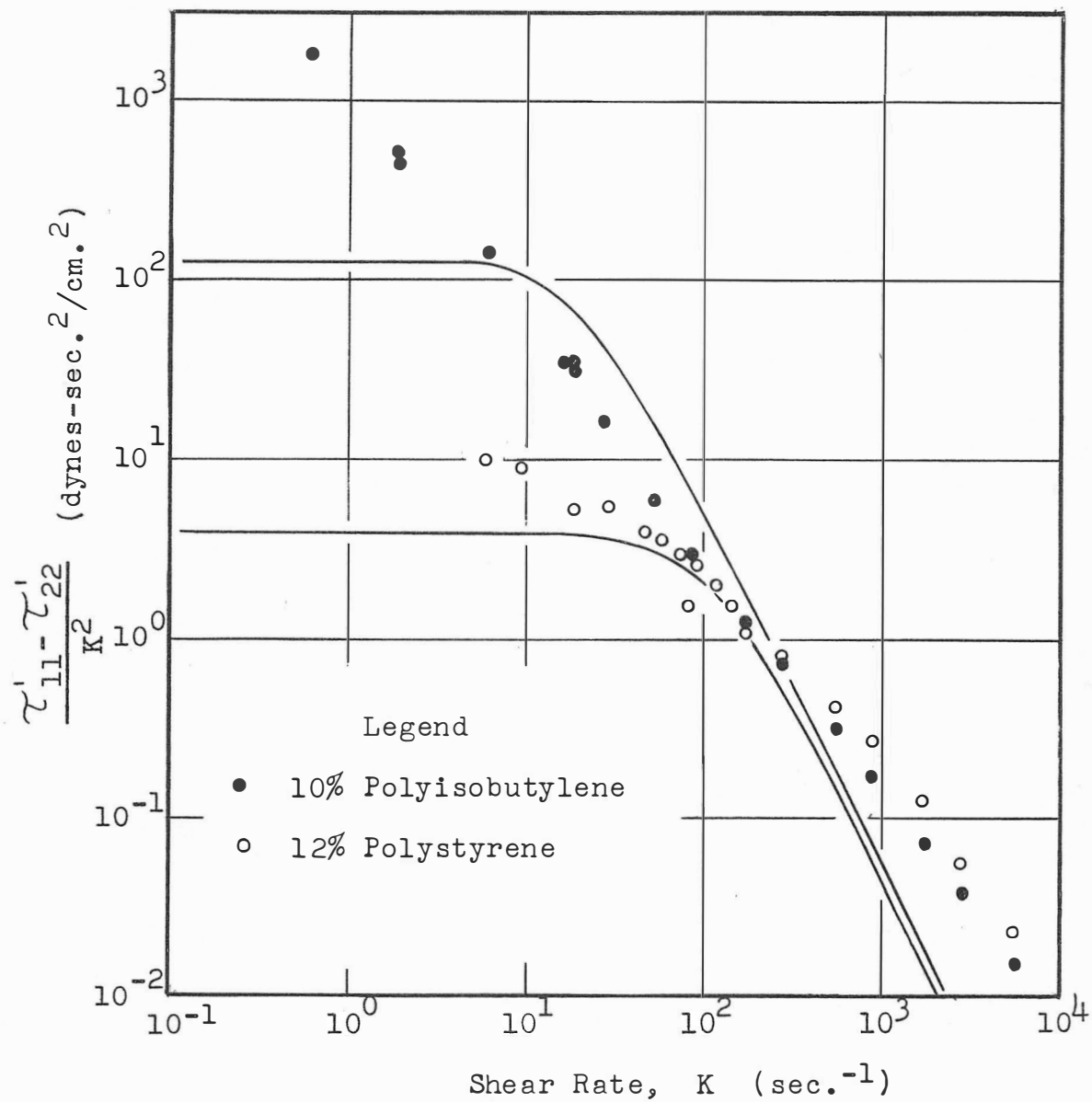


Figure 10. Comparison of Oldroyd's Theory with First Normal Stress Difference Data.

findings of a survey by White (47).

II. PAO'S THEORY

The results predicted by Pao's (34,36) theory for steady shear flow were obtained by integrating Equation II-40 for the viscosity and Equation II-41 for the first normal stress difference. The relaxation spectrum was represented numerically for the integration which was done by computer. (See Appendix C for the program.) Limits for the relaxation spectrum were set by the data available. The results are shown and compared with the polyisobutylene and polystyrene data in Figures 11 and 12.

The theory predicts viscosities that are too large at high shear rates. This agrees with the findings of DeVries (16). A similar result is found for the predicted normal stress difference.

Some insight into the problem can be gained by a study of the two terms in Equation II-41.

$$\frac{\tau'_{12}}{K} = \eta = P_1 + K^2 \frac{(P_2)^2}{P_1} . \quad (\text{II-41})$$

The first term is insignificant at high shear rates, and the second term is insignificant at low shear rates. They are of the same order of magnitude for only a relatively narrow shear rate range. The first term reduces to the zero shear

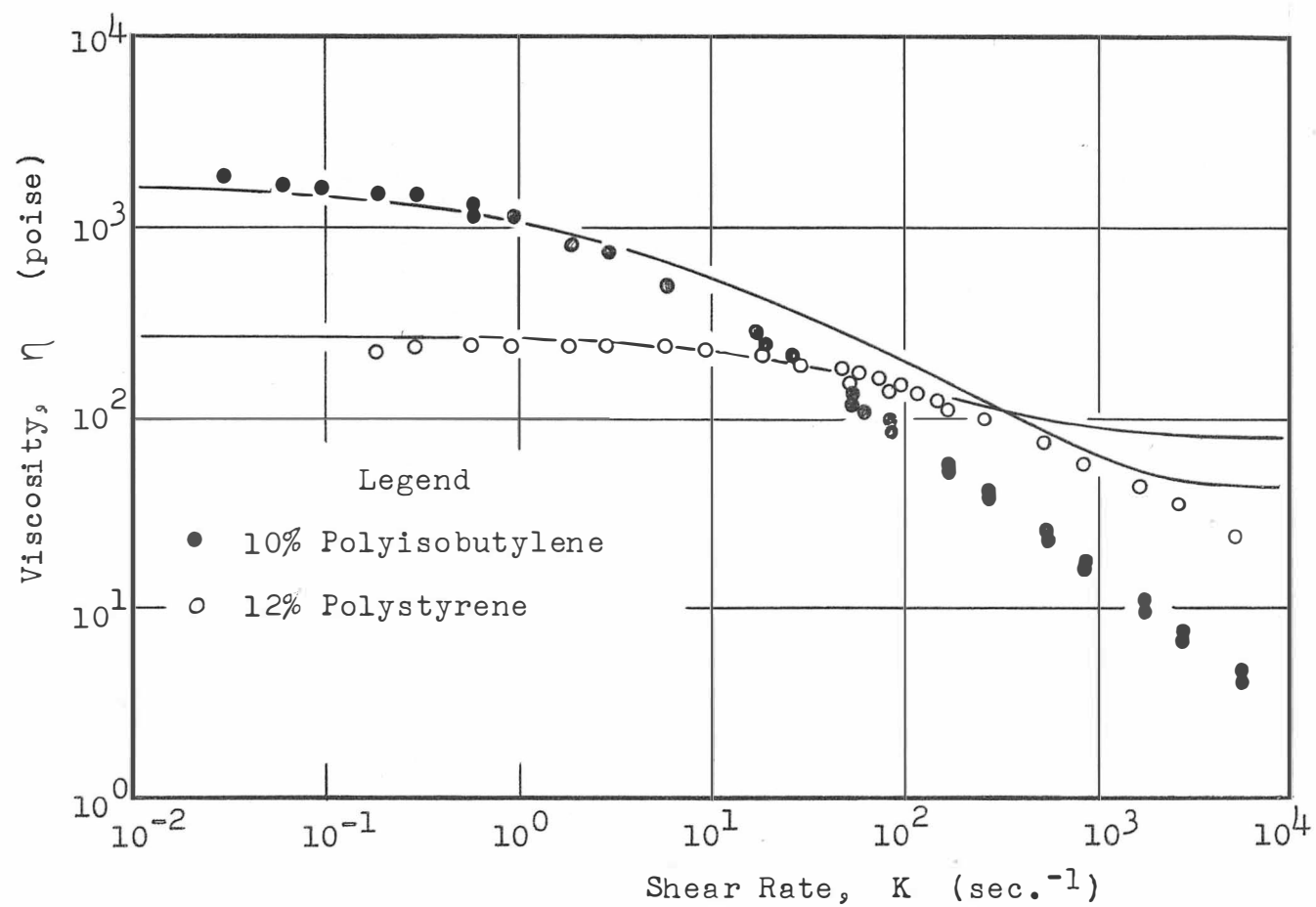


Figure 11. Comparison of Pao's Theory with Viscosity Data.

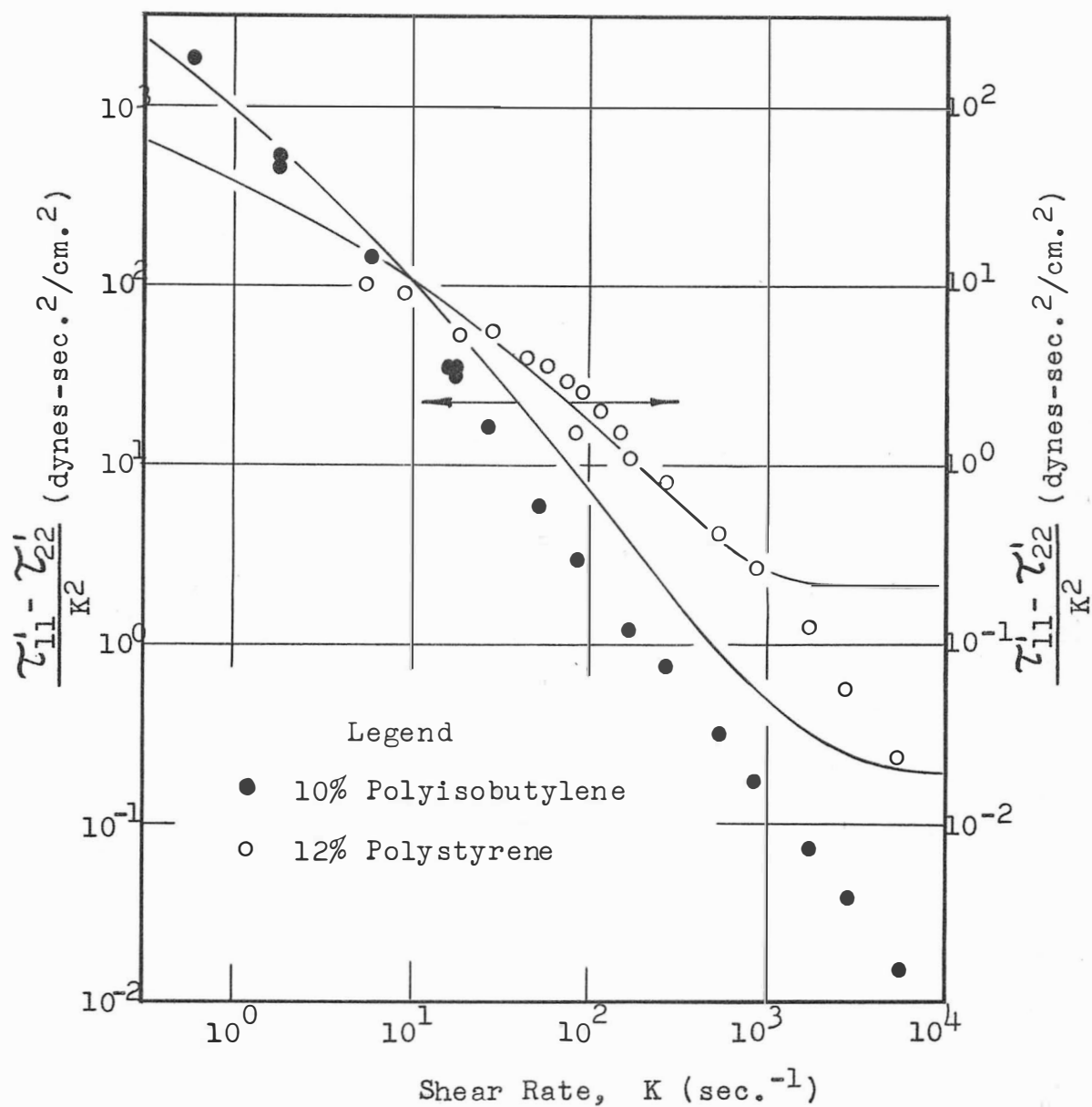


Figure 12. Comparison of Pao's Theory with First Normal Stress Difference Data.

viscosity and, in fact, is identical to an expression by DeWitt (17) that was developed without the use of a convected derivative. The second term becomes independent of shear rate at large shear rates and predicts:

$$\eta_{\infty} = \frac{\left[\int_0^{\infty} \frac{H(\lambda) d\lambda}{\lambda} \right]^2}{\int_0^{\infty} \frac{H(\lambda)}{\lambda^2} d\lambda} \quad . \quad (\text{II-2})$$

Although no data are presented for the high shear rate Newtonian region, it is evident that the value predicted by Equation II-40 is much greater than values obtained for the high shear rate end of the non-Newtonian range. The predictions for the first normal stress difference are also too large for high shear rates.

