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AND LUBRICANTS AT HIGH PRESSURE

A DISSERTATION
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degree of
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BY
TOM TING CHARNG
Norman, Oklahoma

1974

VISCOELASTIC PROPERTIES OF DILUTE POLYMER SOLUTION
AND LUBRICANTS AT HIGH PRESSURE

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To My Parents

ABSTRACT

Torsionally oscillating quartz crystal viscometers with fundamental oscillating frequencies of 20 kHz and 60 kHz were employed to obtain viscosities of lubricants and of polymeric solutions in the pressure range from atmospheric pressure to 120,000 psig and constant temperatures of 77°, 100°, 210° and 300°F. In addition, the effects of temperature and pressure on the density of test liquids were measured.

Four lubricants, Humble FN-3158, Humble FN-3158 + 10 volume percent Kendall 0839 resin, Mobil XRM-109, and DuPont Krytox 143-AB, were tested at constant temperatures of 100°, 210° and 300°F and at pressures from atmospheric pressure to 40,000 psig. Of the lubricants investigated, viscoelastic behavior of Humble FN-3158 plus 10 vol percent 0839, Mobil XRM-109 at 100°F and pressures up to 20,000 psig were detected.

The viscoelastic behavior of a solution of three weight percent polystyrene in toluene was also detected at 77° and 100°F and the entire range of pressures. The pressure effect on the polymer contribution to the solution viscosity was tested. Dynamic viscosity and shear storage modulus are presented as functions of pressure at both 77° and 100°F.

The reduced dynamic viscosity and reduced shear storage modulus are presented as a function of reduced angular frequencies, ranging from 3×10^5 to 2×10^7 radians per second. The data on the polystyrene solution are also compared with theoretical curves calculated from the Rouse and Zimm theories.

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CHAPTER I

INTRODUCTION

In the past two decades, commercial and industrial interests in synthetic polymeric materials have given great impetus to the rapid growth of the science of rheology. The study of flow properties of polymeric fluids is a small part of rheology, which is the study of the time-dependent deformations of a material under the influence of externally imposed forces.

Many theoretical derivations and much experimental work have been devoted to descriptions of the actual response of materials. New requirements and new products in the field of polymer processing and lubrication engineering call for more knowledge on the viscoelastic behavior of polymers and polymer solutions under the combined conditions of high pressure and high temperature. Better understanding of the physical behavior of such fluids under these conditions is needed for the design of the equipment and the processing techniques.

Polymer solutions such as multigraded lubricants used in high-speed bearings and gears are most likely to exhibit

viscoelastic behavior. In practice, the thin oil film in the bearings and gears is subjected to a hydrostatic pressure of several thousand pounds per square inch. Under these high pressures, the apparent viscosity of a lubricant exhibiting viscoelastic behavior can be less than what one would expect from a Newtonian fluid at the same pressure. This decrease in effective viscosity may be the critical factor in determining the ultimate load-bearing capacity.

Among the pressure-viscosity investigations reported in the literature (12), the work of Bridgman on pure compounds (6) and the ASME Pressure-Viscosity Report (3) on oils and polymer-blends are two of the most significant contributions to this field. However, almost all of the experimental work has been done with conventional or modified falling-weight type viscometers. In such apparatuses the shear rate is too low to detect either non-Newtonian or viscoelastic behavior which show up only at high shear rates. Moreover, the high viscosities at high hydrostatic pressures increase fluid friction and consequently produce excessive heat. With a steady-state viscometer, this heating effect introduces serious experimental errors which might be interpreted as non-Newtonian behavior.

The torsionally-oscillating quartz crystal viscometer introduced by Mason (21) has the advantage over steady-state viscometers in that the heat generated by friction at high shear rates is negligible. In addition, the oscillating

crystal method can easily be adapted to high pressure vessels. The disadvantage of this type of viscometer is that each crystal can supply only one frequency, which is the fundamental resonant frequency of the crystal itself. Fortunately, the concept of reduced variables provides a method for relating data measured at different temperatures and pressures and at one frequency to equivalent information at one temperature and pressure and a range of frequencies.

In this study, the torsionally-oscillating quartz crystal technique was used for measuring the viscosity and elasticity of four lubrication fluids and one dilute polymer solution. The experimental objective was to determine the pressure and shear rate effects on the viscoelastic behavior of polymeric materials.

Measurements on the solution of three weight percent S-109 polystyrene in toluene were done with a constant crystal frequency of about 60 kHz at pressures from atmospheric to 120,000 psig and at constant temperature levels of 77° and 100°F. This monodisperse polystyrene was obtained from Dr. H. W. McCormick of Dow Chemical Company. The ratio of its weight average molecular weight, $\bar{M}_W$, to its number average molecular weight, $\bar{M}_N$, is 1.05, with $\bar{M}_W = 1.93 \times 10^5$.

The lubrication fluids, supplied by NASA, were Humble FN-3158, Humble FN-3158 plus 10 volume percent Kendall 0839 resin, Mobil XRM 109-F, and DuPont Krytox 143-AB. The experiments on these fluids were carried out at a constant temperature

of 100°F and pressures from atmospheric pressure to 18,000 psig using a crystal frequency of about 60 kHz, and at pressures from atmospheric pressure to 40,000 psig and at constant temperatures of 100°, 210° and 300°F using a crystal frequency of 20 kHz.

Density measurements of these lubricants and the polymer solution were also made concurrently with the viscosity measurements.

Some mathematical descriptions and correlations on material behavior under shear deformation, the experimental techniques, results on density, viscosity and viscoelastic behavior of the test liquids, and conclusions from this experimental study are presented in the following chapters.

CHAPTER II

THEORETICAL BACKGROUND

Some fundamental rheological phenomena and mathematical descriptions of the linear viscoelastic behavior of materials under shear deformation are presented in the following sections.

Rheological Phenomena

An ideal or perfect fluid is an imaginary liquid which is completely frictionless so that it offers no resistance to shear stress. The classical theory of fluid dynamics for simple fluids is based upon an incompressible substance which undergoes continuous deformation when subjected to a shear stress. The frictional effect is assumed to be confined to a thin fluid layer adjacent to solid surfaces. This layer is called boundary layer. The flow outside the boundary layer may be regarded as essentially frictionless. This class of fluids is commonly referred to as Newtonian fluids. A Newtonian fluid is defined as a fluid that exhibits a direct proportional relation between shear stress and strain rate in laminar flow and the shear stress-strain rate curve is linear through the origin with a constant slope.

However, many materials are non-Newtonian. When subjected to a simple shear motion the flow curve, stress versus strain rate (or velocity gradient), for such materials, is not linear through the origin, i.e., dilatant fluids and pseudoplastic fluids, or is linear through the origin but with a yield stress at a given condition, i.e., Bingham body.

Some materials will flow when subjected to stress but part of their deformation is gradually recovered upon removal of the stress. If such materials are subjected to a constant strain, the stress will gradually relax with time. Such time dependences reflect a behavior which combines liquid-like and solid-like characteristics. This group of materials is called linear viscoelastic fluids because they exhibit time-dependent elasticity in addition to time-dependent viscosity. Non-linear viscoelastic behavior is encountered if the deformation due to shear stresses is a function of position as well as a function of time.

In an external force field viscoelastic behavior is characterized by a combined change in shape and volume. In other words, both the shear stress and normal stresses are relaxed with time. A description of this more complicated type of deformation requires the introduction of a volumetric relaxation modulus as well as the shear stress relaxation modulus. The required information on the volumetric relaxation modulus is related to the normal stress differences, $\sigma_{11} - \sigma_{22}$, $\sigma_{11} - \sigma_{33}$, and $\sigma_{22} - \sigma_{33}$, which cannot be measured

with the torsionally oscillating crystal technique. Despite this limitation on the experimental technique, one fortunate simplification is based on the fact that most polymer melts and polymer solutions are sufficiently soft to support substantial deformations without breaking, i.e., the volumetric relaxation modulus is much greater than the shear stress relaxation modulus, which enables one to neglect the volume changes. Thus, viscoelastic behavior may be described by the shear stress relaxation modulus alone. Viscoelastic behavior of fluids concerned in this investigation is limited to the case in which the ratio of shear stress to strain rate is only a function of time.

A few words must be said about the difference between a viscoelastic fluid and a soft plastic solid. The latter flows only after the yield stress has been exceeded, while the former flows when any shear stress, no matter how small, is applied to it. In a soft plastic solid the elastic component is dominant at very small velocities. On the other hand, the elasticity of a viscoelastic liquid is apparent only at high velocities when no time is given for its elastic stress to relax.

In discussing the viscous and elastic responses of a given fluid it is important to note that, in a given experiment, the responses may depend not only on the material but also on the time scale of the experiment. For instance, water behaves like a Newtonian fluid in ordinary experiments. But

if it is subjected to ultra-high frequency vibrations, water will propagate waves as if it were an elastic body. The reason for this apparent change in behavior lies in the fact that the response is ultimately molecular in nature, which involves the stretching of intermolecular bonds and the motion of molecules past one another. In general, bonds can be stretched very quickly by an imposed stress, since little motion is involved. On the other hand, considerably more time is involved in causing molecules to flow. Thus, in a stress field with a very short time scale the stress may reverse itself before molecules have time to move appreciably, and only mechanisms giving rise to elasticity may have time to be excited. Because material behavior can depend upon the time scale of the experiments and the type of stress field imposed, it is imperative that, when one reports the rheological properties of a material, he also reports the range of conditions over which these properties were measured. Only in this way can rheological properties be used with any assurance of pertinence to the application at hand.

Fundamental Concepts

The shear strain of an ideal elastic solid (Figure 1) subjected to a shear stress can be written as

$$\frac{F}{A} = \sigma = G \frac{\Delta l}{l} = G\gamma \quad (1)$$

where F is the imposed shear force on the top surface with an area of A , ℓ is the original height and $\Delta\ell$ is the horizontal increases in length, G is the shear modulus, and γ is $\Delta\ell/\ell$ or the shear strain response.