III. BOGUE'S THEORY

Figures 13 through 16 show a comparison of Bogue's theory with viscosity and normal stress data. The treatment of the theory was the same as for Pao's (see Appendix C) except for the material parameter a . In earlier work, Bogue (7) used a constant value of 0.6 for the parameter, but more recently he suggested that it be treated as a material

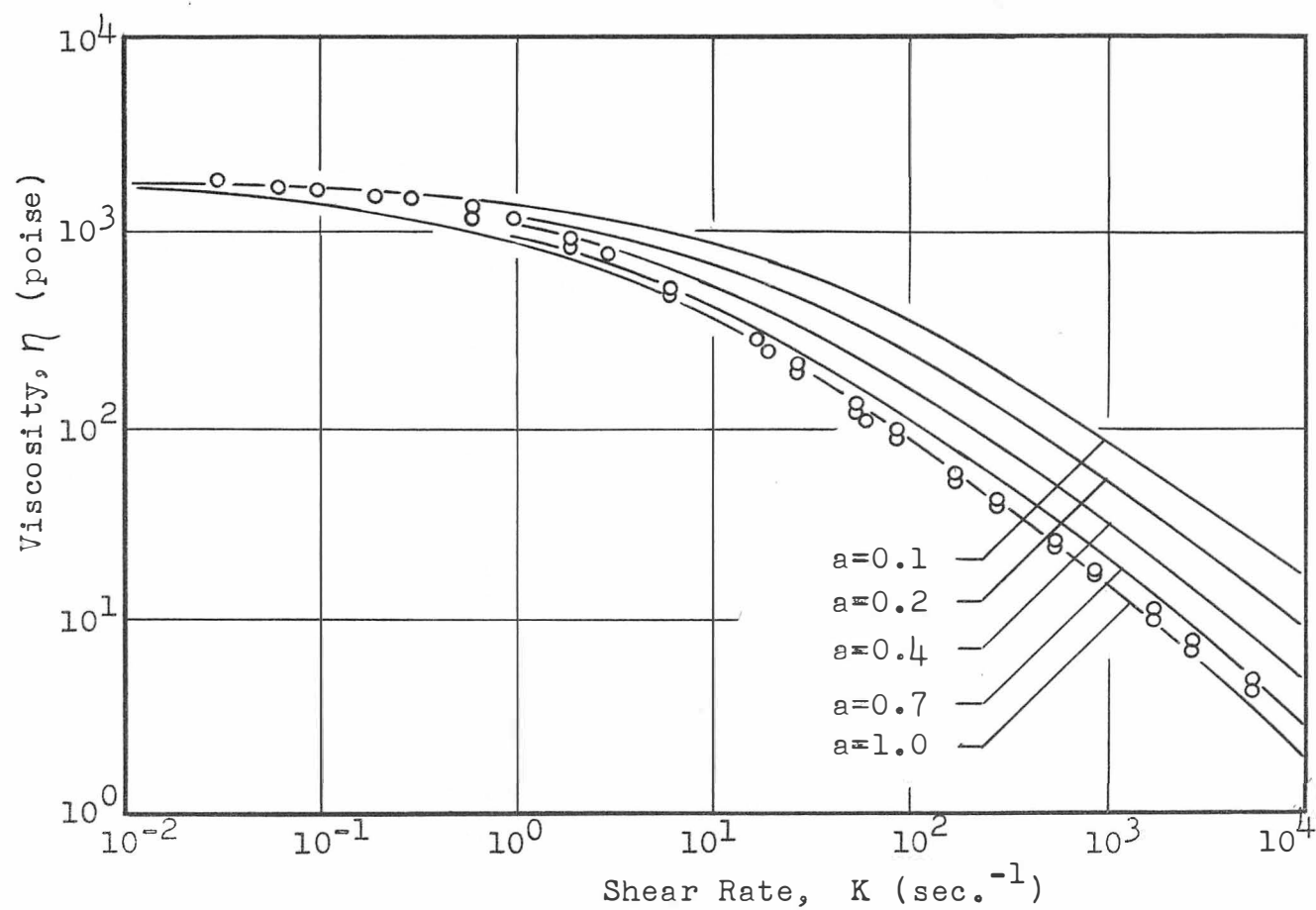


Figure 13. Comparison of Bogue's Theory with Viscosity Data for the Polyisobutylene Solution.

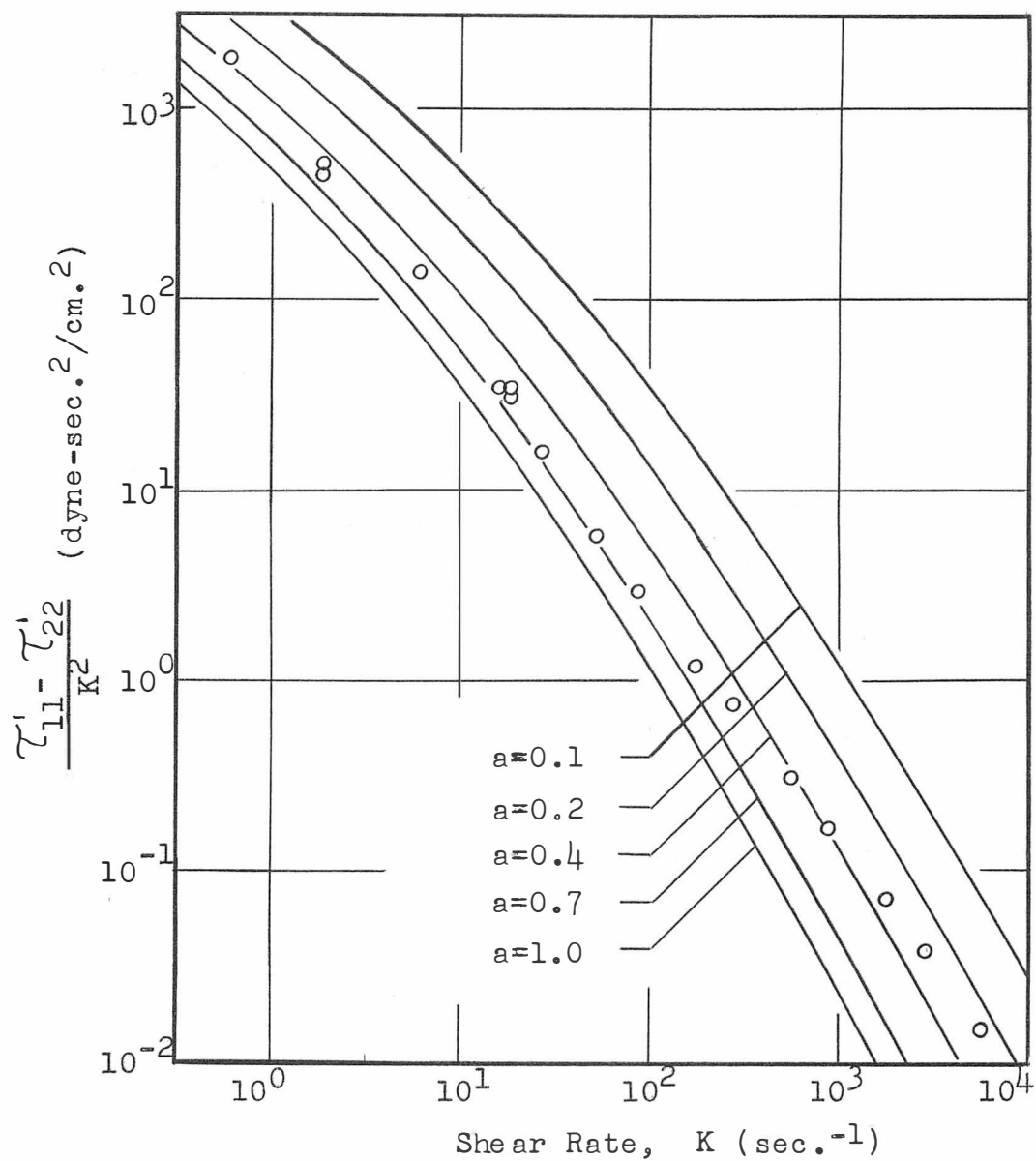


Figure 14. Comparison of Bogue's Theory with First Normal Stress Difference Data for the Polyisobutylene Solution.

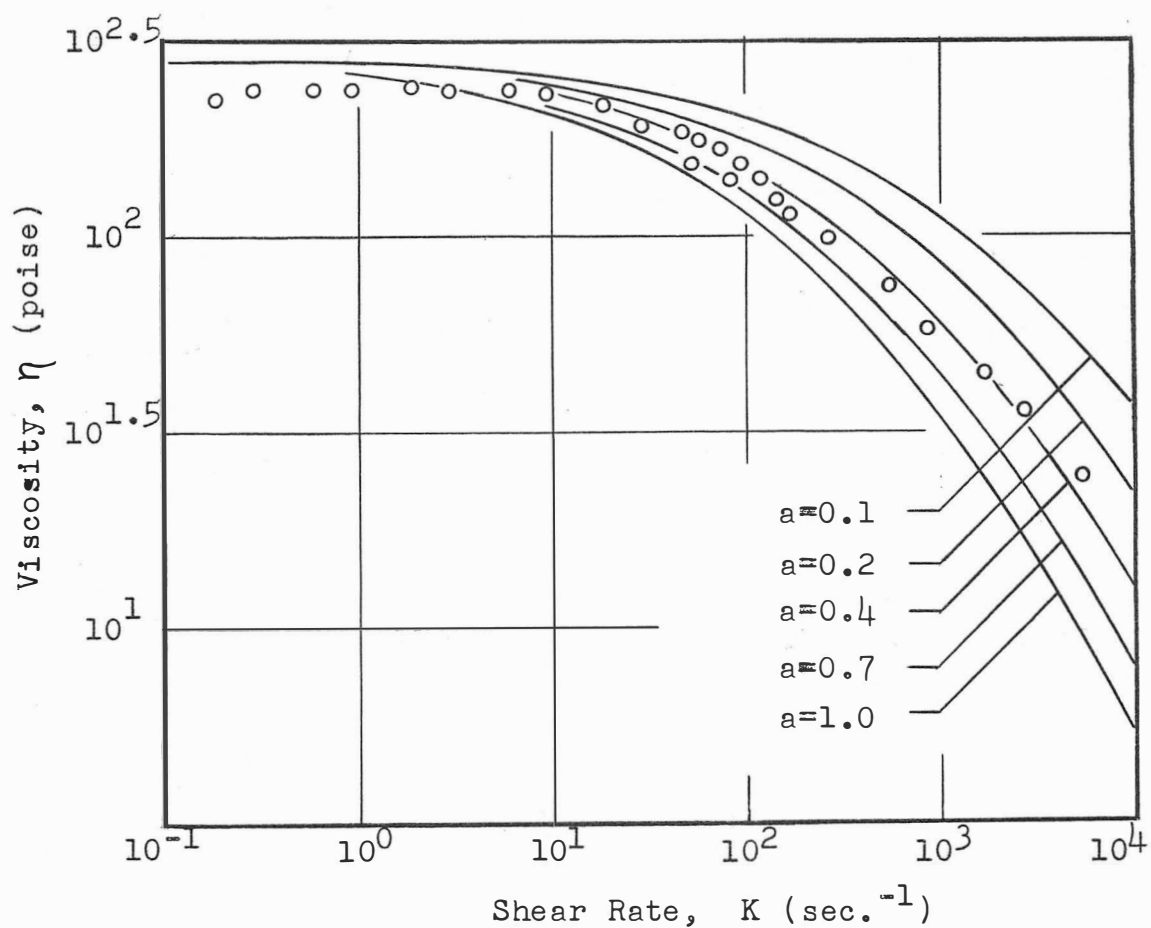


Figure 15. Comparison of Bogue's Theory with Viscosity Data for the Polystyrene Solution.

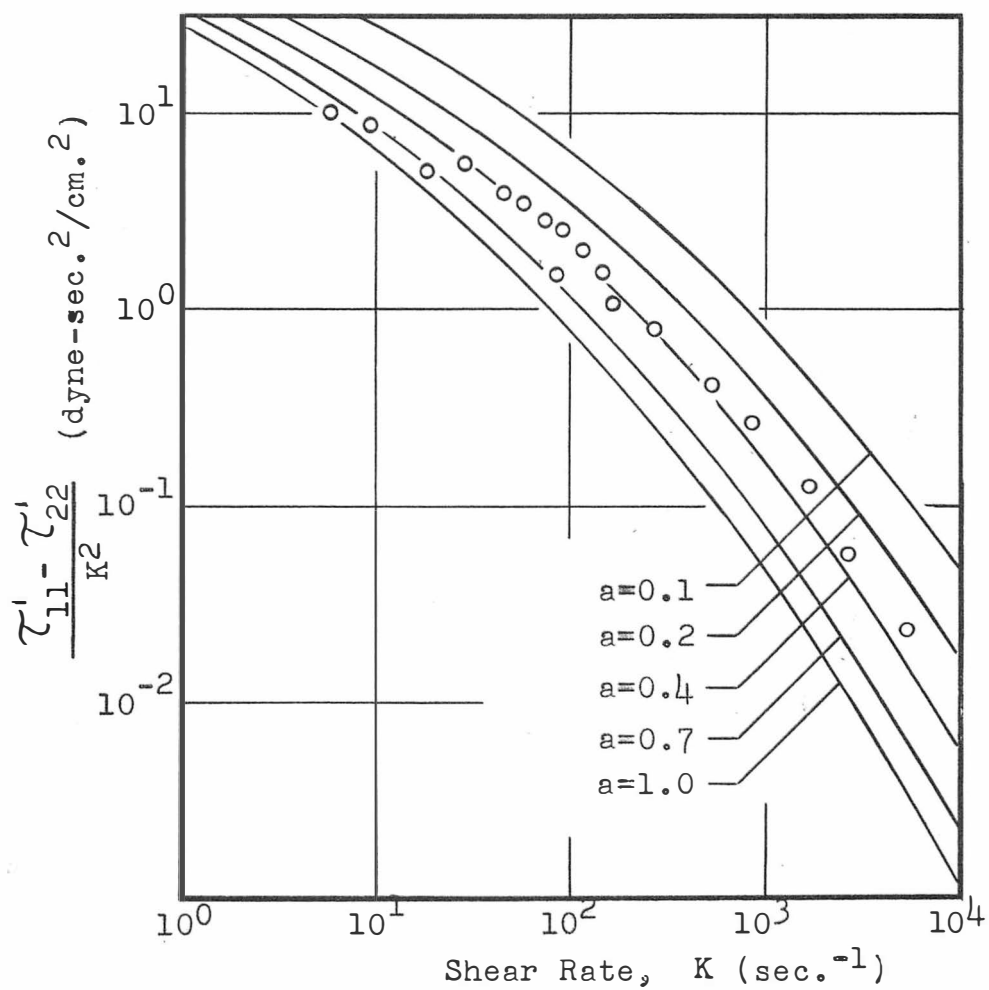


Figure 16. Comparison of Bogue's Theory with First Normal Stress Difference Data for the Polystyrene Solution.

parameter. In keeping with this, predictions of his theory are presented for values of a varying from 0.1 to 1.0.

The latter treatment is borne out by comparison with data. It is found that the data can be approximated over several decades of shear rate if the approximate value for the material constant is employed. Even though the fit is not good enough to select a definite value for the constant, a value of about 0.7 seems to provide the best fit for the polyisobutylene solution, whereas a value of 0.4 appears appropriate for the polystyrene solution.

The major weakness of Bogue's theory applied to viscometric flows is its inability, in the form presented, to predict the high shear rate Newtonian region. Instead, it predicts ever-decreasing values for viscosity and normal stress difference with increasing shear rate. This defect can be artificially corrected by introducing a relaxation time smaller than the reciprocal of the highest conceivable shear rate (7).

IV. THE BERNSTEIN-KEARSLEY-ZAPAS THEORY

Equations II-56 and II-57 were evaluated by numerical integration with the relaxation spectra represented numerically. The evaluation is similar to that of Bogue's theory except that a double integral is involved. The integral limits for integrating over s are not obvious, although

one would expect the maximum significant value of s to be about the same as the maximum value of λ because of the exponential factor, $e^{-s/\lambda}$, in Equations II-56 and II-57. In order to establish reasonable limits, the integrand of Equation II-56 was evaluated for the polyisobutylene solution over a range of s (see Figure 21, page 71). The effective range of the function is greatest for zero shear rate; therefore, one concludes that unless low zero shear rate viscosities are produced by the integration, the effective range has been covered. (The curves shown in Figure 21 are actually for a four-constant representation of the relaxation spectrum which is probably the reason for the "humps," but that should not affect the general trend of the function with shear rate.) The actual limits used in the integrations were from $\log s = -7$ to $\log s = 2$.

Zapas' function (Equation II-48) can be put into a form to include a material parameter similar to the a in Bogue's theory. With α and c still taken as zero, the form is:

$$W = \frac{m(s)}{2A} \ln \left[\frac{A}{2}(I+II-6)+1 \right] + \frac{21}{4} m \ln \frac{I+6}{II+6} . \quad (IV-3)$$

Using this form for his function, along with Equations II-54 and II-55, the following results are obtained for viscometric flows:

$$\frac{\tau'_{12}}{K} = \eta = \int_0^{\infty} \int_{-\infty}^{\infty} \frac{H(\lambda) e^{-s/\lambda} s}{\lambda (1 + AK^2 s^2)} d \ln \lambda ds \quad (\text{IV-4})$$

and

$$\frac{\tau'_{11} - \tau'_{22}}{K^2} = \int_0^{\infty} \int_{-\infty}^{\infty} \frac{H(\lambda) e^{-s/\lambda} s^2}{\lambda (1 + AK^2 s^2)} d \ln \lambda ds . \quad (\text{IV-5})$$

Zapas (53) has used a form for which $A=2/9$, as well as the form shown in Equation II-48, for which $A=2/3$. It was therefore decided to treat the parameter as an adjustable material constant as was done with the a in Bogue's theory. Accordingly, curves are shown for values of A varying between 0.1 and 1.0 (see Figures 17 through 20).

As with Bogue's theory, it is not possible to select a definite value of the material parameter because the shapes of the curves do not exactly fit the data; however, a reasonable fit for both solutions is obtained using a value of 0.1. A slightly better fit for the polyisobutylene solution might result using a value of 0.2.

In the form used, this theory also does not predict a high shear rate Newtonian region, and the fit obtained covers a shear rate range somewhat less than that realized from Bogue's theory. It does, however, appear less dependent on the material parameter. If a universal value for a or

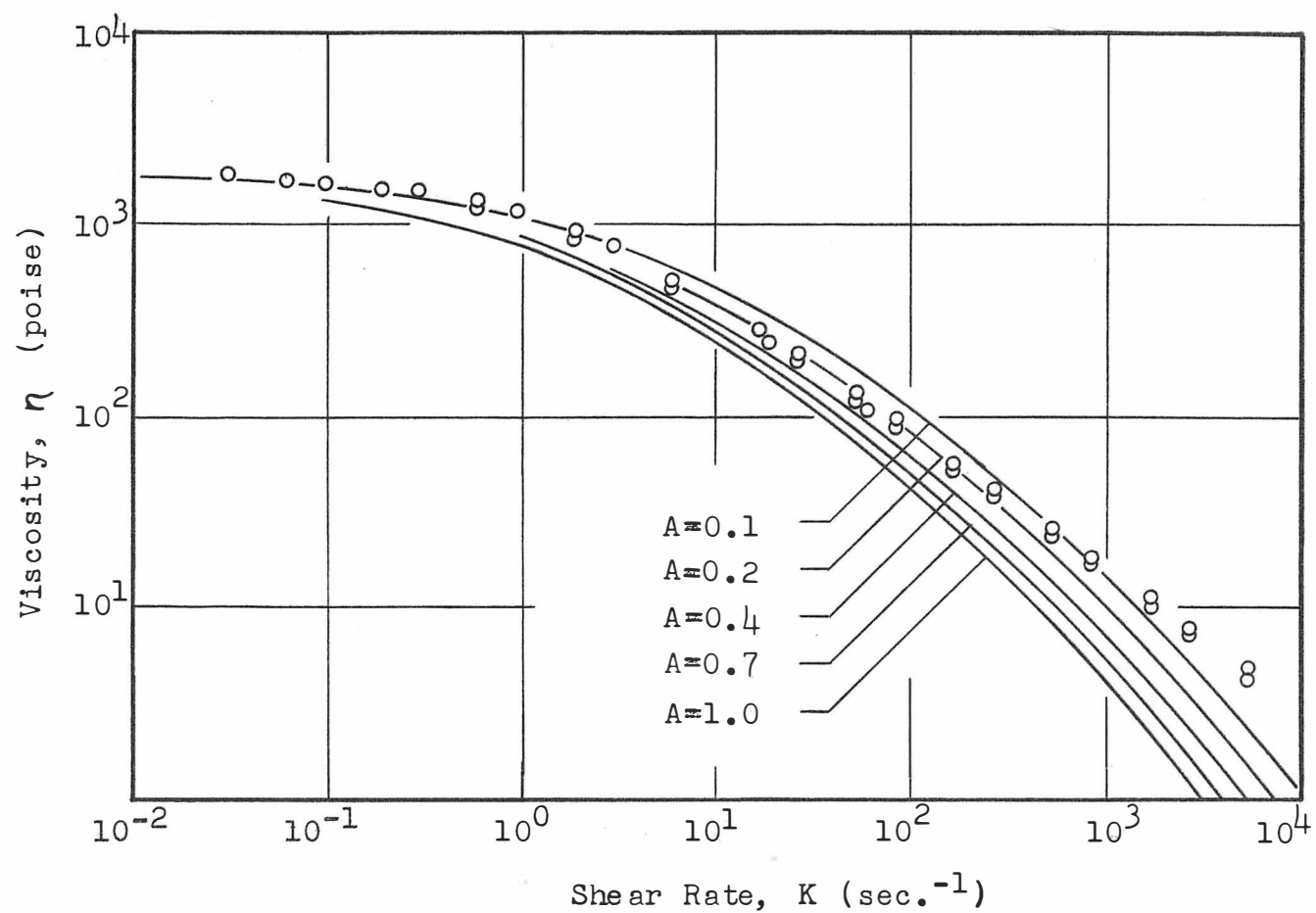


Figure 17. Comparison of the Bernstein-Kearsley-Zapas Theory with Viscosity Data for the Polyisobutylene Solution.

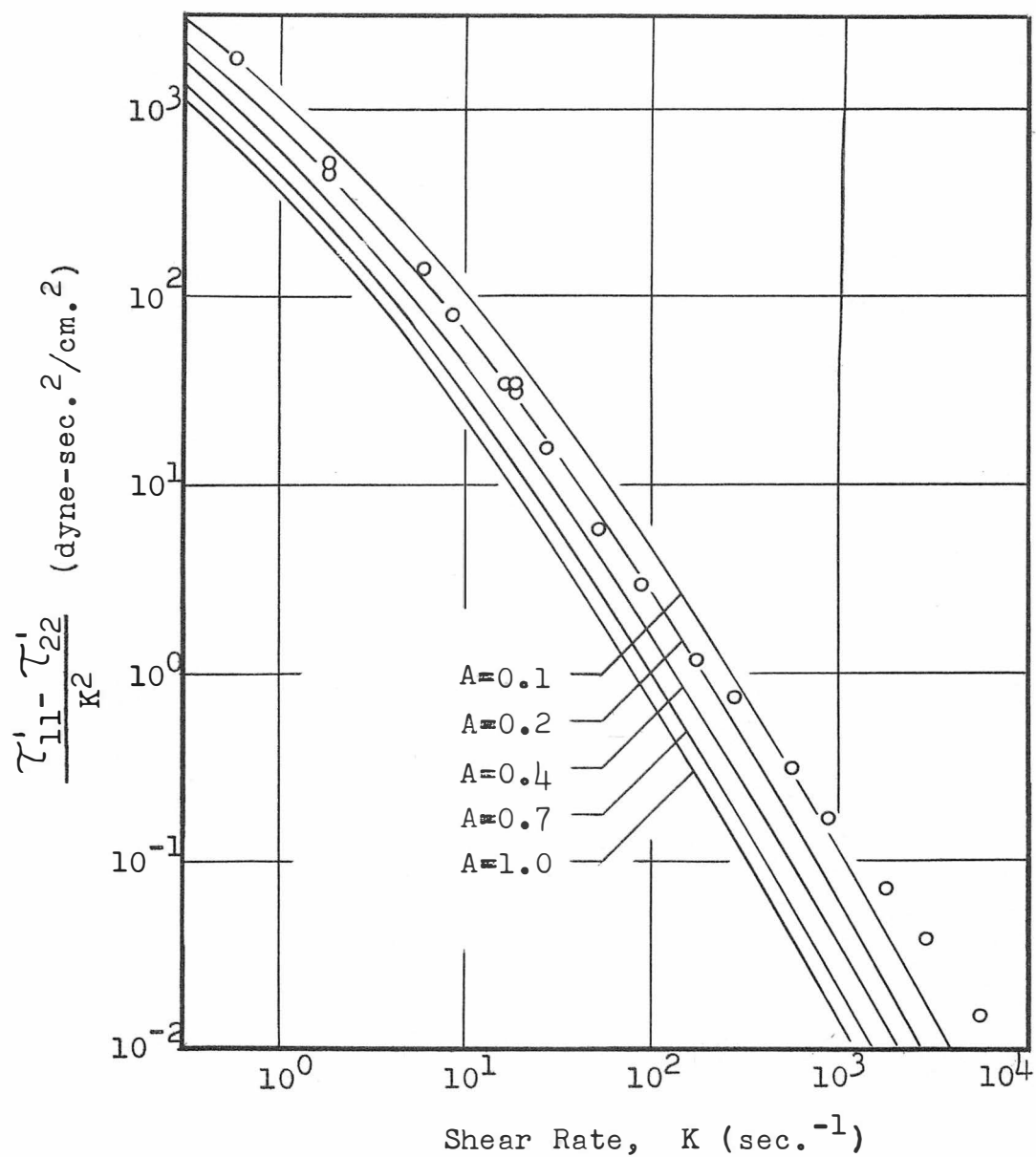


Figure 18. Comparison of the Bernstein-Kearsley-Zapas Theory with First Normal Stress Difference Data for the Polyisobutylene Solution.

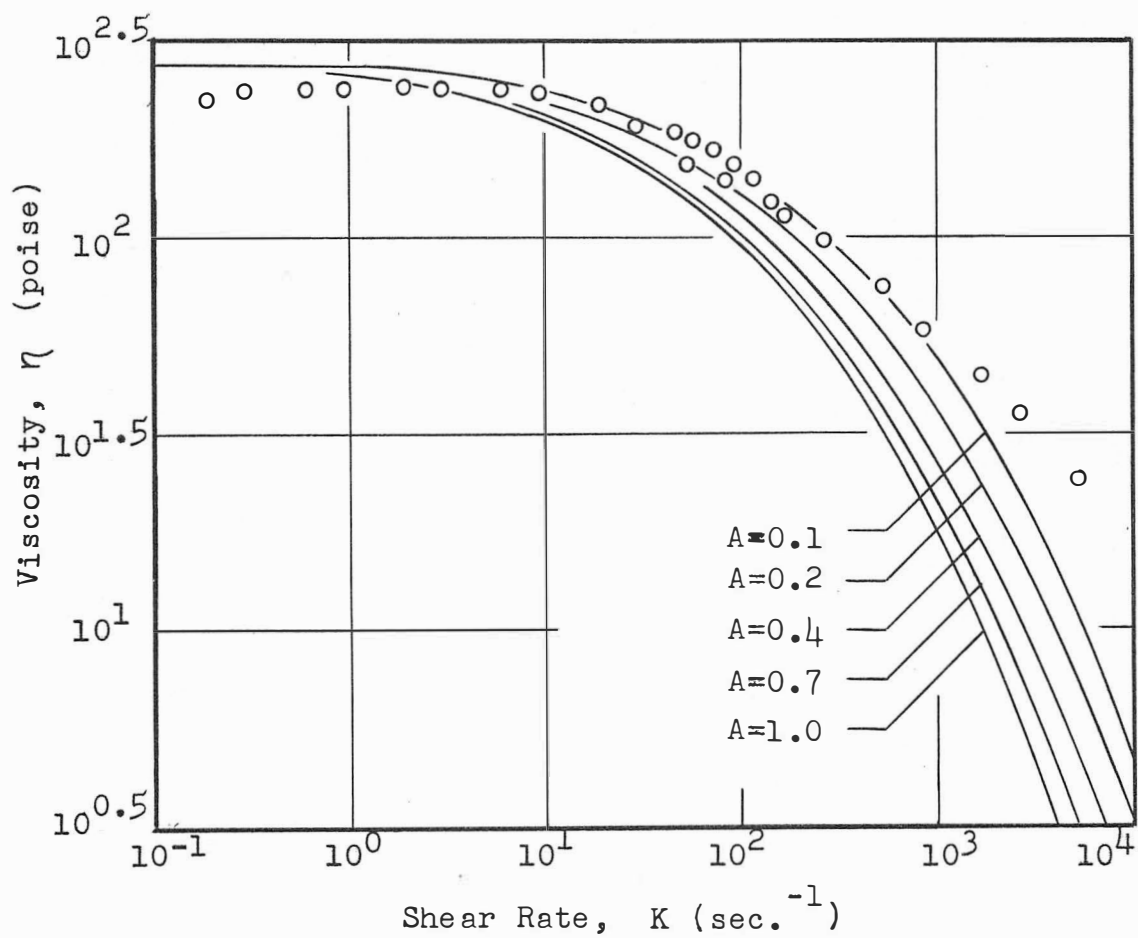


Figure 19. Comparison of the Bernstein-Kearsley-Zapas Theory with Viscosity Data for the Polystyrene Solution.

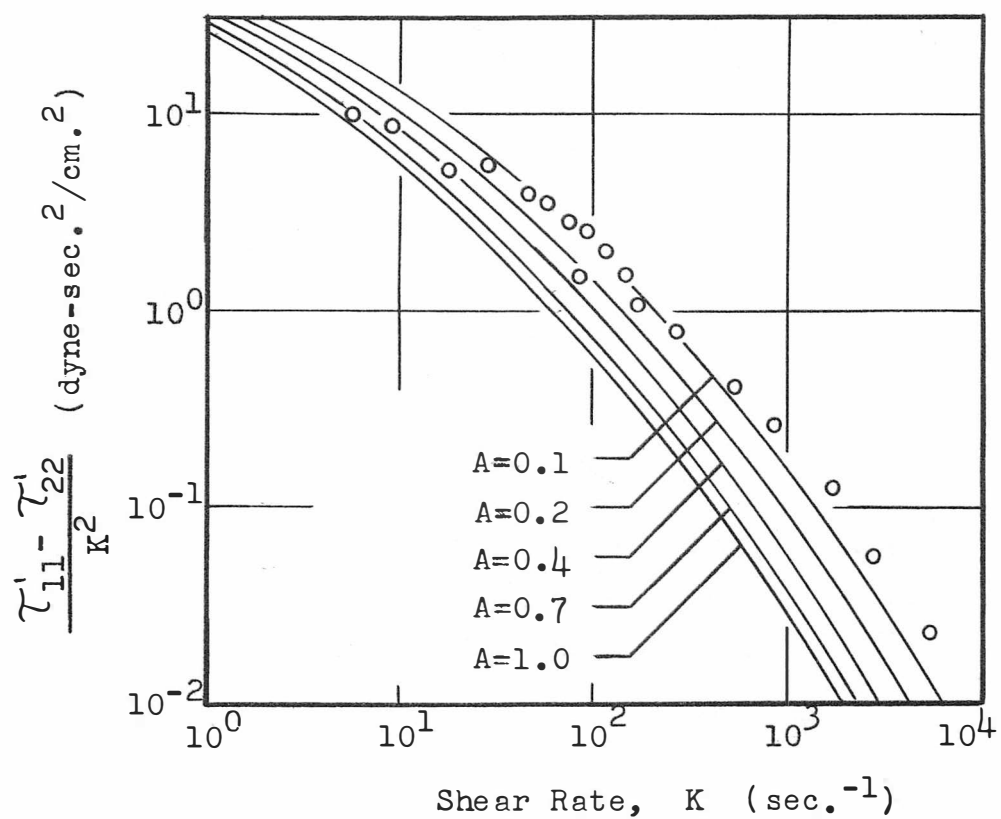


Figure 20. Comparison of the Bernstein-Kearsley-Zapas Theory with First Normal Stress Difference Data for the Polystyrene Solution.