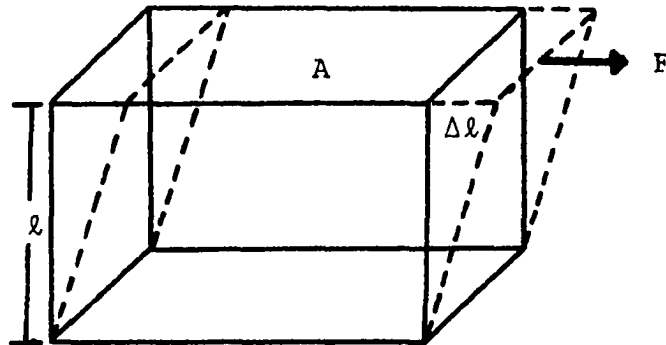


Figure 1. Shear Deformation of an Ideal Elastic Body.

The stress-time and strain-time curves for an ideal elastic body are described in Figure 2a. A constant shear stress is applied at time t_1 , a strain occurs instantaneously and remains constant until the applied constant shear stress is removed at time t_2 . At this moment the strain also drops to zero. Figure 2b is a graphical expression of Equation 1 with the slope being equal to the shear modulus.

The behavior of a Newtonian fluid (as contrasted to a frictionless or ideal fluid) can be illustrated by considering the response to shear forces. Consider a fluid located

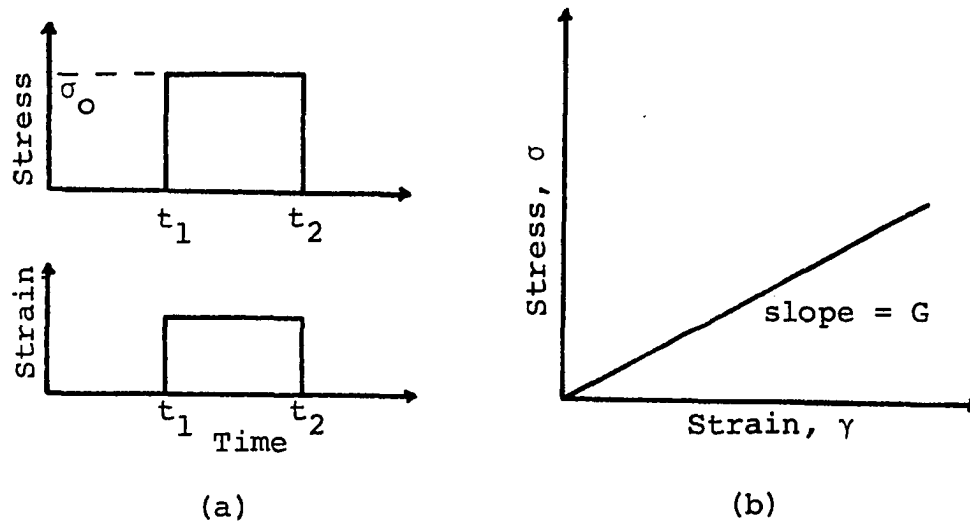


Figure 2. Time-Stress-Strain Relationship for an Ideal Elastic Body.

between two parallel flat plates which are separated by a normal distance, dy , as shown in Figure 3. The upper plate is moving with a constant velocity, du , relative to the stationary lower plate. The arrows indicate the velocity of the various layers of fluid relative to the top and bottom plate velocities.

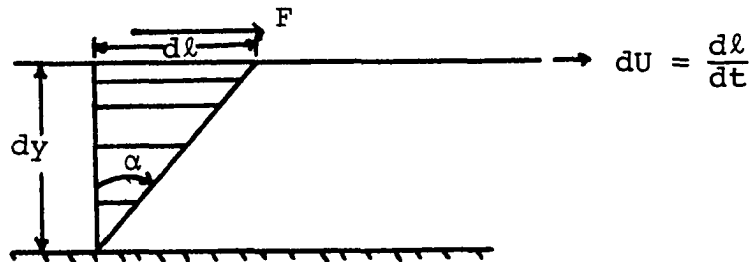


Figure 3. Shear Deformation of a Newtonian Liquid.

Fluids which obey the following simple relation

$$\sigma = \eta \frac{du}{dy} \quad (2)$$

are known as Newtonian fluids. The constant η is the coefficient of viscosity. The deformation of a Newtonian fluid caused by the shear stress is given by

$$\gamma = \frac{d\ell}{dy} \quad (3)$$

By analogy with deformation in an elastic body, γ may be described as the strain. The rate of strain is therefore

$$\dot{\gamma} = \frac{\partial}{\partial t} \left(\frac{\partial \ell}{\partial y} \right) = \frac{\partial}{\partial y} \left(\frac{\partial \ell}{\partial t} \right) = \frac{du}{dy} \quad (4)$$

Thus, the rate of strain is also called the velocity gradient. Hence, the stress-strain relation for a Newtonian fluid may be written as

$$\sigma = \eta \dot{\gamma} \quad (5)$$

The stress-time and strain-time curves for a Newtonian fluid are shown in Figure 4a. Application of a constant shear stress at t_1 causes a deformation which increases steadily with time until t_2 where the shear stress is removed and the deformation becomes constant with time. Figure 4b is a plot of shear stress against shear rate for a Newtonian liquid. The slope of the stress-strain curve is the coefficient of viscosity.

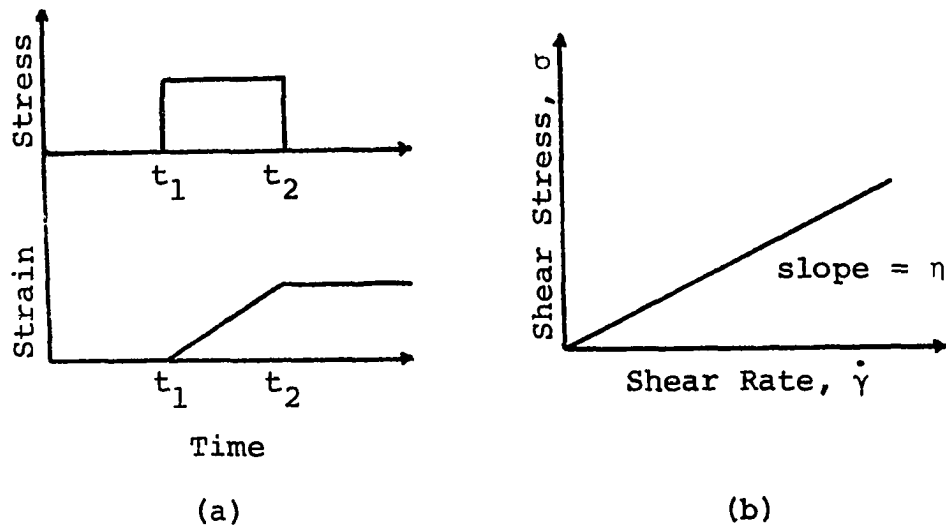


Figure 4. Time-Stress-Strain Relationship for a Newtonian Fluid.

Viscoelastic Fluids and Mechanical Models

Whereas the previous section described the behavior of ideal elastic solids and Newtonian fluids, this section describes the behavior of viscoelastic materials.

As mentioned previously, materials can exhibit viscous or elastic behavior, or a combination of both, depending on the time scale of the process involved. It is necessary to be able to describe the material behavior under any physical condition.

The observed time-dependence of a viscoelastic material can sometimes be understood better physically when viewed

in terms of equivalent mechanical models. Various mechanical models are designed to duplicate, more or less closely, such viscoelasticity qualitatively. These models are made up of combinations of springs and dashpots. The springs and dashpots can be used to represent elastic and viscous responses, respectively, of a material. The force on a spring is proportional to the displacement,

$$F = k_1 x \quad (6)$$

where k_1 is the spring constant. The force on a dashpot is proportional to the rate of displacement,

$$F = k_2 \frac{dx}{dt} \quad (7)$$

where k_2 is the damping constant of the dashpot. Hence, forces applied to the terminals of the model is analogous to σ in Equation 1 for the spring, or in Equation 2 for the dashpot, the relative displacement of the terminals is analogous to γ in Equation 3, and the rate of displacement is analogous to $\dot{\gamma}$ in Equation 4.

Two basic mechanical models are a parallel combination of a spring and a dashpot, known as a Voigt body, and a series combination of a spring and a dashpot, known as a Maxwell body. These two basic models represent the behavior of idealized materials. It has been shown that most viscoelastic liquids cannot be described by such simple models. Consequently,

combinations of Voigt bodies and Maxwell bodies are required to simulate more closely the behavior of real materials.

Voigt Body

Because the total stress is equal to the sum of the stresses on the spring and dashpot, the equation for a Voigt body shown in Figure 5, is

$$\sigma = G\gamma + \eta \dot{\gamma} \quad (8)$$

where η is a Newtonian viscoelasticity and G is a shear modulus.

A general solution of Equation 8 is

$$\gamma(t) = \exp\left(-\frac{G}{\eta}t\right) \left[\gamma_0 + \frac{1}{\eta} \int_0^t \sigma \exp\left(\frac{G}{\eta}t\right) dt\right] \quad (9)$$

where γ_0 is the strain at time $t = 0$.

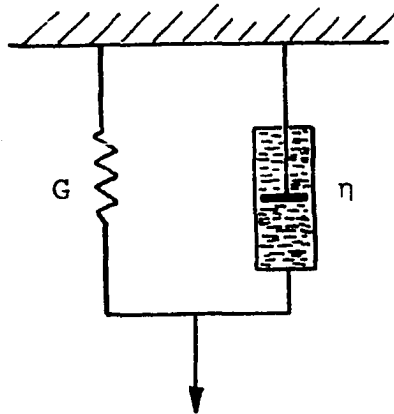


Figure 5. A Voigt Body.

In the special case of constant stress, shown in Figure 6, and zero initial strain, a solution of Equation 8 is

$$\gamma(t) = \frac{\sigma_0}{G} [1 - \exp(-t/\lambda)] \quad (10)$$

where $\lambda = \eta/G$ is called retardation time. If the stress is removed, the strain vanishes exponentially with the time constant λ , i.e., the strain falls to $1/e$ of its initial value in time λ .

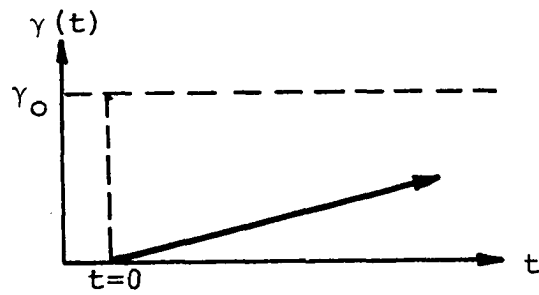
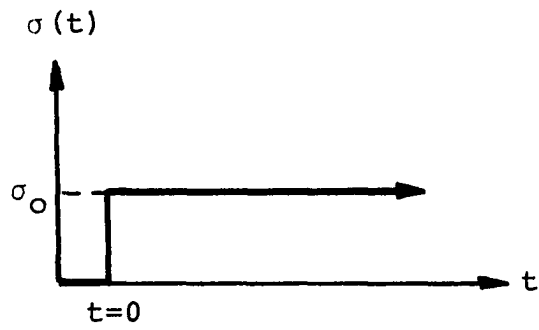
If a constant stress, σ_0 , is suddenly applied to a set of N Voigt bodies in series at time $t = 0$, the total strain will be the sum of the strains of all the elements. Hence,

$$\begin{aligned} \gamma(t) &= \sigma_0 \sum_{n=1}^N \frac{1}{G_n} [1 - \exp(-t/\lambda_n)] \\ &= \sigma_0 \sum_{n=1}^N J_n [1 - \exp(-t/\lambda_n)] \end{aligned} \quad (11)$$

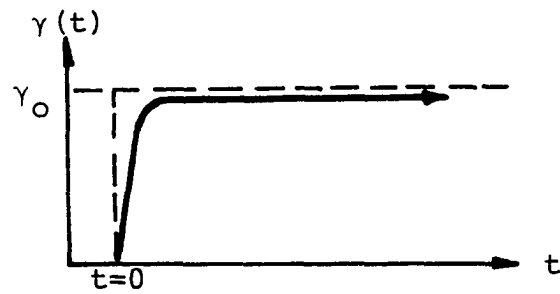
It is customary to write $1/G_n = J_n$ where J_n is called the compliance of the n^{th} element. A creep compliance $J(t)$ is defined as the strain per unit stress expressed as a function of time when the relaxed material is suddenly subjected to a constant stress. Therefore, Equation 11 may be written as

$$J(t) = \sum_{n=1}^N J_n [1 - \exp(-t/\lambda_n)] \quad (12)$$

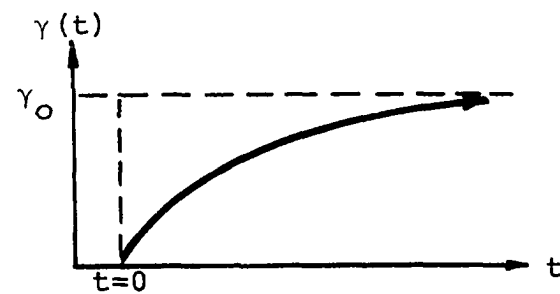
A generalized Voigt element, consisting of an infinite number of elements, is represented by continuous creep function given in accordance with Equation 12 with J_n and λ_n



Behavior like
dash-pot



Behavior like
spring



Both η and G
operative

Figure 6. Response of Voigt Body to a Constant Load σ_0 .

replaced by a retardation function, $B(\lambda)$, which gives the amount of elastic compliance associated with the retardation time, λ . Thus,

$$J(t) = J_g + \int_{-\infty}^{\infty} B(\lambda) [1 - \exp(-t/\lambda_n)] d \ln \lambda + t/\eta \quad (13)$$

The constant J_g corresponds to the elastic compliance at $t=0$. The constant t/η is added to allow one of the elements to have an infinite retardation time.

Maxwell Body

Another simple mechanical model used to describe viscoelastic behavior is the Maxwell body, Figure 7, which consists of a spring and a dashpot in series. Because the total strain rate is equal to the sum of strain rates on the spring and the dashpot, the equation for a Maxwell body is

$$\dot{\gamma} = \frac{\dot{\sigma}}{G} + \frac{\sigma}{\eta} \quad (14)$$

The solution of Equation 14, obtained by integration, is

$$\sigma(t) = \exp\left(-\frac{G}{\eta} t\right) \left[\sigma_0 + G \int_0^t \gamma \exp\left(\frac{G}{\eta} t\right) dt\right] \quad (15)$$

where σ_0 is the stress at time $t = 0$.

Application of a constant strain at zero time, γ_0 , as shown in Figure 8, reduces Equation 14 to

$$\eta \dot{\sigma} + G\sigma = 0 \quad (16)$$

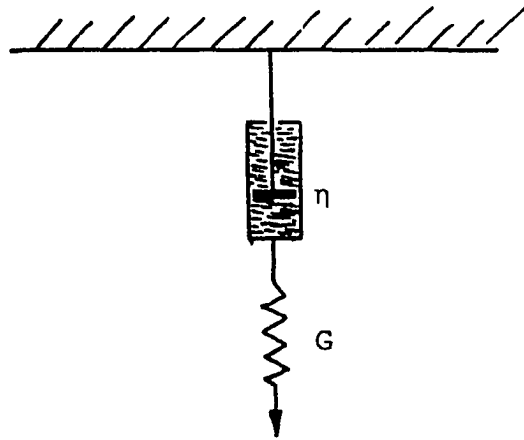


Figure 7. A Maxwell Body.

Solution of Equation 16 with proper boundary values for a constant initial strain gives

$$\sigma(t) = \gamma_0 G \exp(-t/\tau) \quad (17)$$

where $\tau = \eta/G$ is called relaxation time. If the strain is removed, the stress vanishes exponentially with time constant τ , i.e., the stress relaxes to $1/e$ of its original magnitude.

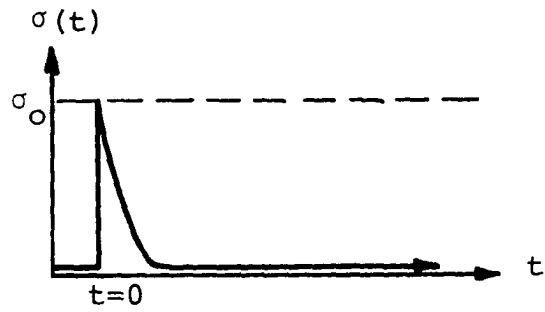
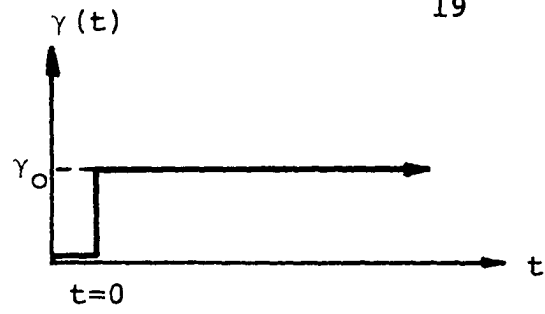
The extension to a set of N Maxwell bodies in parallel results in the total stress being the sum of the individual stresses, i.e.,

$$\sigma(t) = \gamma_0 \sum_{n=1}^N G_n \exp(-t/\tau_n) \quad (18)$$

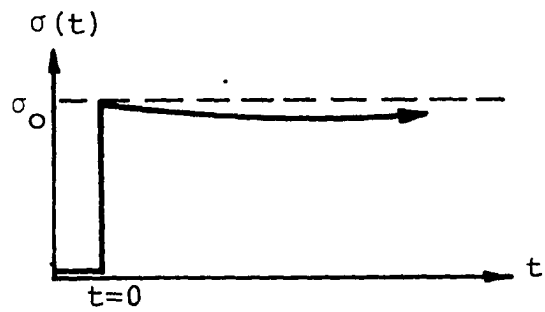
or

$$G(t) = \frac{\sigma(t)}{\gamma_0} = \sum_{n=1}^N G_n \exp(-t/\tau_n)$$

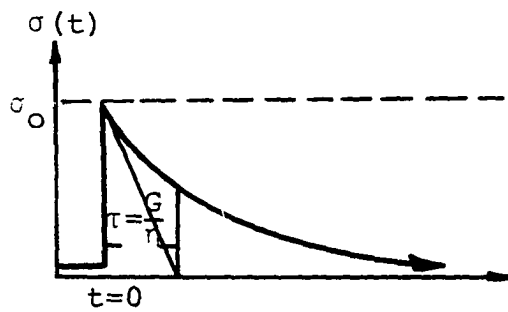
The relaxation function $G(t)$ is defined as the stress per unit strain expressed as a function of the time t when the material has been subjected to an instantaneous strain at $t=0$.



Behavior like
spring



Behavior like
dash-pot



Both η and G
operative

Figure 8. Response of Maxwell Body to a Constant Load γ_0 .