A could be used for all materials or for classes of materials, there would be the obvious advantage of one less constant to evaluate. This would have significance not only in the number of experiments necessary to characterize a fluid, but also for dimensional analysis (see Chapter V).

V. THE FOUR-CONSTANT FIT TO DYNAMIC DATA

With the exception of Oldroyd's theory, the results of the theories must be expressed as series of terms containing viscoelastic constants, G_n and λ_n , or as an integral of the relaxation spectrum, $H(\lambda)$. The question arises then as to the minimum number of constants necessary to describe viscoelastic behavior. If it could be described by a few constants, not only would the calculation and experimental effort be reduced, but also a foundation would be provided for a dimensional analysis treatment of more complicated flow problems (8).

When expressed in terms of discrete spectra, the form of the results of the theories suggests a series truncation. It is necessary to retain two terms in the series (four constants) in order for Pao's theory to retain its essential features, and Bogue (7) has represented the behavior of a polyisobutylene solution over a non-Newtonian shear rate range of about two decades using four constants. Therefore, the theories were evaluated for a series truncation to four

constants which were determined by a fit to the η' curve.

The equations resulting from this truncation are:

$$\eta' = \frac{G_1 \lambda_1}{1 + \omega^2 \lambda_1^2} + \frac{G_2 \lambda_2}{1 + \omega^2 \lambda_2^2} ; \quad (\text{IV-6})$$

Pao's theory:

$$\eta = \frac{G_1 \lambda_1}{1 + K^2 \lambda_1^2} + \frac{G_2 \lambda_2}{1 + K^2 \lambda_2^2} + K^2 \frac{\left[\frac{G_1 \lambda_1^2}{1 + K^2 \lambda_1^2} + \frac{G_2 \lambda_2^2}{1 + K^2 \lambda_2^2} \right]^2}{\frac{G_1 \lambda_1}{1 + K^2 \lambda_1^2} + \frac{G_2 \lambda_2}{1 + K^2 \lambda_2^2}} ; \quad (\text{IV-7})$$

$$\frac{\tau'_{11} - \tau'_{22}}{K^2} = 2 \frac{G_1 \lambda_1^2}{1 + K^2 \lambda_1^2} \frac{G_2 \lambda_2^2}{1 + K^2 \lambda_2^2} + K^2 \frac{\left[\frac{G_1 \lambda_1^2}{1 + K^2 \lambda_1^2} \frac{G_2 \lambda_2^2}{1 + K^2 \lambda_2^2} \right]^3}{\left[\frac{G_1 \lambda_1}{1 + K^2 \lambda_1^2} \frac{G_2 \lambda_2}{1 + K^2 \lambda_2^2} \right]^2} ; \quad (\text{IV-8})$$

the Bernstein-Kearsley-Zapas theory (see Figure 21):

$$\eta = \int_0^\infty \frac{\frac{G_1}{\lambda_1} e^{-s/\lambda_1} + \frac{G_2}{\lambda_2} e^{-s/\lambda_2}}{1 + AK^2 s^2} s \, ds ; \quad (\text{IV-9})$$

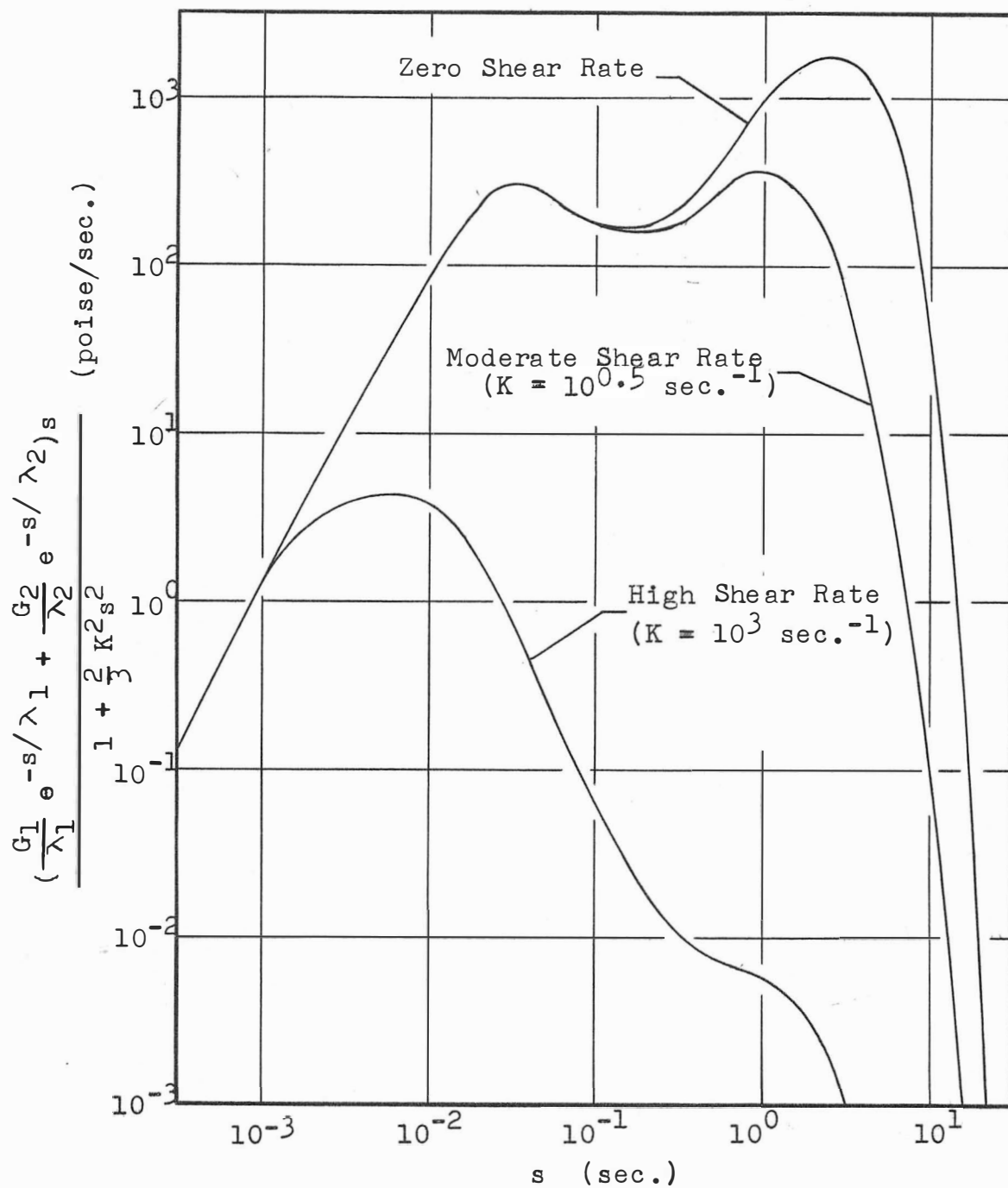


Figure 21. A Plot of the Integrand of Equation IV-9, Using a Four-Constant Relaxation Spectrum.

$$\frac{\tau'_{11} - \tau'_{22}}{K^2} = \int_0^{\infty} \frac{\frac{G_1}{\lambda_1} e^{-s/\lambda_1} + \frac{G_2}{\lambda_2} e^{-s/\lambda_2}}{1 + AK^2 s^2} s^2 ds ; \quad (\text{IV-10})$$

Bogue's theory:

$$\eta = \frac{G_1 \lambda_1}{(1+aK \lambda_1)} + \frac{G_2 \lambda_2}{(1+aK \lambda_2)} ; \quad (\text{IV-11})$$

$$\frac{\tau'_{11} - \tau'_{22}}{K^2} = \frac{G_1 \lambda_1^2}{(1+aK \lambda_1)^2} + \frac{G_2 \lambda_2^2}{(1+aK \lambda_2)^2} . \quad (\text{IV-12})$$

Without a perfect fit there is some arbitrariness in the fit to the η' curve (as in the case with Oldroyd's theory). The fit was made to force the correct value for the zero shear viscosity and then through three points on the η' curve that appeared to provide the best agreement (see Figure 22). The constants obtained are:

$$\begin{aligned} \lambda_1 &= 0.0224 \text{ sec.}, \\ \lambda_2 &= 1.12 \text{ sec.}, \\ G_1 &= 12,770 \text{ dynes/sq.cm.}, \\ G_2 &= 1,415 \text{ dynes/sq.cm.} \end{aligned}$$

Values used for the material parameters were $A=2/9$ (a value used by Zapas which fits the data reasonably) and $a=0.6$

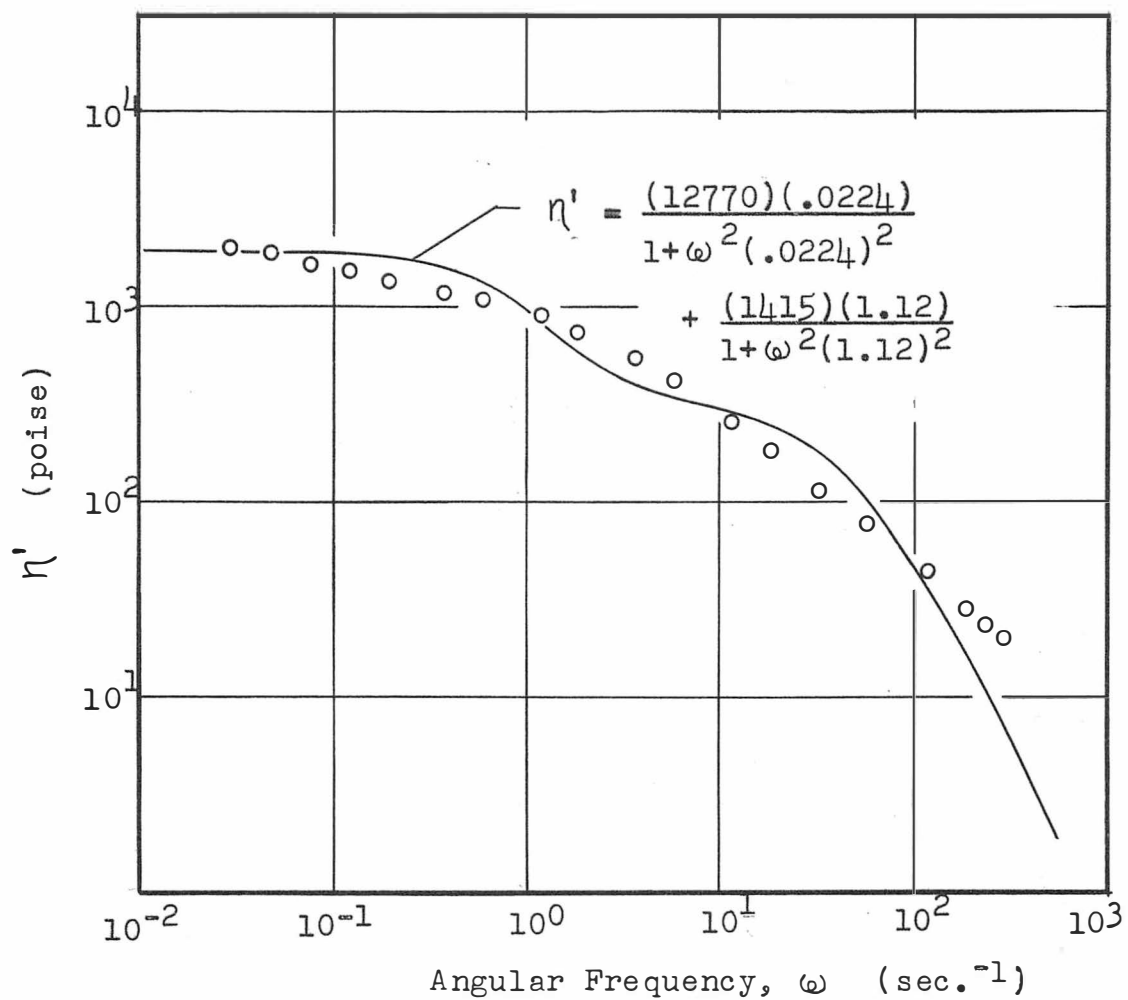


Figure 22. A Fit to the Polyisobutylene Dynamic Velocity Data by Truncating Equation II-14 after the Second Term.

(a value used by Bogue for a polyisobutylene solution, 7).

The viscosity curves produced are shown in Figure 23. Although, for moderate shear rates, the results of Bogue's theory and the Bernstein-Kearsley-Zapas theory do not deviate excessively from the data, there is an undesirable meandering in the curves. It is especially noticeable in the Bernstein-Kearsley-Zapas theory.

The meandering described above may be interpreted as the result of oversimplifying the relaxation spectrum. As was shown by Bogue (7), it has the effect of replacing the relaxation spectrum by two "spikes," which include an area equal to the real spectrum, but which is concentrated at λ_1 and λ_2 . In order to alleviate this situation it was decided to adopt a curve fitting technique to represent the continuous relaxation spectrum. The polyisobutylene spectrum was successfully represented by an equation of the form:

$$H = \frac{H_{CH}}{\left(1 + \frac{\lambda}{\lambda_{CH}}\right)^n}; \quad 0 \leq \lambda \leq \lambda_M. \quad (\text{IV-13})$$

The fit provided is shown in Figure 24 for 10 per cent polyisobutylene and the 6.6 per cent polyisobutylene solution treated by Bogue (7). Obviously, when fed into the theories, there will be no detrimental effect so long as the relaxation spectrum is adequately represented.