In the limit of an infinite number elements, a continuous spectrum $G(t)$ is given in accordance with Equation 18 with G_n and τ_n replaced by the relaxation spectrum $H(\tau)$, which gives the amount of elastic modulus associated with the relaxation time τ , i.e.,

$$G(t) = G_e + \int_{-\infty}^{\infty} H(\tau) \exp(-t/\tau) d \ln \tau \quad (19)$$

Here the constant term G_e is the equilibrium modulus which allows a discrete contribution at $\tau = \infty$.

Since any of the terms, $J(t)$, $B(\tau)$, $G(t)$, and $H(\tau)$, can be used to describe a viscoelastic material, it is useful to know the relationships between these functions. Since the relationships have been fully discussed in the literature (1, 13, 14), only a diagrammatical interrelationship between these viscoelastic functions will be given here as illustrated below.

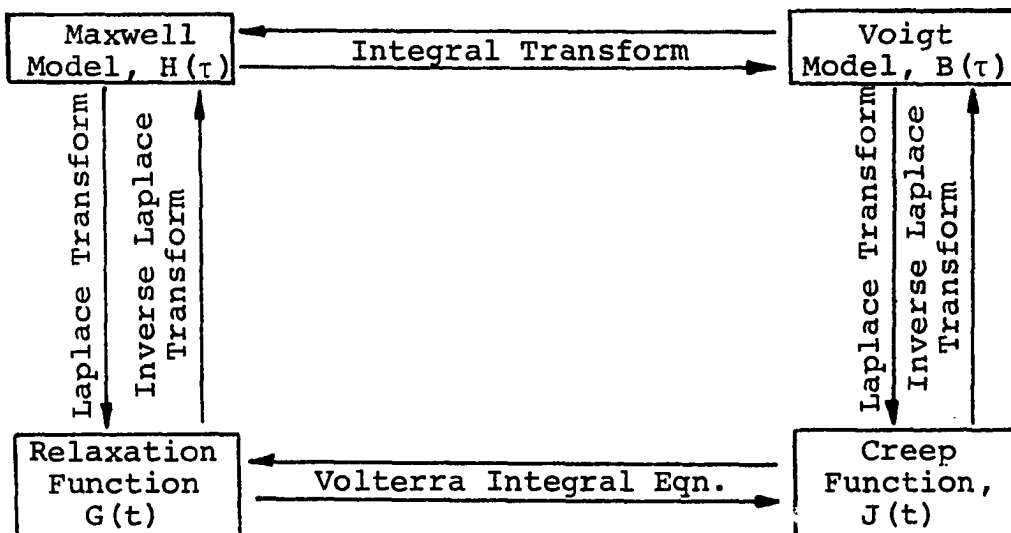


Figure 9. Interrelations Between Viscoelastic Functions.

As mentioned earlier, neither the Voigt body nor the Maxwell body is capable of describing the behavior of real materials. However, a combination of these basic mechanical models, as shown below, can be used to describe a real fluid.

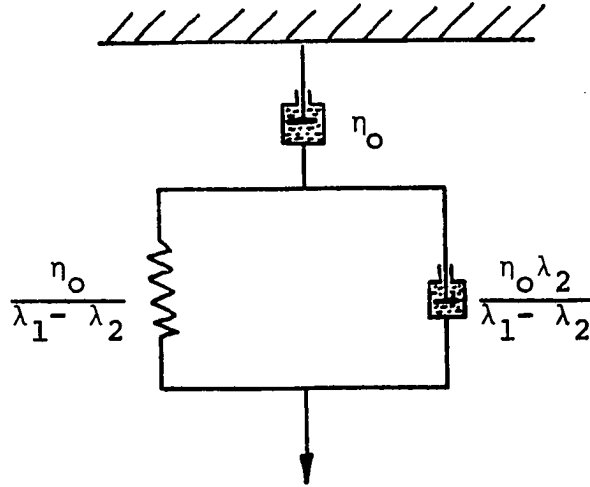


Figure 10. Combination of a Dashpot and a Voigt Body.

The strain of the Voigt body is

$$\gamma_1(t) = \sigma(t) / \left[\frac{\eta_0}{\lambda_1 - \lambda_2} + \frac{\eta_0 \lambda_2}{\lambda_1 - \lambda_2} \frac{d}{dt} \right]$$

The strain of the dashpot is

$$\gamma_2(t) = \sigma(t) / \eta_0 \frac{d}{dt}$$

The total strain $\gamma(t) = \gamma_1(t) + \gamma_2(t)$, i.e.,

$$\gamma(t) = \sigma(t) \left[\frac{\lambda_1 - \lambda_2}{\eta_0 (1 + \lambda_2 \frac{d}{dt})} + \frac{1}{\eta_0 \frac{d}{dt}} \right]$$

$$\gamma(t) = \sigma(t) \left[\frac{1 + \lambda_1 \frac{d}{dt}}{\eta_0 \frac{d}{dt} (1 + \lambda_2 \frac{d}{dt})} \right]$$

which may be written as

$$\sigma + \lambda_1 \dot{\sigma} = \eta_0 (\dot{\gamma} + \lambda_2 \ddot{\gamma})$$

The above equation is of the same form as the Oldroyd equation derived for certain polymer solutions.

Oscillatory Load

The determination of the response of viscoelastic materials to steady-state shear and to dynamic shear entails two types of experiments. In the steady-state experiment the short-time behavior of materials does not show up clearly because only relatively low shear rates can be obtained with the experimental equipment. Therefore, the dynamic shear method is often used to study the short-time behavior of viscoelastic materials.

If a sinusoidal stress is applied to a viscoelastic material, the strain will also respond sinusoidally, but the strain will be out-of-phase with the stress, as sketched in Figure 11. The response of a viscoelastic material to sinusoidally varying stresses is determined by the ratio of peak stress to peak strain accompanying the change in phase angle. The complex quantities derived from sinusoidally varying stress and strain are given in the following.

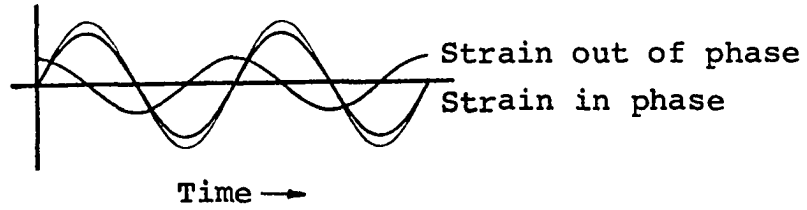


Figure 11. Sinusoidally Alternation of Stress with Strains In Phase and Out of Phase.

A sinusoidally varying complex strain, γ^* , is defined as

$$\gamma^* = \gamma_0 \exp(i\omega t) \quad (20)$$

where γ_0 is the maximum amplitude of the strain, ω is the angular frequency, and t is time. Because the stress associated with this strain is also sinusoidal but out-of-phase with the strain by phase angle δ ,

$$\sigma^* = \sigma_0 \exp[i(\omega t + \delta)] = \sigma_0 [\exp(i\omega t) \cos \delta + i \exp(i\omega t) \sin \delta] \quad (21)$$

where σ_0 is equal to the initial amplitude of the stress. The dynamic shear modulus is defined as

$$G^* = \frac{\sigma^*}{\gamma^*} = G' + iG'' \quad (22)$$

in which G' is the storage modulus and G'' is the loss modulus. The complex dynamic viscosity, η^* , is defined as

$$\eta^* = \frac{\sigma^*}{\dot{\gamma}^*} = \eta' - i\eta'' \quad (23)$$

The rate of strain, $\dot{\gamma}^*$, is found from Equation 20,

$$\dot{\gamma}^* = i\omega \gamma_0 \exp(i\omega t) = i\omega \gamma^* \quad \text{or} \quad \gamma^* = \dot{\gamma}^*/i\omega \quad (24)$$

Combining Equations 22 and 24, the resulting equation is

$$\sigma^* = G^* \dot{\gamma}^*/i\omega = \frac{G^*}{i\omega} \dot{\gamma}^* \quad (25)$$

By comparing Equation 25 with Equation 23,

$$G^*/i\omega = \eta^* \quad (26)$$

or

$$G' + iG'' = \omega\eta'' + i\omega\eta' \quad (27)$$

The relationships between η 's and G 's are readily provided by separating the real and imaginary parts of Equation 27,

$$\eta' = G''/\omega \quad (28)$$

and

$$\eta'' = G'/\omega \quad (29)$$

A vectorial representation of the complex quantities is given in Figure 12.

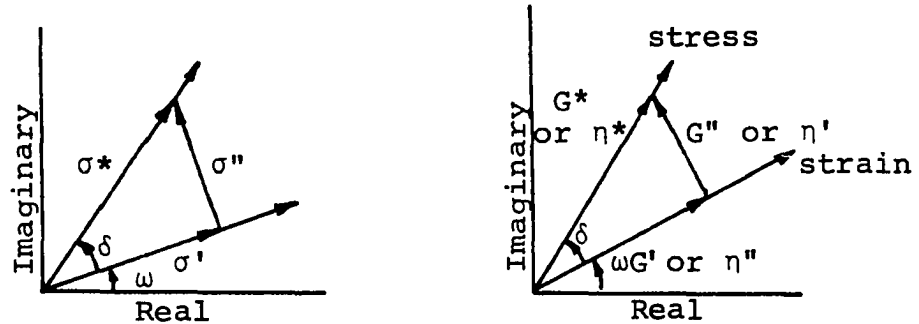


Figure 12. Vectorial Representation of Complex Quantities.

Another expression of the complex viscosity can be obtained by combining Equations 21, 23 and 24,

$$\eta^* = \sigma_o \exp [i(\omega t + \delta)] / i\omega \gamma_o \exp(i\omega t)$$

or

$$\eta' = \frac{\sigma_o}{\omega \gamma_o} \sin \delta; \quad \eta'' = \frac{\sigma_o}{\omega \gamma_o} \cos \delta \quad (30)$$

In the case of an ideal elastic body, the stress and strain are in phase with each other, in which case the phase angle, δ , is equal to zero. Therefore,

$$\eta'' = \frac{\sigma_o}{\omega \gamma_o} \quad \text{or} \quad G' = \frac{\sigma_o}{\gamma_o} \quad (31)$$

Equation 31 provides a measure of the elastic effects, or energy storage, which is given by G' or η'' .

For a Newtonian fluid, the stress and strain are out of phase with each other, in which case the phase angle is equal to ninety degrees. Therefore,

$$\eta' = \frac{\sigma_o}{\omega \gamma_o} \quad \text{or} \quad G'' = \frac{\sigma_o}{\gamma_o} \quad (32)$$

Equation 32 provides a measure of the Newtonian viscosity.

If a sinusoidally varying load is imposed upon a Maxwell body, Equation 14 may be written as

$$\eta \dot{\gamma}^* = \sigma^* + \tau \dot{\sigma}^* = (1 + \omega \tau) \sigma^*$$

or

$$\sigma^* / \dot{\gamma}^* = \eta / (1 + i\omega \tau) \quad (14a)$$

Equation 14a can be separated into real and imaginary parts to give

$$\eta' = \eta / (1 + \omega^2 \tau^2) \quad (33)$$

and

$$\eta'' = \omega \tau \eta / (1 + \omega^2 \tau^2) \quad (34)$$

The storage modulus is readily converted from Equation 34 with $G' = \omega \eta''$ and $\tau = \eta / G$,

$$G' = G \omega^2 \tau^2 / (1 + \omega^2 \tau^2) \quad (35)$$

A generalized Maxwell body may be represented by the sum of the individual responses of all elements as

$$G' = \sum_{i=1}^N [G_i \omega^2 \tau_i^2 / (1 + \omega^2 \tau_i^2)] \quad (36)$$

$$\eta' = \sum_{i=1}^N [\eta_i / (1 + \omega^2 \tau_i^2)] \quad (37)$$

Characteristic Impedance Measurement

There is a close mathematical similarity between the mechanical response of a viscoelastic material and the electrical response of a two-terminal electrical network. Such electrical-mechanical analogies are listed in Reference 1. By analogy with the concept of impedance used in the mathematical analysis of electrical network the viscoelastic properties of fluids can be related to the measurements of the characteristic impedance of fluids.

Consider a fluid with viscosity, η , and density, ρ , subjected to a tangential shearing stress produced by a torsionally oscillating crystal. The viscoelastic properties of

the medium can be deduced from the complex characteristic impedance (mechanical impedance/unit area), Z_M^* , defined as the ratio of the stress on a fluid particle to the partical velocity,

$$Z_M^* = R_M + iX_M \quad (38)$$

The in-phase component, R_M , and the out-of-phase component, X_M , of the characteristic impedance are related to the shear storage modulus, G' , and shear loss modulus, G'' , by

$$G' = (R_M^2 - X_M^2)/\rho = \eta''\omega \quad (39)$$

$$G'' = 2R_M X_M/\rho = \eta'\omega \quad (40)$$

The mechanical resistance, R_M , and the mechanical reactance, X_M , are related to the resonant frequency of the crystal and the resistance at resonance by

$$R_M = (R_E - R_{EO})/K_r \quad (41)$$

$$X_M = (f_o - f)/K_f \quad (42)$$

R_E is the electrical resistance of the crystal at resonance in a given liquid, and R_{EO} is the electrical resistance of the crystal at resonance in air. Likewise, f is the resonant frequency of the crystal in a given liquid, and f_o is the resonant frequency of the crystal in air. The crystal constants K_r and K_f can be determined experimentally by calibrating the crystal with Newtonian fluids of known viscosity and density. Because

$\eta'' = 0$, $X_M = R_M$ for Newtonian fluids, combining Equations 40 and 41, and Equations 40 and 42, gives

$$R_E = R_{EO} + K_r (\omega\rho\eta/2)^{1/2} \quad (43)$$

$$f = f_o - K_f (\omega\rho\eta/2)^{1/2} \quad (44)$$

Thus, a plot of R_E versus $(\omega\rho\eta/2)^{1/2}$ will give a straight line with slope K_r and intercept R_{EO} . Likewise, a plot of f versus $(\omega\rho\eta/2)^{1/2}$ will give a straight line with slope $-K_f$ and intercept f_o .

Theoretical values of the crystal constant can be related to the physical and electrical properties of the crystal by (2, 33)

$$K_f = \frac{1}{\pi\rho_c} \left(\frac{1}{r} + \frac{1}{l} \right) \quad (45)$$

$$K_f = 4\pi L_c K_f \quad (46)$$

$$L_c = (2\pi \Delta f G_c)^{-1} \quad (47)$$

where r = crystal radius, cm

l = crystal length, cm

ρ_c = crystal density, 2.60 g/cc

G_c = conductance at resonance or the reciprocal of
the resistance at resonance

Δf = difference between the two frequencies at which
the conductance is one-half of the maximum value

The torsionally oscillating crystal viscometer was first introduced by Mason (21). When a voltage is applied to

the crystal, a torsional vibration is generated by the piezo-electric effect of the crystal. The oscillating crystal technique was modified by Rouse, et al. (34), used by Philippoff (27), Rouse and Sittel (36), Harrison, et al. (15), and Appeldoorn, et al. (2). Rein (30, 31) extended the techniques used by Philippoff for pressures up to 8,000 atmospheres. This type of viscometer has been successfully used to obtain viscosity and viscoelastic data at extreme pressures and at high shear rates which correspond to conditions existing in many applications of lubrication fluids and polymer solutions. The disadvantages of the oscillating crystal viscometer are that the fluid being measured must be non-conducting or of very low conductivity, and only one frequency can be obtained with each crystal.

Dependence on Temperature and Pressure

As mentioned earlier, the characteristic impedance measurements are made only at the fundamental crystal frequency. Measurements at various frequencies must be taken with crystals having different fundamental resonant frequencies. To circumvent this limitation, the concept of reduced variables can be used to correlate the measurements at a single frequency but over a range of temperatures and pressures in the form of a single reduced curve in the following manner:

For non-crosslinking polymers, the dependence of viscoelastic behavior on temperature can be represented by

defining a shift factor, a_T , (13)

$$a_T = (T_O/T) (\rho_O/\rho) (\eta_T/\eta_O) \quad (48)$$

and a set of reduced variables, f_r , G'_r and η'_r ,

$$r_r = a_T f; \quad \omega_r = a_T \omega = a_T (2\pi f) \quad (49)$$

$$G'_r = G' (T_O/T) (\rho_O/\rho) \quad (50)$$

$$\eta'_r = \eta' (\eta_O/\eta_T) \quad (51)$$

Thus, Equations 49 through 51 reduce measurements made at temperature T to a reference temperature T_O .

Many efforts have been devoted to formulating the temperature dependent properties of viscoelastic materials. However, the pressure dependence is not as well studied due to relatively limited experimental work at high pressures. Philippoff (27) introduced a set of reduced variables which provided correlations for both the pressure and temperature dependence of viscoelastic fluids. The expressions are identical with Equations 48 through 51, except for a new shift factor, a_{TP} , and a combined viscosity, $(\eta_T/\eta_O)_P (\eta_P/\eta_O)_T$, instead of a_T and (η_T/η_O) , respectively.

$$a_{TP} \equiv (T_O/T) (\rho_O/\rho) (\eta_T/\eta_O)_P (\eta_P/\eta_O)_T \quad (52)$$

$$f_r = a_{TP} f; \quad \omega_r = a_{TP} \omega = a_{TP} (2\pi f) \quad (53)$$

$$G'_r = G' (T_O/T) (\rho_O/\rho) \quad (54)$$

$$\eta'_r = \eta' (\eta_O/\eta_T)_P (\eta_O/\eta_P)_T \quad (55)$$

where the subscripts T and P refer to the temperature and pressure of the measurements and the subscript o refers to values at a common temperature and pressure to which all measurements are being reduced. The viscosities η_o , $(\eta_o)_T$, and $(\eta_o)_P$ are those measured in the limit of zero shear rate. This technique has been verified by other workers (2, 27, 30, 33).

An additional advantage of the concept of reduced variables is that the measurements taken at higher pressures can be transferred into a set of measurements which correspond to atmospheric pressure and much higher shear rates. This advantage is significant since higher shear rates give more definitive information on the properties of viscoelastic materials.

Molecular Theory

Mathematical models based upon statistical mechanics have been used to describe the complicated motion of polymer molecules. Although the molecular models were often proved inadequate due to over-simplified modelling and mathematical complexities, these models are capable of predicting the dependence of rheological parameters on concentration and molecular weight, and on occasion, of making explicit numerical predictions for coefficients and functions of the flow properties of polymeric materials.

Theories on the dynamic viscosity of dilute polymer solutions developed by Rouse (35) and Zimm (39) are the two most widely accepted mathematical models. Rouse introduced a model of a randomly coiled macromolecule which was assumed to be a series of $N + 1$ equal length submolecules consisting of q monomeric units connected with N perfect springs. This model is called a free draining coil because the hydrodynamic interaction between the motions of the submolecule junctions and the monomer inertia are ignored. In a sinusoidally varying force field, the delay in the movement of monomers encountered by each simulated spring moving through its surroundings is characterized by an average friction coefficient. This averaged coefficient is assumed to be valid for all submolecule junctions. The motion of each mass is described by $N + 1$ simultaneous differential equations and is normalized through a transfer of the position coordinates. The energy dissipation and storage of each monomer are calculated based on the change in free energy associated with the entropy decrease from non-random configurations and the tendency of the macromolecule to diffuse toward a random state. The result for the complex viscosity may be written as

$$\eta^* = \eta_s + NkT \sum_{j=1}^N \frac{\tau_j}{1 + \omega^2 \tau_j^2} \quad (56)$$

or

$$\eta' = G''/\omega = \eta_s + kNT \sum_{j=1}^N \tau_j / (1 + \omega^2 \tau_j^2) \quad (57)$$

$$\eta'' = G'/\omega = kNT \sum_{j=1}^N \omega^2 \tau_j^2 / (1 + \omega^2 \tau_j^2) \quad (58)$$

where N = number of polymer molecules per cm^3

k = Boltzmann's constant

T = absolute temperature in $^\circ\text{K}$

η_s = viscosity of solvent

The values of the relaxation times τ_j of the different modes of motion of the polymer chain are

$$\tau_j = \frac{6(\eta - \eta_s)}{\pi^2 j^2 kNT} = \frac{6}{\pi^2 j^2} \frac{(\eta - \eta_s)M}{cRT} \quad (59)$$

where η is the static viscosity of the solution, M is the molecular weight of the polymer, c is the concentration of the solution in grams per cubic centimeter, and R is the gas constant.