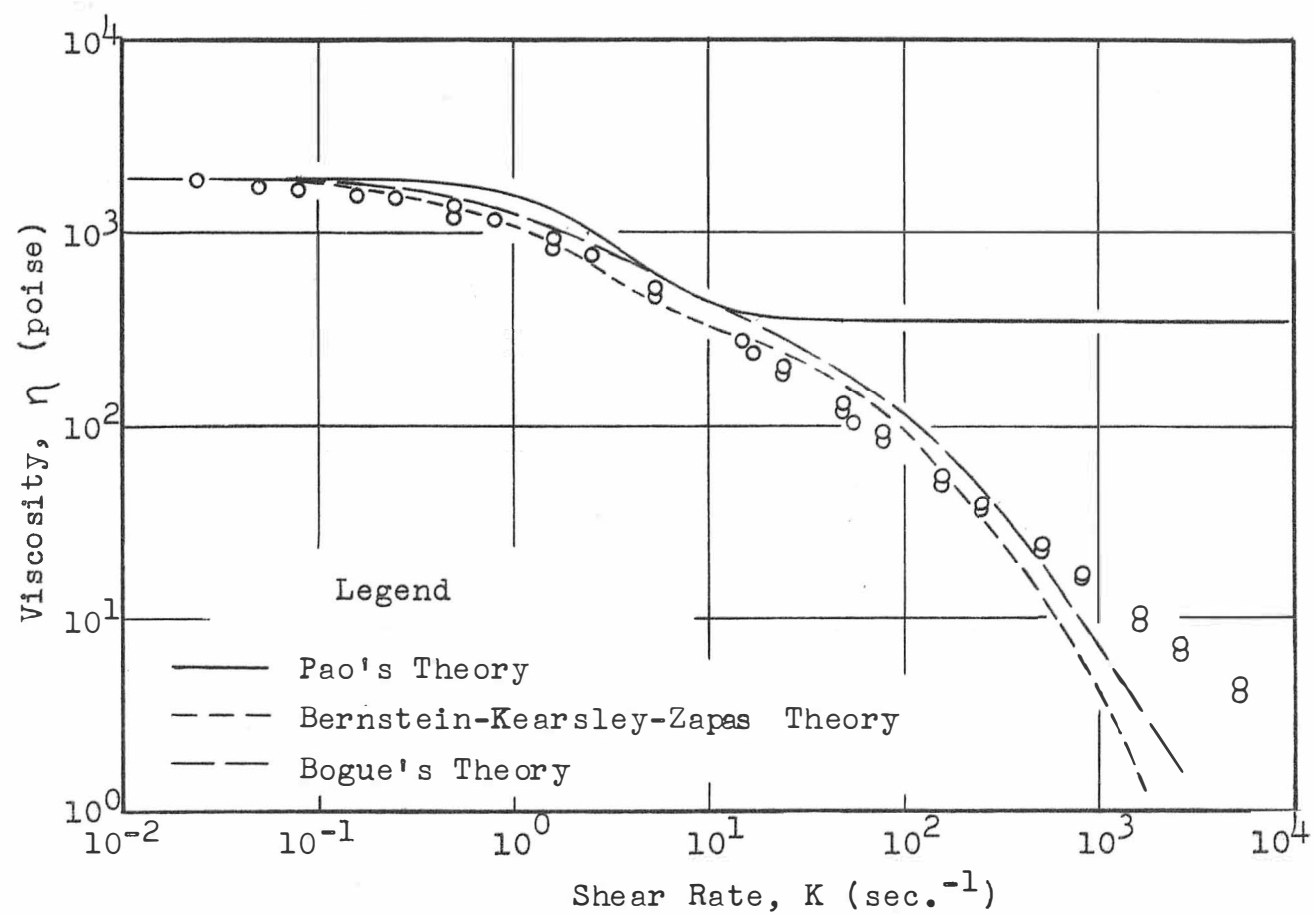


Figure 23. Viscosity Curves Predicted by Utilizing Two Terms To Represent the Relaxation Spectrum for the Polyisobutylene Solution.

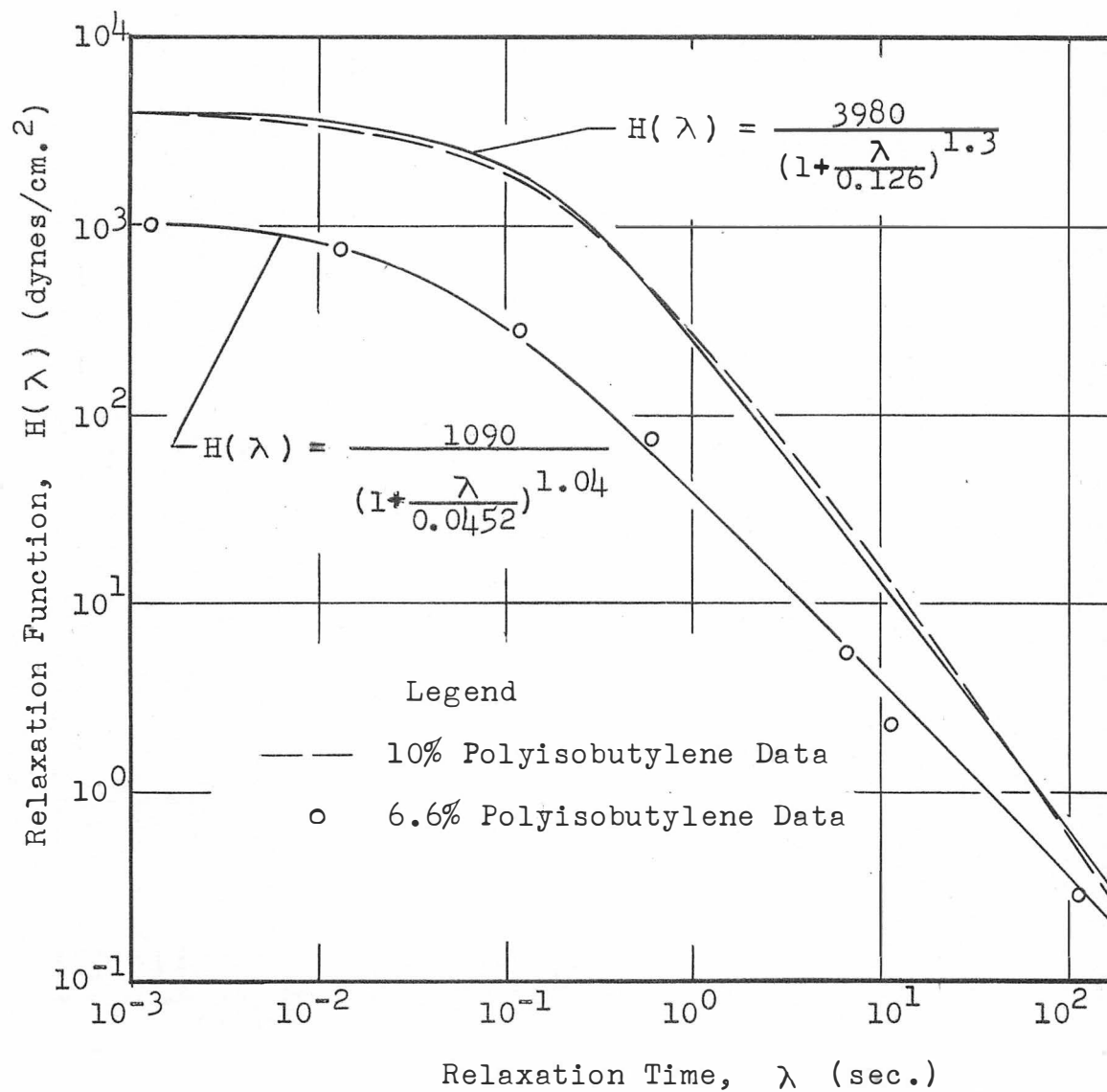


Figure 24. Representation of Polyisobutylene Relaxation Spectra with Equation IV-13.

An added advantage of this representation of the relaxation spectrum is that the expressions for zero shear viscosity and normal stress difference can be integrated analytically:

$$\begin{aligned} \eta_0 &= \int_{-\infty}^{\ln \lambda_M} H(\lambda) \lambda d \ln \lambda \\ &= H_{CH} \lambda_{CH} \left[\frac{1 - (1 + \frac{\lambda_M}{\lambda_{CH}})^{1-n}}{n-1} \right]; \quad (n \neq 1) \quad (\text{IV-14}) \end{aligned}$$

$$\begin{aligned} \left[\frac{\tau'_{11} - \tau'_{22}}{K^2} \right]_{K \rightarrow 0} &= 2 \int_{-\infty}^{\ln \lambda_M} H(\lambda) \lambda^2 d \ln \lambda \\ &= H_{CH} \lambda_{CH}^2 \left[\frac{(1 + \frac{\lambda_M}{\lambda_{CH}})^{2-n} - 1}{2-n} \right. \\ &\quad \left. - \frac{1 - (1 + \frac{\lambda_M}{\lambda_{CH}})^{1-n}}{n-1} \right] \cdot \quad (n \neq 1) \quad (\text{IV-15}) \end{aligned}$$

It is obvious that the relaxation spectrum for polystyrene cannot be fitted by an equation of the form used to fit the polyisobutylene. However, because the curve is linear over significant shear rate ranges, it would seem reasonable to fit sections of the curve with equations of

the form:

$$H = H_{CH} \left(\frac{\lambda}{\lambda_{CH}} \right)^n \quad . \quad (IV-16)$$

For spectrum fitting of this type to be most useful, it would be desirable to have the various spectrum shapes classified and fitted with simple equations. Ferry (20) describes seven different spectrum shapes for solid visco-elastic materials and Tobolsky (43) suggests using a "wedge-box" shaped spectrum for polymer solutions with a sharp molecular weight distribution.

VI. RECAPITULATION AND DISCUSSION

Of the theories examined here, Bogue's theory and the Bernstein-Kearsley-Zapas theory are the most satisfactory for the purpose of making quantitative predictions for non-Newtonian behavior. By quantitative predictions is meant the ability to correlate linear data with viscosity and normal stress data. It is unfortunate that Oldroyd's and Pao's theories do not produce comparable results because they do possess several desirable features. They do not contain adjustable material parameters relating the linear and non-linear data, and both predict high shear rate Newtonian viscosities as have been reported by Brodnyan, et al. (10), and others. Also, Oldroyd's theory is appealing

because it contains only three material constants. In recent work Spriggs and Bird (41) have generalized the Rouse (40) molecular theory in the framework of Oldroyd's notation.

The correlation obtained using Bogue's theory and the Bernstein-Kearsley-Zapas theory is about the same. Bogue's theory produces a reasonable fit over a slightly greater shear rate range; whereas, the Bernstein-Kearsley-Zapas theory shows slightly less dependence on the material parameter. Both theories fail to predict high shear rate Newtonian viscosities unless an additional adjustable function is added, and both predict viscosity curves that do not bend sharply enough in the initial non-Newtonian region. The viscometric predictions of Bogue's theory are mathematically simpler. The ratio of computer time for corresponding calculations is roughly 10:1 (on the IBM 7040). The Bernstein-Kearsley-Zapas theory is conceptually a more general theory which includes compressibility and energetic effects (3).

It should be emphasized again that the test of the theories was rather demanding in that very different types of data were correlated with, at most, one experimental constant. It seems particularly significant that non-linear normal stress data were reasonably predicted from linear data that in no direct way involved normal stress.

Also, it should be said that the failure to predict the correct zero shear viscosity for the polystyrene solution is not a theoretical failing because all three integral theories reduce to the classically accepted expression for zero shear viscosity (20):

$$\eta(0) = \int_0^{\infty} H(\lambda) d\lambda \quad . \quad (\text{IV-17})$$

Of the two attempts to simplify the theories, the more promising seems to be that of curve-fitting directly to the relaxation spectrum with convenient functional forms. Because of the large range of the elastic moduli and relaxation times for polymer solutions, one cannot hope to describe behavior with one or two relaxation times.

CHAPTER V

VISCOELASTIC CHARACTERIZATION FOR ENGINEERING ANALYSIS

If one is to deal with complicated flow problems of practical interest (such as flow in a spinnerette), it is clear that considerable qualitative understanding of viscoelastic behavior is necessary. In this chapter an attempt is made to set down some of the qualitative observations that might be of value in an engineering analysis.

I. EXPERIMENTAL CHARACTERIZATION

A basic question in the area of viscoelasticity is, "What is the minimum number of measurements necessary to characterize a viscoelastic fluid?" As with the various equations of state for gases, the answer will depend on the situation. For instance, Bogue (9) has shown that non-Newtonian effects are relatively unimportant in many turbulent flows; and Metzner, White, and Denn (28) have approached engineering problems with power-law fits to viscosity and normal stress data. However, it seems clear that if problems are to be treated in which normal stresses as well as shearing stresses are significant, a constitutive equation relating both of them to the basic kinematics is necessary.

Coleman and Noll (12) show that three viscometric

functions are sufficient to characterize any viscometric flow, but their analysis does not lead to functional forms or to functional interdependence. In contrast, the theories considered here give explicit functional forms and also express interdependencies. If one examines Equations II-67, II-68, IV-4, and IV-5, one finds that if a or A is specified, then one needs to determine only the relaxation function, $H(\lambda)$, to predict rheological behavior generally. However, the theories have not been examined for the second normal stress effect, and it is possible that additional constants may be needed. Also, other classes of materials, or any material at very high shear rate, may require additional relaxation functions (such as the functions $\alpha(s)$ and $c(s)$ in Zapas' equation).

While use of the relaxation spectrum is the most direct from the standpoint of the theories, it is also possible to determine the spectrum from either the viscosity or the first normal stress function. One would use methods similar to those by which it is determined from dynamic data. That is, one would determine a function that is involved as a factor in an integrand.

In summation (again with the reservations concerning high shear rates and the second normal stress difference): if the material parameters a and A are constant for classes of materials, the relaxation spectrum or any

viscometric function of shear rate describes a fluid completely and predicts the other functions. If a and A vary from fluid to fluid, then any function and one point in the non-linear region of another function is required. It would seem then that viscoelastic characterization requires some quantity with stress units as a function of some quantity with time units.

II. DATA RANGE

The fluids tested exhibit a relaxation function that decreases sharply with increasing relaxation time. For such a fluid, the most significant portion of the spectrum associated with a shear rate is a range that is centered about a relaxation time equal to the reciprocal of the shear rate. Also, dynamic data are needed in a region centered about $\omega = 1/\lambda$ to produce a point on the relaxation spectrum at λ . Therefore, if one is taking dynamic data to make predictions over a certain shear rate range, the dynamic data should cover a somewhat greater range in ω and be centered about the shear rate range.

Since the more successful theories examined here involve the integration of the relaxation spectrum, it need not be represented with absolute precision at each point. It is more important to have the general shape represented with a curve bounding the proper area. Therefore, some

liberty can be taken in representing and extrapolating the spectrum. On the other hand, the original dynamic data must be as accurate as possible since data reduction generally involves derivations of these curves.

III. THE MOMENTUM EQUATION AND DIMENSIONAL ANALYSIS

A viscoelastic constitutive equation combined with a momentum balance produces the viscoelastic equivalent of the Navier-Stokes equations. Because of the mathematical complexity of such equations, it is unlikely that any boundary value problems, except for the very simplest, can be solved analytically. However, such equations are of value in providing a framework for numerical solutions and dimensional analysis.

Using a relaxation spectrum fit in the form of Equation IV-16, Bogue's theory can be combined with a momentum balance to produce the following result (9):

$$\frac{DV_i^*}{Dt^*} = - \frac{\partial p^*}{\partial x_i^*} + \frac{H_{CH}}{\rho v^2} \frac{\partial}{\partial x_i^*} \left[\int_0^\infty J_{ij}(s^*) \right]$$

(continued on page 85)

$$\begin{aligned}
& \cdot \int_{-\infty}^{\ln(\frac{\lambda_M}{\lambda_{CH}})} \left[\frac{1 + aK^* \lambda^* (\frac{\lambda_{CH}^V}{L})}{(1 + \lambda^*)^n \lambda^*} \right] \\
& \cdot \exp \left\{ - s^* \left[1 + aK^* \lambda^* (\frac{\lambda_{CH}^V}{L}) \right] \right\} d \ln \lambda^* ds^* \Bigg] \\
& + \text{double integral term,} \tag{V-1}
\end{aligned}$$

where

$$\begin{aligned}
v_i^* &= \frac{v_i}{V}, & s^* &= s / \lambda_{CH}, \\
t^* &= \frac{tV}{L}, & \lambda^* &= \lambda / \lambda_{CH}, \\
x_i^* &= \frac{x_i}{L}, & K^* &= \frac{1}{s^*} \int_0^{s^*} \left| \frac{II_d L}{V} \right|^{\frac{1}{2}} ds'^*, \\
p^* &= \frac{p}{\rho V^2}, \\
L &= \text{characteristic length,} & V &= \text{characteristic velocity.}
\end{aligned}$$

The equation produces six dimensionless parameters:

$$\frac{H_{CH}}{\rho V^2}, \quad \frac{\lambda_{CH}^V}{L}, \quad \frac{\lambda_M}{\lambda_{CH}}, \quad n, \quad a, \quad a'. \tag{V-2}$$

The first parameter can be put into the form of a Reynolds number by combining it with the second group and inverting:

$$\frac{LV\rho}{H_{CH} \lambda_{CH}}, \quad \frac{\lambda_{CH}^V}{L}, \quad \frac{\lambda_M}{\lambda_{CH}}, \quad n, \quad a, \quad a'. \tag{V-3}$$

A similar result would be obtained from the Bernstein-

Kearsley-Zapas theory.