Zimm assumed the macromolecule was suspended in a viscous medium which offered dominant hydrodynamic interaction between the moving segments of the $N + 1$ submolecules in the same manner as calculated by Kirkwood and Riseman (19). In the theory of Zimm, the contribution of the dissolved polymer molecules to the shear stress for oscillating deformations is calculated based on the force on each submolecule as the sum of the hydrodynamic drag force by the solvent, the force associated with the Brownian motion, and the perfect spring-like forces exerted by the two neighboring submolecules. Zimm employed an approach different from that of Rouse but reached

the same expression for complex viscosity as Equation 56.

With the assumption of dominant hydrodynamic interaction, the relaxation times are given by

$$\tau_j = \frac{1.71 (\eta - \eta_s)}{C_j kNT} = \frac{1.71 (\eta - \eta_s)M}{C_j cRT} \quad (60)$$

where C_j 's are coefficients which allow the solution to satisfy the boundary conditions on the eigenvalue equations for the model of the polymer chain set up by Zimm (40). For vanishing hydrodynamic interaction Zimm found the expression on relaxation times are identical as Equation 59.

Both the Rouse and Zimm theories predict that the relaxation time of j^{th} mode is proportional to $(\eta - \eta_s)M/cRT$ and shear storage modulus, G' , to cRT/M . Therefore, it is possible to normalize the results for polymers of different molecular weights, concentrations, and temperatures to a single curve for the dynamic viscosity, to a single curve for the shear storage modulus and to a single curve for the shear loss modulus by using the dimensionless variables $(\eta' - \eta_s)/(\eta - \eta_s)$, $G'M/cRT$, $(G'' - \omega\eta_s)M/cRT$ and $\omega(\eta - \eta_s)M/cRT$.

It is worth relating the Rouse and Zimm results (dynamic shear) to a generalized Maxwell model (steady-state shear) because the Maxwell model is still widely accepted for its simplicity. Furthermore, established terminology is still based upon the Maxwell model. By combining Equations 57 and 59,

$$\eta' - \eta_s = \frac{6(\eta - \eta_s)}{\pi^2} \sum_{j=1}^N \frac{1/j^2}{1 + \omega^2 \tau_j^2} \quad (61)$$

If η_j is set equal to $6(\eta - \eta_s)/j^2 \pi^2$, then Equation 61 may be written as

$$\eta' - \eta_s = \sum_{j=1}^N \frac{\eta_j}{1 + \omega^2 \tau_j^2} \quad (62)$$

which is identical with the dependence of dynamic viscosity, η' , on relaxation time predicted by a generalized Maxwell model, as Equation 37, except for the subtraction of the solvent viscosity. Hence, the Rouse theory may be interpreted as equivalent to a generalized Maxwell model with a discrete set of relaxation times.

Correlation Between Steady Shear and Dynamic Viscosity

Predictions on the relationships between steady shear and dynamic viscosities are made by the continuum theory of Spriggs (37) which suggests that

$$\eta(\dot{\gamma}) = \eta'(b\omega) = G''(b\omega)/b\omega \quad (63)$$

Equation 63 stated that η and η' have the same shape but are shifted with respect to each other along the $\dot{\gamma}$ - ω axis by a factor of b .

Osaki (23) and Onogi (22) observed a good agreement between steady shear and dynamic viscosities with a shift factor of one although some studies indicated $b = 0.7$, (10).

A similar comparison of data for a polymethyl methacrylate solution (23) could not be shifted into coincidence, and Equation 63 is clearly refuted. There is substantial experimental support for Equation 63, although data obtained over a wide range of $\dot{\gamma}$ and ω indicated failure at high rates of deformation (22, 23, 28).

Other theoretical correlations (13, 24) have been proposed. Although the work done by DeWitt, et al. (11) and Pao's theory (25) imply close relationships between flow as characterized by steady shear and by dynamic loading, there is no rigorous theoretical prediction as to how the dynamic and steady shear viscosities are related in concentrated solutions. Much needs to be done before any definitive conclusion can be made in this field.

CHAPTER III

EXPERIMENTAL EQUIPMENT

The three major groups of equipment used in this experiment were the quartz crystal viscometer, electronic components, and pressure generation and storage system. Details are described in the following sections.

Quartz Crystal

Quartz rods with their axes parallel to the X crystal direction were purchased from P. R. Hoffman Company. The Y crystal axis was indicated on the crystals by the Company. The crystal dimensions and approximate fundamental frequencies are:

60 kHz: 0.375 ± 0.001 inches OD x 1.300 ± 0.001 inches

20 kHz: 0.375 ± 0.001 inches OD x 3.875 ± 0.001 inches

These final dimensions were obtained by grinding with No. 600 abrasive. This work was performed by P. R. Hoffman Company. A ninety degrees cone was machined onto both ends of the quartz rod as the seat for the sapphire bearing of the crystal holder.

The final preparations of these crystals were the same as described by Rein (32) except for the following:

1. The ring of silver paint midway between the ends of the crystals was omitted because of a different method of mounting.
2. Silver and gold, used as the electrical conductive materials, were vacuum evaporated onto the 20 kHz and 60 kHz crystals, respectively.
3. The separation of conductive film on the cylindric surface of the crystal was accomplished by tape strips before the vacuum evaporation. These tapes, about 1/16 inches in width, were removed after depositing the conductive film. Electrical isolation of the separated electrodes was checked with an ohmmeter. The resistance between electrodes was at least 100 megohms. This technique of electrode separation was superior to the earlier technique because the former eliminated unnecessary crystal surface abrasion.
4. Following the film deposition, the crystal was allowed to sit overnight to stabilize the conductive coat.

Since the quartz crystal is the sensor of the viscometer, the crystal must be securely mounted to insure reproducible measurements. Even the slightest slippage of the crystal can cause a change in the resonant frequency (as determined by calibration) sufficient to introduce an appreciable error in viscosity calculations. Soldered electrical leads on the conductive surface of the crystal had been found to be unreliable mounting because the leads often broke from the

crystal. For this reason subsequent investigators (2, 32) have employed a spring-clamp mounting.

In this study a superior mounting, developed by Rein (33), was used. A detail drawing of this crystal holder is given in Figure 13. The quartz rod was held in place on its ends by sapphire bearings which were backed with spring in the set screws. The main advantage was that the weight of the rod was supported at the ends of the crystal rather than being suspended on tiny electrical leads. Electrical contacts to the crystal was attained by set screws which can be advanced to maintain good contact with the crystal. The teflon insulator was found to be inadequate. When the viscometer was cooled from temperatures above 210°F, the contraction forced the insulators to slip along the crystal surface. A similar problem was also found after the viscometer had been subjected to pressures over 80,000 psig. This problem appears to have been solved by using silver epoxy to make direct electrical connections to the crystal. In the earlier stage of this experiment, it was observed that the silver electrodes on the 20 kHz crystal tended to flake-off after pressurization at temperatures above 300°F, thus breaking the electrical circuit. This problem now appears to have been resolved by maintaining closer control of the thickness of the conductive film.

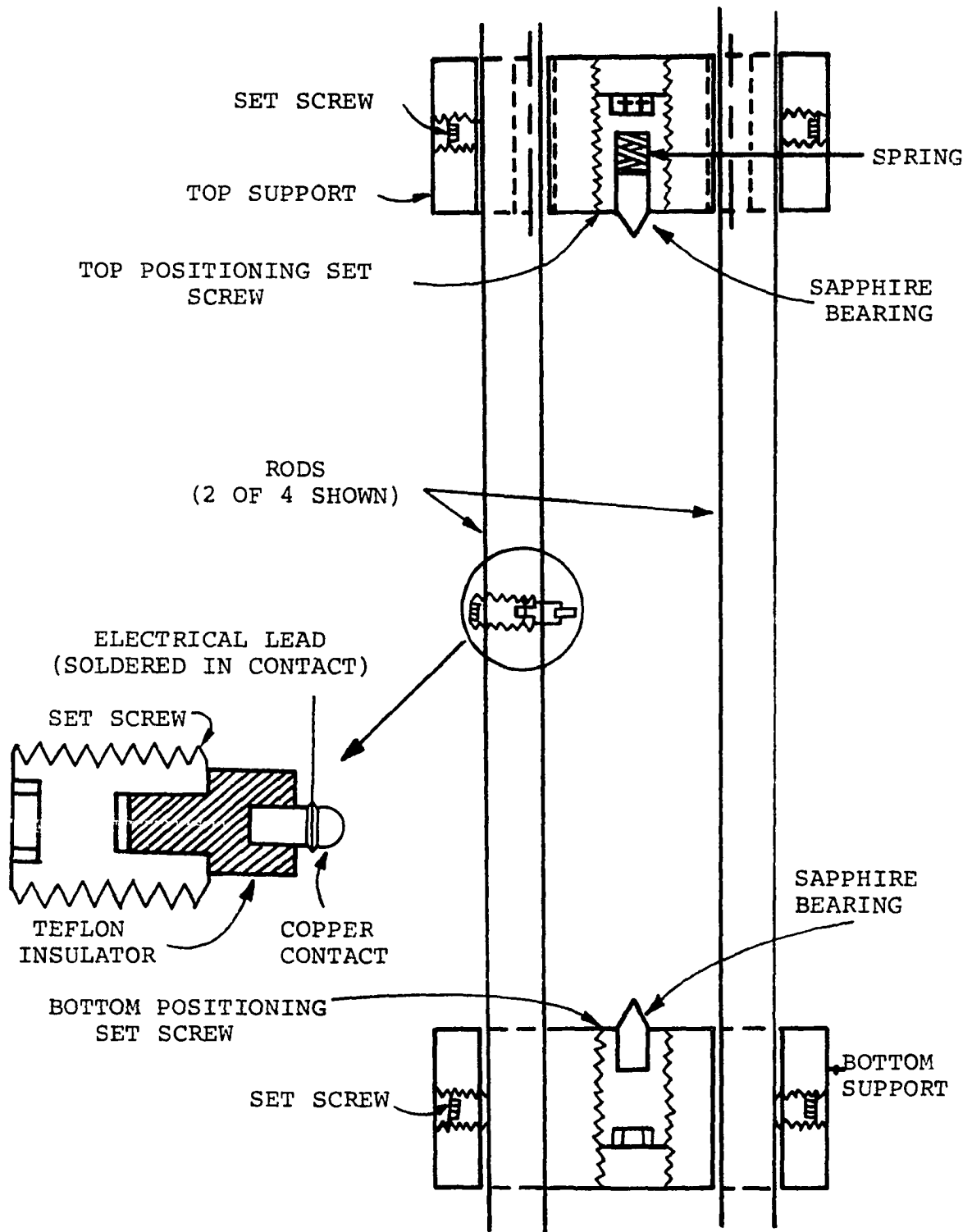


Figure 13. Details of an Improved Crystal Mounting.

Electronic Components

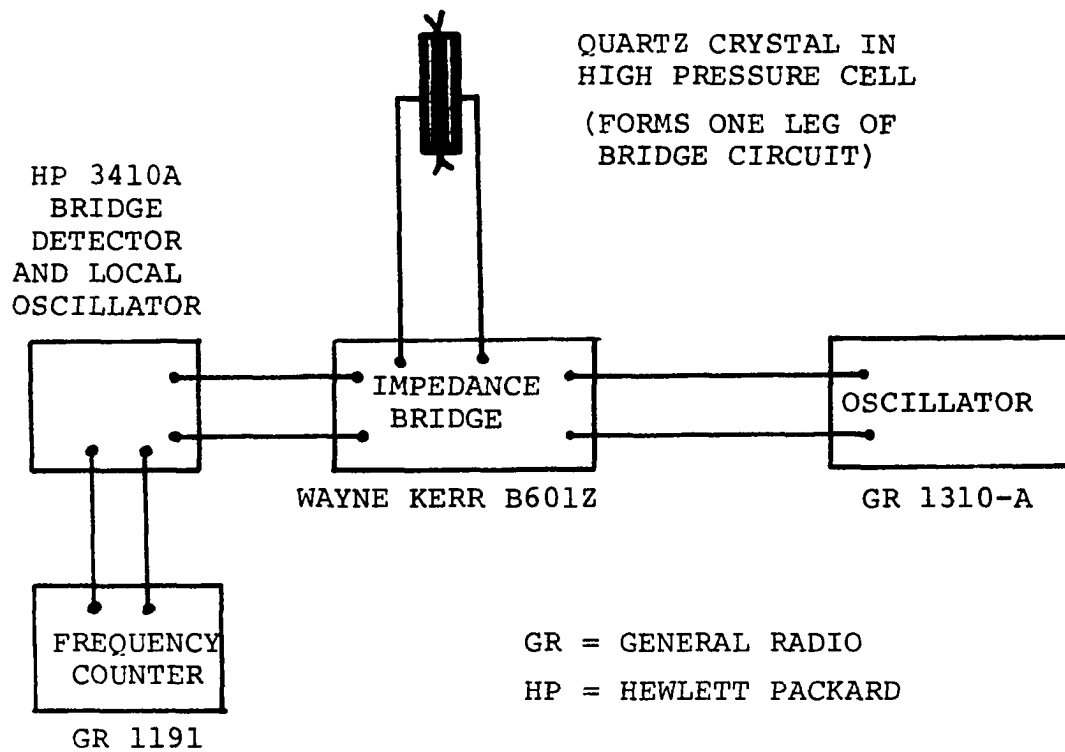
Figure 14 gives a schematic diagram of the electronic components used in this study. The function of these components is to measure the resonant frequency and the resistance at the resonant frequency of the quartz crystal with respect to various fluids. Details are described in the following paragraphs.

Oscillator

High stability on the output of an oscillator is one of the most important factors dominating the accuracy of frequency measurement. A General Radio Model 1310-A oscillator with a frequency range from 3 Hz to 2 MHz was used in this study. The manufacturer claimed that the drift is less than 0.003 percent after a 20-minute warm-up period. Harmonic distortion is no greater than 0.25 percent. Noise is below 0.02 percent of the output, which is satisfactory for this experiment.

Impedance Bridge

An impedance bridge, Wayne Kerr Model B-601, with a frequency range from 15 kHz to 5 MHz and a resistance range from 10 ohms to 10 megohms was used. This bridge has the advantage that the undesirable shunt effect of long cables is eliminated by the bridge design. A simplified diagram of this impedance bridge circuit is given in Figure 14.



NOTE: ALL LEADS ARE SHIELDED.

Figure 14. Electronic Equipment Required for Measurements.

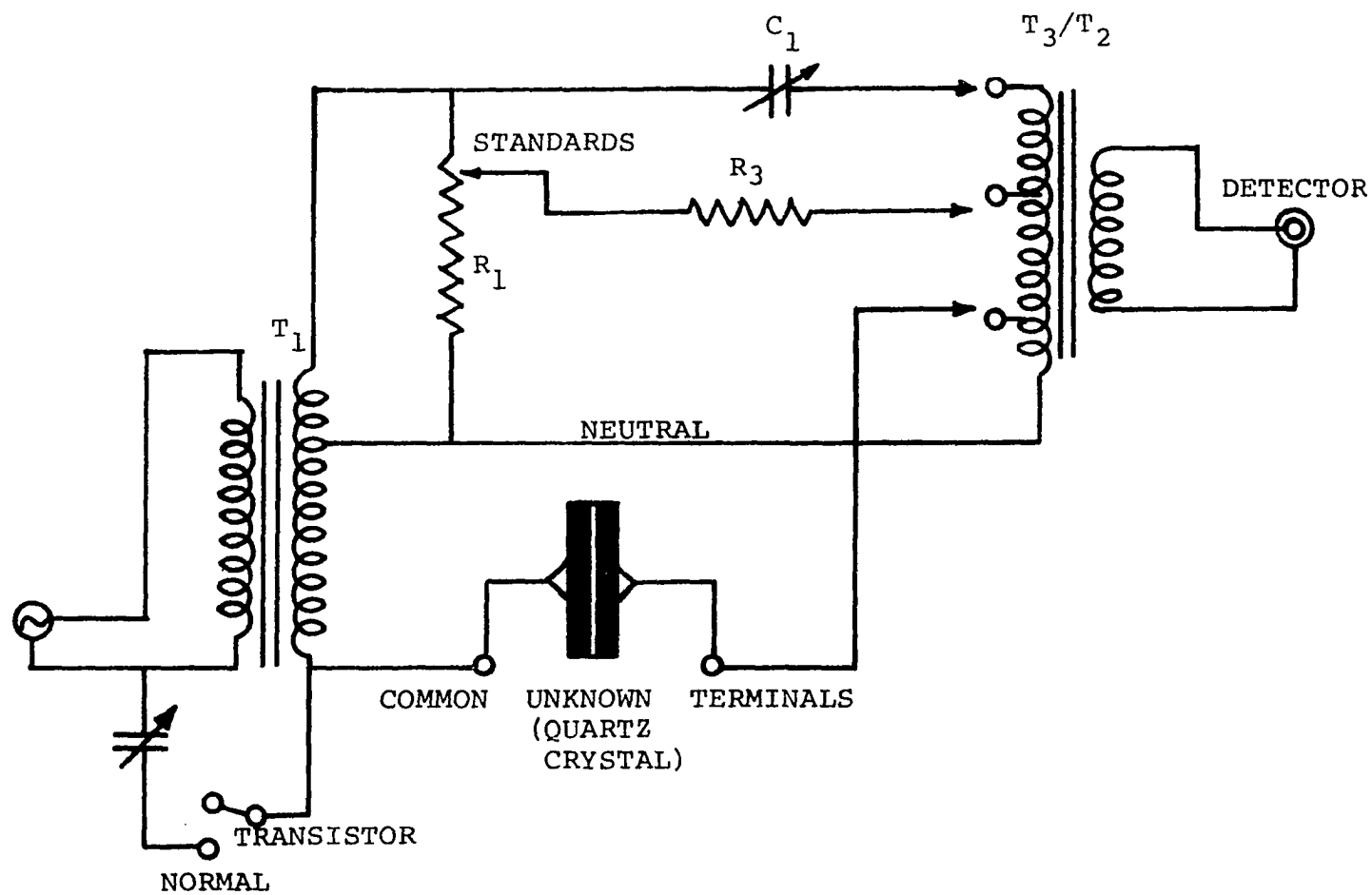


Figure 15. Simplified Schematic Diagram of Wayne Kerr Impedance Bridge.