Since only the first two groups in V-3 contain flow variables, they are sufficient to characterize a flow field. Unfortunately, the form prohibits scaling with a single fluid because the first group requires

$$L_1 V_1 = L_2 V_2 , \quad (V-4)$$

and the second group requires

$$\frac{V_1}{L_1} = \frac{V_2}{L_2} . \quad (V-5)$$

This condition is impossible to achieve with different size models (i.e., there is only one experiment to satisfy both constants). One would hope then that only one of the groups would be important for a given flow problem. Otherwise, it might be possible to show that some effects are predominantly associated with one group and vice-versa. This is done in scaling ship models where the Reynolds number is controlled to study viscous effects and the Froude number is controlled for surface wave effects. The discussion above is restricted to situations where geometric similarity is maintained. If this restriction were relaxed, one might be able to correlate effects between large and small flows although this would not be scaling in the usual sense of the word.

CHAPTER VI

CONCLUSIONS

The following conclusions were made on the basis of this investigation:

1. Pao's theory and Oldroyd's three-constant model produce viscometric stress functions of shear rate that are qualitatively correct but not quantitatively correct.

2. Bogue's theory and the Bernstein-Kearsley-Zapas theory correlate data for the relaxation spectrum, viscosity function, and second normal stress difference up to moderate shear rates. One adjustable parameter is involved in both theories; however, it is possible that they are constant for classes of materials.

3. The latter theories predict stress behavior at moderate shear rates from the relaxation spectrum assuming prior knowledge of a material constant (a or A). Possibly another constant is required to predict the second normal stress difference.

4. The most direct function to use to characterize a fluid is the relaxation spectrum; however, the viscosity function and the normal stress function can also be used. In general, one must have experimental data of something with stress units versus something with time units.

5. For non-linear predictions from linear dynamic

data one needs data over a range of angular frequency corresponding to the shear rate range of interest. In terms of the relaxation spectrum, the range of interest would be centered about relaxation times equal to the reciprocal of the shear rates.

6. A momentum balance produces six dimensionless parameters, only two of which contain flow variables (V and L). The form of the parameters prohibits direct scaling with one material so that other possibilities need investigating, such as the relative importance of the parameters in various flows and the possibility of correlation with more than one characteristic length.

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APPENDICES

APPENDIX A

FLOW ANALYSIS FOR A CONE AND PLATE RHEOMETER

The kinematic flow in a cone and plate can be easily described if the cone angle, α , is assumed to be very small so that the velocity profile is linear, $\sin \alpha \approx \alpha$, and $\cos \alpha \approx 1.0$. (See Figure 25 for illustrations of geometric nomenclature used here.) For this condition the shear rate is constant throughout the sample and is given by:

$$K = \frac{\omega}{\alpha} . \quad (A-1)$$

Then laminar flow can be analyzed with the following assumptions:

1. The deviatoric stresses are functions of shear rate only.
2. There is no secondary flow ($V_\theta = V_\phi = 0$).
3. Axial symmetry exists ($\frac{\partial}{\partial \phi} = 0$).
4. Inertia effects are negligible ($\rho \frac{D\bar{V}}{Dt} = 0$).
5. There are no body forces.
6. The environment exerts only normal stress at the outer circumferential boundary.

With these assumptions the r-directed equation of motion in spherical coordinates (5) reduces to:

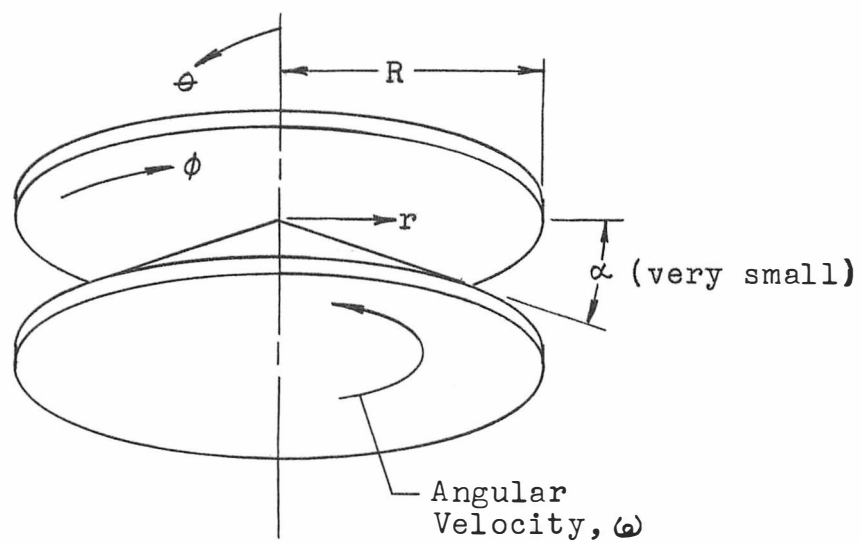


Figure 25. Illustration of Cone and Plate Nomenclature.

$$0 = -\frac{\partial p}{\partial r} + \frac{2\tau'_{rr} - \tau'_{\theta\theta} - \tau'_{\phi\phi}}{r}, \quad (\text{A-2})$$

or

$$-\frac{\partial p}{\partial(\ln r)} = \tau'_{\theta\theta} + \tau'_{\phi\phi} - 2\tau'_{rr}. \quad (\text{A-3})$$

The right side of Equation A-3 is independent of r ;
therefore,

$$\int_{p(R)}^{p(r)} -dp = (\tau'_{\theta\theta} + \tau'_{\phi\phi} - 2\tau'_{rr}) \int_{\ln R}^{\ln r} d(\ln r). \quad (\text{A-4})$$

Integration of Equation A-4 yields:

$$p(R) - p(r) = (\tau'_{\theta\theta} + \tau'_{\phi\phi} - 2\tau'_{rr}) \ln\left(\frac{r}{R}\right). \quad (\text{A-5})$$

The net force exerted on the plate is the difference in the integral of the total normal stress and the force of atmospheric pressure acting on the outside of the plate.

Thus,

$$F = - \int_0^R \tau_{\theta\theta} (2\pi r \, dr) - \pi R^2 p_0, \quad (\text{A-6})$$

where p_0 is ambient pressure. Since

$$\tau_{\theta\theta} = -p(r) + \tau'_{\theta\theta} \quad , \quad (A-7)$$

the integral becomes

$$F = -2\pi \int_0^R \left[-p(r) + \tau'_{\theta\theta} \right] r \, dr - \pi R^2 p_0 \quad . \quad (A-8)$$

Combining Equation A-5 with A-8 gives

$$\begin{aligned} F &= -2\pi \int_0^R \left[-p(R) + \tau'_{\theta\theta} + (\tau'_{\theta\theta} + \tau'_{\phi\phi} - 2\tau'_{rr}) \right. \\ &\quad \left. \cdot \ln\left(\frac{r}{R}\right) \right] r \, dr - \pi R^2 p_0 \\ &= \pi p(R) R^2 - \pi R^2 p_0 \\ &\quad - 2\pi \int_0^R \left[\tau'_{\theta\theta} + (\tau'_{\theta\theta} + \tau'_{\phi\phi} - 2\tau'_{rr}) \right. \\ &\quad \left. \cdot \ln\left(\frac{r}{R}\right) \right] r \, dr \\ &= \pi R^2 (p(R) - p_0 - \tau'_{\theta\theta}) \\ &\quad - 2\pi (\tau'_{\theta\theta} + \tau'_{\phi\phi} - 2\tau'_{rr}) \int_0^R \ln\left(\frac{r}{R}\right) r \, dr \\ &= R^2 (p(R) - p_0 - \tau'_{\theta\theta}) + \frac{\pi R^2}{2} (\tau'_{\theta\theta} + \tau'_{\phi\phi} - 2\tau'_{rr}) \quad . \quad (A-9) \end{aligned}$$

Then rearranging:

$$\frac{F}{\pi R^2} = p(R) - \tau'_{rr} - p_0 + \frac{\tau'_{\phi\phi} - \tau'_{\theta\theta}}{2} . \quad (A-10)$$

Combining $p(R)$ with τ'_{rr} , which does not vary with r , one has:

$$\frac{F}{\pi R^2} = - \tau'_{rr}(R) - p_0 + \frac{\tau'_{\phi\phi} - \tau'_{\theta\theta}}{2} .$$

At the circumferential free surface the total radial stress must be balanced by atmospheric pressure so that

$$- \tau'_{rr}(R) - p_0 = 0 . \quad (A-11)$$

Thus,

$$F = \frac{\pi R^2}{2} [\tau'_{\phi\phi} - \tau'_{\theta\theta}] , \quad (A-12)$$

and the measured force is related to the first normal stress difference without any assumptions about the rheological behavior of the fluid.

Equation A-3 can be shown to be in agreement with the experimental findings of Roberts (39), i.e., the total normal stress perpendicular to the shear planes varies logarithmically with radius in a cone and plate. From Equation A-3, for a given experiment,

$$\frac{\partial p}{\partial (\ln r)} = \text{const.} , \quad (\text{A-13})$$

and since

$$\frac{\partial \tau'_{\theta\theta}}{\partial (\ln r)} = 0 , \quad (\text{A-14})$$

then

$$\frac{\partial \tau_{\theta\theta}}{\partial (\ln r)} = - \frac{\partial p}{\partial (\ln r)} + \frac{\partial \tau'_{\theta\theta}}{\partial (\ln r)} = \text{const.} \quad (\text{A-15})$$

With the assumptions already noted, the shear stress can be related to the net torque by:

$$T = \int_0^R \tau'_{\theta\phi} \, 2\pi r^2 \, dr = 2\pi \tau'_{\theta\phi} \int_0^R r^2 \, dr . \quad (\text{A-16})$$

Integration of Equation A-16 results in:

$$\tau'_{\theta\phi} = \frac{3T}{2\pi R^3} .$$

APPENDIX B

DISCUSSION OF PAO'S THEORY

The basic concept in Pao's (34,35,36) theory is that there is a "natural state" from which strain is measured. While this natural state is defined mathematically, it is still useful to attempt to assign a physical interpretation to it. Because strains so defined are later given the meaning of "recoverable strain," it is reasonable to associate the natural state with the state to which the fluid would return if the external stress were removed. There is some confusion concerning the notation, however, and it seems worthwhile to present Pao's definitions (35) and to discuss some of the more subtle points of the theory.

The symbol $(r^{-1})_{ij}$ represents the strain components taken from the natural state and in Cartesian coordinates is defined by:

$$(r^{-1})_{ij} = \delta_{mn} \frac{\partial x^i}{\partial X^m} \frac{\partial x^j}{\partial X^n}, \quad (B-1)$$

where the x^i are the present coordinates and the X^j are the material coordinates. In simple shear the relationship between coordinates is given by:

$$\left. \begin{aligned} x_1 &= X_1 + KX_2(t-t_0) \\ x_2 &= X_2 \\ x_3 &= X_3 \end{aligned} \right\}, \quad (\text{B-2})$$

where $(t-t_0)$ is the time lag between the present state and the natural state. Then in steady shear:

$$\left. \begin{aligned} (r^{-1})_{11} &= 1 + K^2(t-t_0)^2 \\ (r^{-1})_{22} &= 1 \\ (r^{-1})_{12} &= K(t-t_0) = (r^{-1})_{21} \end{aligned} \right\}. \quad (\text{B-3})$$

The confusion concerning the nomenclature centers around the meaning of the symbol $(d/dt)(r^{-1})_{ij}$ (see Equation II-38). Although it appears to be the time derivative of the recoverable strain (which would be zero in the steady state case), it is not intended as such. Instead, it is the instantaneous strain rate measured relative to the natural state. Thus,

$$\frac{d}{dt}(r^{-1})_{11} = \frac{d}{dt} \left[\frac{\partial x_1}{\partial X_1} \frac{\partial x_1}{\partial X_1} + \frac{\partial x_1}{\partial X_2} \frac{\partial x_1}{\partial X_2} + \frac{\partial x_1}{\partial X_3} \frac{\partial x_1}{\partial X_3} \right], \quad (\text{B-4})$$

where the X^i coordinates are taken to be independent of time. Writing similar expressions for derivatives of the other components, one finally obtains:

$$\left. \begin{aligned} \frac{d}{dt}(r^{-1})_{11} &= 2K^2(t-t_0) \\ \frac{d}{dt}(r^{-1})_{22} &= 0 \\ \frac{d}{dt}(r^{-1})_{12} &= \frac{d}{dt}(r^{-1})_{21} = K \end{aligned} \right\} . \quad (B-5)$$

In describing strain with respect to the natural state, the fluid is tracked through a finite angle of rotation. An orthogonal rotating coordinate system is used to do this with the y -coordinates tracking the fluid and the x -coordinates fixed. The angle between the systems is ϕ , where $\phi = (K/2)t$. Pao then assumes that the fluid is described in the rotating system by (see Chapter II):

$$(\tau'_{ab} + p \delta_{ab})_y = \sum_n G_n e^{-t/\lambda_n} (\Delta r_{ab}^{-1})_y . \quad (B-6)$$

The strain increment affecting the fluid at any time is assumed to be the summation of all the increments over past time, summed after adjustment for the decay which took place because of the different initial time associated with each infinitesimal strain. Expressing this notion mathematically, one has:

$$(\tau'_{ab} + p \delta_{ab})_y = \int_0^t \sum_n G_n e^{-\frac{(t-\xi)}{\lambda_n}} \frac{d(r^{-1})_{ab}}{d\xi} d\xi . \quad (B-7)$$

This equation is assumed to describe viscoelastic behavior with respect to the rotating coordinate system. The transformation back to the fixed coordinate system is accomplished by:

$$\tau'_{ij} + p \delta_{ij} = \frac{\partial x_i}{\partial y_a} \frac{\partial x_j}{\partial y_b} \int_0^t \sum_n G_n e^{-\frac{(t-\epsilon)}{\lambda_n}} \cdot \frac{d}{d\epsilon} \left[(r^{-1})_{ij} \frac{\partial y_a}{\partial x_i} \frac{\partial y_b}{\partial x_j} \right] d\epsilon, \quad (B-8)$$

where

$$\left. \begin{aligned} \frac{\partial x_1}{\partial y_1} &= \frac{\partial y_1}{\partial x_1} = \cos \phi \\ \frac{\partial x_2}{\partial y_1} &= \frac{\partial y_1}{\partial x_2} = \sin \phi \\ \frac{\partial x_1}{\partial y_2} &= \frac{\partial y_2}{\partial x_1} = -\sin \phi \\ \frac{\partial x_2}{\partial y_2} &= \frac{\partial y_2}{\partial x_2} = -\cos \phi \end{aligned} \right\} \cdot \quad (B-9)$$

If the fluid were being tracked for a small time increment, one would have $\cos \phi \approx 1$, $\sin \phi \approx \phi$. This linearization leads to a viscosity that is independent of shear rate. Thus it is essential to use the transformation relationships in their non-linear form ($\cos \phi$ and $\sin \phi$) to achieve a

shear-dependent viscosity.

In order to achieve Pao's explicit results, a final assumption must be made that he refers to as the "isotropic" assumption. This involves assuming that in the fixed coordinate system, τ'_{11} depends only on $(r^{-1})_{11}$ and $(d/d\varepsilon)(r^{-1})_{11}$; τ'_{12} depends only on $(r^{-1})_{12}$ and $(d/d\varepsilon)(r^{-1})_{12}$; etc. It is clear from the original statement of the theory that this is true in the rotating system but not obvious for the fixed system since generally, in a transformation from one coordinate system to another, each strain component in one system is a function of all components in another. Stated mathematically, Pao's isotropic assumption is:

$$\begin{aligned} \tau'_{ij} + p\delta_{ij} = & \frac{\partial x_i}{\partial y_a} \frac{\partial x_j}{\partial y_b} \int_0^t G_n \sum_n e^{-\frac{t-\varepsilon}{\lambda_n}} \\ & \cdot \frac{d}{d\varepsilon} \left[(r^{-1})_{ij} \frac{\partial y_a}{\partial x_i} \frac{\partial y_b}{\partial x_j} \right] d\varepsilon \\ & (i \text{ and } j \text{ not summed}) . \quad (B-10) \end{aligned}$$

Using both Equations B-8 and B-10, one can, in principle, obtain Pao's explicit predictions for steady viscometric flow. (Writing out Equation B-8 gives a number of extra terms which are set equal to zero.)

It would be more satisfying if the isotropic assumption were a result of the theory rather than an assumption made near the end of the analysis. Some additional constitutive relationship is needed at the beginning which manifests itself as the isotropic assumption in the final result.

APPENDIX C

COMPUTER PROGRAMS

All computer processing done in connection with this dissertation was coded in Fortran II and processed on an IBM 7040 computer. The most significant programs are listed in this Appendix. A subroutine is used with all programs except the one for calculating $H(\lambda)$ (see Section VI).

I. PROGRAM FOR CALCULATING THE RELAXATION SPECTRUM FROM G''

This program fits parabolas through short segments of the G'' curve and incorporates the method of Staverman and Schwarzl (42) to calculate a first approximation to the relaxation spectrum. The input data are defined as follows:

NP = number of points used to represent the
 G'' curve,
W(1) = logarithm of the least value of angular
frequency,
G(I) = NP numerical values of G'' spaced in
increments of $\log \omega = 0.2$.

The output yields $H(\lambda)$ and $\log H(\lambda)$; running time, including compilation, is about 2 minutes. The program is listed in Table III.

TABLE III

PROGRAM FOR CALCULATING THE RELAXATION
SPECTRUM FROM G"

```

C      PROGRAM FOR CALCULATING LOG H FROM GDOUBLEPRIME
      DIMENSION W(100),G(100),VLH(100),VH(100),VL(100)
      READ 100,NP
      READ 101, W(1)
      READ 101, (G(I),I=1,NP)
      PRINT 104
      DO 10 I=2,NP
        J=I-1
10     W(I)=W(J)+.2
        K=NP-2
        DO 20 I=3,K
          U=W(I-2)
          Z=W(I)
          Y=W(I+2)
          A=G(I-2)
          C=G(I)
          E=G(I+2)
          DN=Z*Y*Y-Y*Z*Z+U*Z*Z-U*Y*Y+U*U*Y-U*U*Z
          ADN=A*Z*Y*Y-A*Z*Z*Y-U*C*Y*Y+U*E*Z*Z+U*U*C*Y-U*U*E*Z
          BDN=C*Y*Y-E*Z*Z-A*Y*Y+A*Z*Z+E*U*U-C*U*U
          CDN=E*Z-C*Y-E*U+C*U+A*Y-A*Z
          A=ADN/DN
          B=BDN/DN
          C=CDN/DN
          VH(I)=.637*(10.**G(I))*(1.-(B+2.*C*Z)**2.-2.*C)
          VLH(I)=ALOG10(VH(I))
          VL(I)=-W(I)
20     PRINT 103,VL(I),VH(I),VLH(I)
100    FORMAT(I2)
101    FORMAT(16F5.0)
103    FORMAT(1H9,4X,F6.3,8X,E10.3,5X,F6.3)
104    FORMAT(1H9,38H      LOG LAMBDA      H OF LAMBDA      LOG H)
      END

```

II. PROGRAM FOR REPRODUCING DYNAMIC DATA FROM THE RELAXATION SPECTRUM

This program reproduces G' , G'' , and η' from the relaxation spectrum using Equations II-18, II-20, and II-21. The input is as follows:

NP = number of points used to represent the
relaxation spectrum,
A(1) = the logarithm of the least relaxation
time used,
DEL = the logarithmic spacing of points on the
relaxation spectrum,
H(I) = NP values of the logarithm of $H(\lambda)$.

The output includes $\log G'$, $\log G''$, and $\log \eta'$.
Running time is about 2 minutes, including compilation.
The program is listed in Table IV.

III. PROGRAM FOR CALCULATING VISCOSITY AND NORMAL STRESS WITH PAO'S THEORY

This program calculates the shear dependent viscosity and first normal stress difference by Pao's theory using Equations II-40 and II-41. Calculations are made from a numerically represented relaxation spectrum. The input data are defined as follows:

TABLE IV

PROGRAM FOR REPRODUCING DYNAMIC DATA
FROM THE RELAXATION SPECTRUM

```

C      CALCULATE G-PRIME, G-DOUBLEPRIME, AND ETA-PRIME FROM H
      DIMENSION A(100),W(100),H(100),X(100),Y(100),Z(100),
      ID(100)
      READ 100,NP
      READ 101,A(1)
      READ 101,DEL
      READ 101,(H(I),I=1,NP)
      PRINT 104
      DO 10 I=2,NP
      J=I-1
10     A(I)=A(J)+.2
      DO 20 I=1,NP
      W(I)=-A(I)
      DO 30 J=1,NP
      D(J)=1.+10.** (2.*(W(I)+A(J)))
      X(J)=10.** (H(J)+W(I)+W(I)+A(J)+A(J))
      X(J)=(ALOG(10.)*X(J))/D(J)
      Y(J)=10.** (H(J)+W(I)+A(J))
      Y(J)=(ALOG(10.)*Y(J))/D(J)
      Z(J)=10.** (H(J)+A(J))
30     Z(J)=(ALOG(10.)*Z(J))/D(J)
      CALL SIM(X,NP,DEL,SUMX)
      CALL SIM(Y,NP,DEL,SUMY)
      CALL SIM(Z,NP,DEL,SUMZ)
      SUMX=ALOG10(SUMX)
      SUMY=ALOG10(SUMY)
      SUMZ=ALOG10(SUMZ)
20     PRINT 103,W(I),SUMX,SUMY,SUMZ
100    FORMAT(12)
101    FORMAT(13F6.3)
103    FORMAT(1H9,5X,F6.3,7X,F6.3,8X,F6.3,10X,F6.3)
104    FORMAT(1H9,28H      LOG OMEGA      LOG G PRIME,
133H      LOG G DPRIME      LOG ETA PRIME)
      END

```

NP = number of points used to represent the
 relaxation spectrum,
 A(1) = logarithm of the least relaxation time used,
 DEL = the logarithmic spacing of points on the
 relaxation spectrum,
 H(1) = NP values of the logarithm of $H(\lambda)$,
 S(1) = the logarithm of the least shear rate used,
 DELS = the logarithmic spacing of values of shear
 rate,
 NS = number of shear rate values used.

The program is listed in Table V. Run time is about 1.5 minutes.

IV. PROGRAM FOR CALCULATING VISCOSITY AND NORMAL STRESS WITH BOGUE'S THEORY

This program calculates the shear dependent viscosity and first normal stress difference by Bogue's theory using Equations II-67 and II-68. The material parameter a is varied in increments of 0.1 through a range of $a=0.1$ to $a=1.0$. Input data are identical to those for Pao's theory (see Section III of this Appendix). Total run time is about 2 minutes. A listing of the program is given in Table VI.

TABLE V

PROGRAM FOR CALCULATING VISCOSITY AND
NORMAL STRESS WITH PAO'S THEORY

```

C      CALCULATE VISCOSITY AND NORMAL STRESS BY PAO
      DIMENSION A(100),H(100),X(100),Y(100),S(100),D(100)
      READ 100,NP
      READ 101,A(1)
      READ 101,DEL
      READ 101,(H(I),I=1,NP)
      READ 101,S(1)
      READ 101,DELS
      READ 100,NS
      PRINT 104
      DO 10 I=2,NP
        J=I-1
10     A(I)=A(J)+.2
        DO 11 I=2,NS
          J=I-1
11     S(I)=S(J)+DELS
          DO 20 I=1,NS
            DO 30 J=1,NP
              D(J)=1.+10.** (2.*(A(J)+S(I)))
              X(J)=(10.** (AUJ)+H(J))/D(J)
30     Y(J)=(10.** (A(J)+A(J)+H(J)))/D(J)
          CALL SIM(X,NP,DEL,SUMX)
          CALL SIM(Y,NP,DEL,SUMY)
          ETA=ALOG(10.)M(SUMX+(10.** (2.*S(I))*SUMY*SUMY)/SUMX)
          TOVT=(2.*(10.**S(I))*SUMY)/SUMX
          TDIF=(ETA*TOVT)/(10.**S(I))
          TDIF=ALOG10(TDIF)
          TOVT=ALOG10(TOVT)
          ETA=ALOG10(ETA)
20     PRINT 102,S(I),ETA,TOVT,TDIF
100    FORMAT(I2)
101    FORMAT(13F6.3)
102    FORMAT(1H9.5X,F6.3,7X,F6.3,5X,F6.3,7X,F6.3)
104    FORMAT(1H9.37H   LOG SHEAR   LOG ETA   LOG T-T/T,
114H   LOG T-T/K2)
      END

```

TABLE VI

PROGRAM FOR CALCULATING VISCOSITY AND
NORMAL STRESS WITH BOGUE'S THEORY

```

C      CALCULATE VISCOSITY AND NORMAL STRESS BY BOGUE
      DIMENSION A(100),H(100),X(100),Y(100),S(100),D(100),
1C(100)
      READ 100,NP
      READ 101,A(1)
      READ 101,DEL
      READ 101,(H(I),I=1,NP)
      READ 100,NS
      READ 101,S(1)
      READ 101,DELS
      PRINT 104
      DO 10 I=2,NP
        J=I-1
10     A(I)=A(J)+.2
        DO 11 I=2,NS
          J=I-1
11     S(I)=S(J)+DELS
          C(I)=.0
          DO 50 L=2,11
            M=L-1
            C(L)=C(M)+.1
            B=ALOG10(C(L))
            DO 20 I=1,NS
              DO 30 J=1,NP
                D(J)=1.+10.**((S(I)+A(J)+B)
30          X(J)=(10.**((A(J)+H(J)))/D(J)
                Y(J)=(10.**((A(J)+A(J)+H(J)))/(D(J)*D(J))
              CALL SIM(X,NP,DEL,SUMX)
              CALL SIM(Y,NP,DEL,SUMY)
              ETA=ALOG(10.)*SUMX
              TDIF=2.*ALOG(10.)*SUMY
              TOVT=(TDIF*(10.**S(I)))/ETA
              ETA=ALOG10(ETA)
              TDIF=ALOG10(TDIF)
              TOVT=ALOG10(TOVT)
20          PRINT 102,S(I),ETA,TOVT,TDIF
50          CONTINUE
100         FORMAT(I2)
101         FORMAT(13F6.3)
102         FORMAT(1H9,5X,F6.3,7X,F6.3,5X,F6.3,7X,F6.3)

```

TABLE VI (continued)

104	FORMAT(1H9,37H	LOG SHEAR	LOG ETA	LOG T-T/T.
	114H	LOG T-T/K2)		
	END			

V. PROGRAM FOR CALCULATING VISCOSITY AND NORMAL
STRESS WITH THE BERNSTEIN-KEARSLEY-ZAPAS
THEORY

This program calculates the shear dependent viscosity and first normal stress difference by the Bernstein-Kearsley-Zapas theory using Equations II-56 and II-57. The material parameter A is varied through a range of 0.1 to 1.0 in increments of 0.1. Input data are as follows:

NP = number of points used to represent the
 relaxation spectrum,
A(1) = the logarithm of the least relaxation time
 used,
DEL = the logarithmic spacing of points on the
 relaxation spectrum,
H(I) = NP values of the logarithm of $H(\lambda)$,
NS = number of shear rate values used,
S(1) = the logarithm of the least shear rate used,
DELS = the logarithmic spacing of values of shear
 rate,
NZ = the number of values of s used in
 integrating over time,
DELZ = the logarithmic spacing of s ,
Z(1) = the logarithm of the least value of s used.

This program is listed in Table VII. The run time is approximately 20 minutes. When running this program, some method of suppressing underflow errors must be used. Extremely small values for the integrand are generated when integrating over time at each end of the integration (see Figure 21, page 72).

VI. SUBROUTINE FOR NUMERICAL INTEGRATION

This subroutine, identified as SIM, performs numerical integration by utilizing Simpson's rule. The variables which link it with the mainline program appear in the subroutine argument in the order listed below:

Y = NP ordinates of the function being
 integrated,
NP = number of ordinates used in the integration,
DEL = the spacing of the ordinates,
SUM = the final value of the integral.

The number of ordinates used should be odd for maximum accuracy; however, in the case where the value of the ordinates approaches zero on each end of the integration, as is the case with many functions encountered here, this is of no consequence. See Table VIII for a listing of Subroutine SIM.

TABLE VII

PROGRAM FOR CALCULATING VISCOSITY AND NORMAL STRESS
WITH THE BERNSTEIN-KEARSLEY-ZAPAS THEORY

```

C      CALCULATE VISCOSITY AND NORMAL STRESS BY BKZ
      DIMENSION A(100),H(100),X(1000),Y(1000),S(100),Z(1000),
1X2(100),Y2(100),C(100)
      READ 100,NP
      READ 101,A(1)
      READ 101,DEL
      READ 101,(H(I),I=1,NP)
      READ 100,NS
      READ 101,S(1)
      READ 101,DELS
      READ 100,NZ
      READ 101,DELZ
      READ 101,Z(1)
      PRINT 104
      DO 10 I=2,NP
        J=I-1
10     A(I)=A(J)+.2
        DO 11 I=2,NS
          J=I-1
11     S(I)=S(J)+DELS
          DO 12 I=2,NZ
            J=I-1
12     Z(I)=Z(J)+DELZ
            DO 13 I=1,NP
              A(I)=10.**A(I)
13     H(I)=10.**H(I)
              DO 14 I=1,NS
                S(I)=10.**S(I)
14     S(I)=10.**S(I)
                DO 15 I=1,NZ
                  Z(I)=10.**Z(I)
15     Z(I)=10.**Z(I)
          C(I)=.0
          DO 50 L=2,11
            M=L-1
            C(L)=C(M)+.1
            DO 20 I=1,NS
              DO 30 J=1,NP
                DO 40 K=1,NZ
                  E=-(Z(K)/A(J))
                  E=EXP(E)
                  D=A(J)*(1.+C(L)*S(I)*S(I)*Z(K)*Z(K))

```

TABLE VII (continued)

```

      X(K)=(H(J)*E*Z(K)*Z(K))/D
40    Y(K)=X(K)*Z(K)
      CALL SIM(X,NZ,DELZ,SUMX)
      CALL SIM(Y,NZ,DELZ,SUMY)
      X2(J)=SUMX
30    Y2(J)=SUMY
      CALL SIM(X2,NP,DEL,SUMX)
      CALL SIM(Y2,NP,DEL,SUMY)
      ETA=5.304*SUMX
      TDIF=5.304*SUMY
      TOVT=(TDIF*S(I))/ETA
      ETA=ALOG10(ETA)
      TDIF=ALOG10(TDIF)
      TOVT=ALOG10(TOVT)
      SHEAR=ALOG10(S(I))
20    PRINT 102,SHEAR,ETA,TOVT,TDIF
100   FORMAT(I3)
101   FORMAT(13F6.3)
50    CONTINUE
102   FORMAT(1H9,5X,F6.3,7X,F6.3,5X,F6.3,7X,F6.3)
104   FORMAT(1H9,37H LOG SHEAR LOG ETA LOG T-T/T,
114H LOG T-T/K2)
      END

```

TABLE VIII

SUBROUTINE FOR NUMERICAL INTEGRATION

```
SUBROUTINE SIM(Y,NP,DEL,SUM)
  DIMENSION Y(1000)
  SUM = Y(1) + Y(NP)
  M = NP-1
  DO 2 I = 2,M,2
2 SUM = SUM + 4.*Y(I)
  N = NP-2
  DO 3 I = 3,N,2
3 SUM = SUM + 2.*Y(I)
  SUM = (DEL*SUM)/3.
  RETURN
END
```

APPENDIX D

EXPERIMENTAL DATA

The experimental data for the 12 per cent polystyrene solution are tabulated in the following tables:

Table IX tabulates dynamic data.

Table X tabulates the relaxation spectrum.

Table XI tabulates viscometric data.

The experimental data for the 10 per cent polyisobutylene solution are tabulated as follows:

Table XII tabulates dynamic data.

Table XIII tabulates the relaxation spectrum.

Table XIV tabulates viscometric data.

Viscometric data taken for a 3 per cent napalm solution are given in Table XV.

TABLE IX
DYNAMIC DATA FOR A 12 PER CENT POLYSTYRENE
SOLUTION IN AROCLOR

$\log \omega$ rad./sec.	$\log \eta'$ poise	$\log G''$ dynes/cm. ²
-1.224	2.416	1.193
-.924	2.418	1.494
-.722	2.415	1.694
-.428	2.450	2.025
-.224	2.389	2.167
.076	2.394	2.471
.278	2.389	2.668
.576	2.332	2.930
.776	2.384	3.162
1.076	2.316-2.346	3.391-3.424
1.275	2.290-2.301	3.566-3.576
1.576	2.215-2.241	3.791-3.821
1.678	2.207	3.882
1.776	2.133-2.146	3.907-3.924
1.877	2.090	3.964
1.974	2.061	4.034
2.076	2.038-2.083	4.114-4.158
2.179	1.980	4.158
2.278	1.908-1.924	4.185-4.201
2.378	1.830-1.860	4.210-4.238
2.476	1.794	4.269-4.270
2.576	1.742	4.318

TABLE X
RELAXATION SPECTRUM FOR 12 PER CENT
POLYSTYRENE IN AROCLOR

$\log \lambda_{-1}$ sec.	$\log H$ dynes/cm. ²
-3.2	4.710
-3.0	4.530
-2.8	4.360
-2.6	4.190
-2.4	4.030
-2.2	3.850
-2.0	3.670
-1.8	3.490
-1.6	3.290
-1.4	3.090
-1.2	2.860
-1.0	2.600
-0.8	2.310
-0.6	2.010
-0.4	1.690
-0.2	1.270
0.0	0.720
0.2	0.320
0.4	-0.010
0.6	-0.240
0.8	-0.430
1.0	-0.590
1.2	-0.740
1.4	-0.900
1.6	-1.130

TABLE XI
 VISCOMETRIC DATA FOR 12 PER CENT
 POLYSTYRENE IN AROCLOR

$\log K$ sec. ⁻¹	$\log \eta$ poise	$\log \frac{\tau'_{11} - \tau'_{22}}{K^2}$ dynes-sec. ² /cm. ²
-1.728	2.432	
-1.428	2.418	
-1.223	2.415	
-.952	2.405	
-.735	2.348	
-.728	2.402	
-.535	2.373	
-.428	2.389	
-.236	2.375	
-.223	2.402	
-.034	2.376	
.070	2.398	
.265	2.380	
.272	2.402	
.465	2.373	
.572	2.405	
.764	2.375	1.000
.776	2.396	
.966	2.358	.941
1.070	2.373	
1.265	2.330	.717
1.272	2.352	
1.465	2.281	.733
1.572	2.310	
1.664	2.267	.600
1.776	2.262	
1.732	2.179	
1.865	2.220	.456
1.932	2.143	.175
1.966	2.185	.405
2.064	2.143-2.168	.305
2.164	2.087	.218
2.232	2.051-2.054	.021
2.334	2.021	
2.432	1.981-1.986	-.105
2.532	1.950	

TABLE XI (continued)

$\log K$ sec. ⁻¹	$\log \eta$ poise	$\log \frac{\tau'_{11} - \tau'_{22}}{K^2}$ dynes-sec. ² /cm. ²
2.632	1.906	
2.732	1.871-1.874	-.379
2.832	1.845	
2.932	1.766-1.815	-.586
3.028	1.782	
3.134	1.724	
3.232	1.645-1.673	-.917
3.432	1.548	-1.226
3.732	1.382	-1.640

TABLE XII

DYNAMIC DATA FOR A 10 PER CENT POLYISOBUTYLENE
SOLUTION IN DECALIN

$\log \omega$ rad./sec.	$\log \eta'$ poise	$\log G''$ dynes/cm. ²
-1.522	3.290	1.767
-1.322	3.274	1.954
-1.122	3.216	2.097
-.924	3.181	2.259
-.722	3.124	2.414
-.428	3.071	2.648
-.224	3.032	2.811
.076	2.949	3.039
.278	2.862	3.142
.576	2.728	3.306
.776	2.607	3.385
1.076	2.394	3.594
1.275	2.257	3.532
1.576	2.041	3.619
1.776	1.888	3.665
2.076	1.641	3.718
2.276	1.437	3.717
2.378	1.364	3.738
2.476	1.292	3.766

TABLE XIII
RELAXATION SPECTRUM FOR 10 PER CENT
POLYISOBUTYLENE IN DECALIN

$\log \lambda$ sec. ⁻¹	$\log H$ dynes/cm. ²
-3.4	3.600
-3.2	3.600
-3.0	3.600
-2.8	3.600
-2.6	3.600
-2.4	3.585
-2.2	3.556
-2.0	3.496
-1.8	3.458
-1.6	3.404
-1.4	3.408
-1.2	3.344
-1.0	3.283
-0.8	3.187
-0.6	3.044
-0.4	2.870
-0.2	2.687
0.0	2.440
0.2	2.242
0.4	2.044
0.6	1.801
0.8	1.499
1.0	1.131
1.2	0.889
1.4	0.652
1.6	0.360
1.8	0.020
2.0	-0.240
2.2	-0.510

TABLE XIV
VISCOMETRIC DATA FOR 10 PER CENT
POLYISOBUTYLENE IN DECALIN

$\log K$ sec. ⁻¹	$\log \eta$ poise	$\log \frac{\tau_{11} - \tau_{22}}{K^2}$ dynes-sec. ² /cm. ²
-1.533	3.255	
-1.235	3.215	
-1.032	3.193	
-.732	3.165	
-.533	3.165	
-.235	3.057-3.107	3.26
-.032	3.055	
.268	2.905-2.950	2.645-2.700
.467	2.870	
.765	2.655-2.684	2.140-2.145
.968	2.528	
1.232	2.438-2.445	1.523
1.268	2.301-2.387	1.520-1.530
1.432	2.292-2.326	1.196
1.467	2.149	
1.732	2.097-2.116	0.766
1.765	1.892-2.042	0.820
1.932	1.962-1.975	0.475
2.232	1.726-1.752	0.061
2.432	1.592-1.614	-0.128
2.732	1.367-1.428	-0.520
2.932	1.218-1.255	-0.780
3.232	0.992-1.053	-1.161
3.432	0.848-0.895	-1.438
3.732	0.600-0.698	-1.841

TABLE XV
VISCOMETRIC DATA FOR A 3 PER CENT
NAPALM SOLUTION

$\log K$ sec. ⁻¹	$\log \eta$ poise
-2.755	4.502
-2.452	4.316
-2.153	4.214
-1.955	4.122
-1.674	3.922
-1.354	3.522
-1.081	3.352
-0.754	3.336
-0.339	3.394
-0.237	3.197
-0.037	2.948
0.261	2.603
0.562	2.412
0.763	2.229

LIST OF SYMBOLS

LIST OF SYMBOLS

- a - material constant, dimensionless.
- a' - material constant, dimensionless.
- A - material constant, dimensionless.
- $A_{ij}^{(2)}$ - second Rivlin-Ericksen tensor.
- b - time constant, T.
- b_k - material function, FL^{-2} .
- c - decay function, T.
- c' - derivative of c with respect to time, dimensionless.
- c_k - material function, FL^{-2} .
- C_{ij}, C_{ij}^{-1} - non-linear strain tensor.
- $d_{ij} = V_i|j + V_j|i$, deformation rate tensor.
- D/Dt - substantive time derivative.
- $\partial/\partial t$ - the Jaumann time derivative.
- g_{ij} - metric tensor.
- $G(\lambda)$ - material function, $FL^{-2}T^{-1}$.
- $G_1, G_2, G_3 \dots$ - material constants, FL^{-2} .
- G^* - complex dynamic shear modulus, FL^{-2} .
- G' - shear storage modulus, FL^{-2} .
- G'' - shear loss modulus, FL^{-2} .
- $H(\lambda)$ - relaxation function, FL^{-2} .
- H_{CH} - characteristic stress, FL^{-2} .
- I - first invariant of the Finger strain tensor.
- II - second " " " " " " .

- II_d - second invariant of the deformation rate tensor.
 II_J - second invariant of the deformation history tensor.
 J_{ij} - deformation history tensor.
 k - thermal conductivity, $FL^{-1}\Theta^{-1}$.
 K - shear rate, T^{-1} .
 K^* - complex shear rate, T^{-1} .
 L - characteristic length, L .
 m - decay function, FL^{-2} .
 m' - derivative of m with respect to time.
 m_k - shear dependent decay function, FL^{-2} .
 n - material parameter, dimensionless.
 p - scalar pressure, FL^{-2} .
 p_0 - ambient pressure, FL^{-2} .
 P_1 - see Equation II-42.
 P_2 - see Equation II-43.
 r - radial coordinate, L .
 $(r^{-1})_{ij}$ - Pao's strain tensor.
 R - cone and plate radius, L .
 s - a backward running time index, T .
 S_a - " " " " " "
 S_b - " " " " " "
 t - time, T .
 t' - a dummy time index, T .
 T - temperature, Θ ; or torque, FL .
 U - a scalar function, $FL^{-2}T^{-1}$.

- V - characteristic velocity, LT^{-1} .
 V^i - velocity vector.
 W - strain energy or an arbitrary scalar, FL^{-2} .
 x^i - coordinates at time t .
 X^i - coordinates at some past time.
 y^a - laboratory coordinates in Pao's theory.

Greek Letters

- α - material function, or cone angle.
 α_n - decay function.
 β - material function.
 γ - shear strain, dimensionless.
 γ_o - amplitude of dynamic shear strain, dimensionless.
 γ^* - complex shear strain, dimensionless.
 δ_{ij} - Kronecker delta.
 $\mathcal{E}$ - time measured from a reference state in Pao's theory, T .
 η - apparent viscosity, FTL^{-2} .
 η^* - complex viscosity, FTL^{-2} .
 η' - dynamic viscosity, FTL^{-2} .
 η'' - imaginary component of the complex viscosity, FTL^{-2} .
 θ - spherical coordinate.
 λ - relaxation time, T .
 $\lambda_1, \lambda_2, \lambda_3 \dots$ - discrete relaxation times, T .
 λ_{CH} - characteristic relaxation time, T .

- λ_M - maximum relaxation time, T.
 μ - viscosity, FTL^{-2} .
 μ_1, μ_2, μ_3 - material constants, FTL^{-2} .
 ρ - mass density, FT^2L^{-4} .
 τ - shear stress, FL^{-2} .
 τ_{ij} - stress tensor.
 τ'_{ij} - deviator stress tensor.
 ϕ - phase angle shift, or spherical coordinate.
 ω - angular frequency, T^{-1} ; or angular velocity, T^{-1} .
 ω_{ij} - vorticity tensor.

Subscripts and Superscripts

- 1 - flow direction in Cartesian coordinates.
 2 - direction perpendicular to a boundary in Cartesian coordinates.
 3 - direction perpendicular to flow and parallel to boundary.
 r - radial direction in spherical coordinates.
 θ - direction perpendicular to boundary in spherical coordinates.
 ϕ - circumferential direction in spherical coordinates.

VITA

The author was born in Tuscaloosa, Alabama, on June 11, 1933. He was the oldest child of four. His father, Orus Doughty, has a retail furniture business in West Point, Mississippi.

The author holds a Bachelor of Science (Mississippi State University--1956) and Master of Science (Mississippi State University--1960) in Aeronautical Engineering. He is a member of Lambda Chi Alpha social fraternity, Sigma Xi, and The American Association for Engineering Education. During his senior undergraduate year, he served as chapter president of Epsilon Chi Zeta of Lambda Chi Alpha.

After receiving his B.S., he worked as a design engineer on the F4H, Phantom II aircraft at McDonnell Aircraft Corporation in St. Louis, Missouri. He has taught Engineering Graphics at Mississippi State University and has taught Engineering Graphics, Basic Engineering, and Engineering Mechanics at The University of Tennessee. He will be on the staff of the Aerospace Engineering Department of The University of Alabama, Tuscaloosa, Alabama, after receiving his Ph.D. in Engineering Science from The University of Tennessee. The author's hobbies include golf, in which he shoots in the low 120's, and sketching. In high school he lettered in basketball and baseball.

The author capitalized on a moment of weakness and persuaded Miss Barbara Ann Parr to become his wife in 1956. This blissful union has produced two children, Glenn (nine) and Diane (four), each more perplexing than the other.