This bridge employs the transformer ratio-arm principle. Sinusoidal frequency applied to the Standards and the Unknown (which was the torsionally oscillating quartz crystal) from the secondary of transformer T_1 are equal in magnitude but of opposite phase. The standards are adjusted to provide a null indication on a detector and, in this condition, the ampere-turns produced in the primary of transformer T_3/T_2 by the current from the Standards is cancelled exactly by that produced by the current from the crystal side of the bridge. Different ranges are provided on the Standards side by separate multiplier switches which connect the resistive and capacitive standards to different taps on the primary of transformer T_3/T_2 . Different ranges on the Unknown side are provided by alternative terminal connections to the primary of transformer T_3/T_2 with range factors of $\times 0.1$, $\times 1.0$, and $\times 10.0$.

In general the resistance measurements were accurate to plus or minus one percent as the manufacturer specified. As the viscosity of test fluid increases, the sensitivity of the bridge decreases. The sensitivity, which is given by the ratio of the change in bridge output to the change in the resistance, was compromised as the resistance increased with increasing viscosity. Because of the arrangement of divisions on the resistance dial, the read-out resistance from the high end was probably not more than plus or minus five percent accurate.

The limitation on dial resolution was circumvented by inserting a 1.5-megohm resistor in parallel with the crystal, thus lowering the measured resistance and thereby keeping the measured resistance within a readable range on the dial. This technique was used throughout the experiments wherever applicable. Of course, this adaptation further reduced the sensitivity of the bridge output to crystal resistance changes, but the deleterious effect was more-than-compensated-for by the increased ability to read the dial. With the parallel resistor the actual crystal resistance had to be calculated from the resistance relation for parallel resistors. Fortunately, the limitation on the bridge resistance dial resolution was not encountered on measuring the polymer solution because of its relatively low viscosity.

Detector

A Hewlett Packard Model 3410-A AC microvoltmeter was used as the impedance bridge detector. This detector has a tunable narrow band filter to reject noises that would interfere with the desired signal from the bridge. The Model 3410-A also has a local oscillator. The local oscillator, which furnishes four volts square wave output at the tuned frequency, is locked in phase with the input signal from the impedance bridge. The output of this local oscillator was used to drive the electronic frequency counter to assure precise frequency reading.

Frequency Counter

Since the viscosities of liquids were calculated from the change in resonant frequency of the quartz crystal with respect to the liquids, great accuracy on frequency measurement is required. A General Radio Model 1191 frequency counter, which employs an eight-digit visual register comprised of high density gas-readout tubes, was used to measure the frequency of the quartz crystal.

Accuracy of the frequency counter is affected in direct proportion to the setting of the gate (or counting) time because frequency is measured in terms of pulses occurring within a known time interval. The longer the gate time, the greater the accuracy because more pulses are accumulated.

For fluids with low viscosities, the resonant frequency in the test fluid differs from the resonant frequency in the inviscid fluid (air) by a small value, e.g., 10 to 20 Hz. Therefore, if a gate time of ten seconds is used, the resulting frequency measurements would be precise to ± 0.1 Hz. This precision is necessary because viscosity calculations depend on the difference between the resonant frequency in the test fluid and the inviscid fluid, or $f - f_0$. For more viscous fluids the difference between f and f_0 is larger. In this case a gate time of one second was used and the resulting frequency measurements were precise to within plus or minus one Hz.

Pressure Equipment

A flow diagram for the pressure equipment is sketched in Figure 16. All valves, fittings, and tubing (1/4-inch OD by 0.083-inch ID, 304 stainless steel) used on the low pressure side of the system had a minimum pressure rating of 30,000 psig. For minimizing the number of bulky high pressure fittings, three "frozen valves" were employed to isolate the low pressure equipment from the high pressure side of the system. The concept of using liquid nitrogen to freeze liquid in a small section of transfer line as an ultra-high pressure valve was introduced by Babb (4) and was used by Rein (30). The high pressure side of the system was equipped with stainless steel tubing, 3/16-inch OD by 1/32-inch ID. The service of frozen valves was found to be excellent.

Pressure Generation and Storage

Major items in this group were the air-driven hydraulic pump, liquid separator, high pressure intensifier, and high pressure vessel.

Primary pressurization was obtained with a SC Model 40-500-16 air-driven hydraulic pump. The pump was designed to deliver hydraulic fluid at a maximum pressure of 27,500 psig with an air supply of 100 psig. The discharge rate of the hydraulic fluid can be regulated by adjusting the pressure of the air supply. The hydraulic fluid, Phexol 201, was stored in an oil reservoir and was filtered before being admitted into the pump.

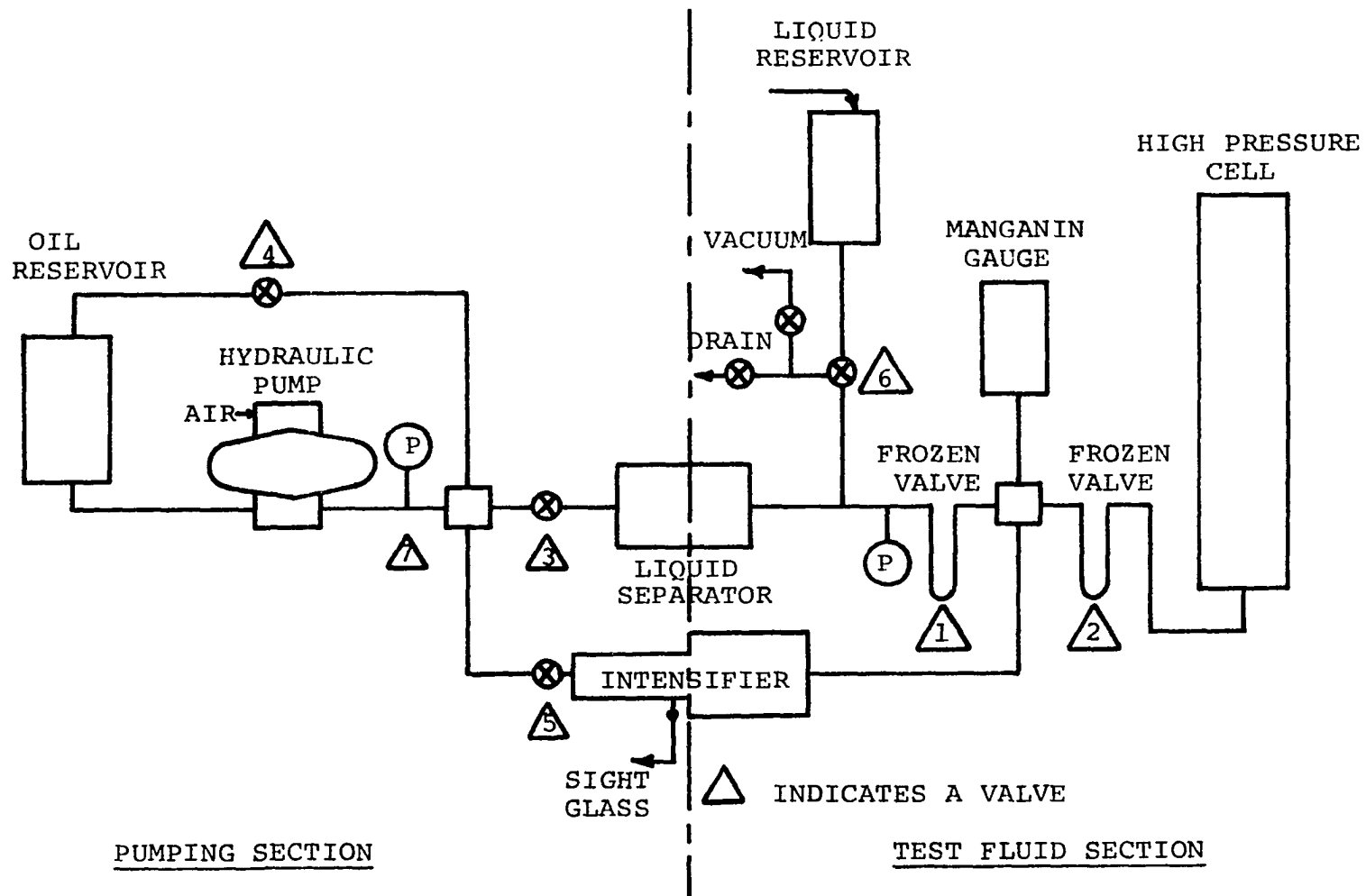


Figure 16. Flow Diagram of High Pressure Equipment and Accessories.

The liquid separator, 1-1/2 inch ID by 4 inch OD by 17 inch internal length, rated at 20,000 psig, was made of plain carbon steel and was machined at the University of Oklahoma Central Shop. The dimensions of the separator were determined in accordance with the internal volume of the 150,000 psig high pressure vessel. The design philosophy was taken from Lott (20). The bore of the separator was reamed and honed to a mirror finish. Both ends of the cylinder were closed with coarse, buttress-thread plugs incorporated with an O-ring seal. A copper free-moving piston was used to separate the hydraulic oil from the test liquid. The seal between the piston and the bore was accomplished with a single Buna-N, 90 shore O-ring accompanied with a double spiral, teflon back-up ring on both sides of the O-ring. Details of the separator are shown in Figure 17.

Pressures higher than 20,000 psig were obtained by driving the intensifier with the hydraulic pump. This high pressure intensifier, rated at 200,000 psig working pressure, was designed and manufactured by Harwood Engineering Company, Incorporated. The high pressure section of the intensifier was of shrink-fit construction, 0.625-inch ID by 6-inch OD by 4 inches in internal length. The high-pressure outlet was equipped with a 3/4-inch high pressure connection. A 1/4-inch AE-cone connection fitted at the end of low pressure section of the intensifier was provided for the pump discharge line. On the other end of the low pressure section (in the middle

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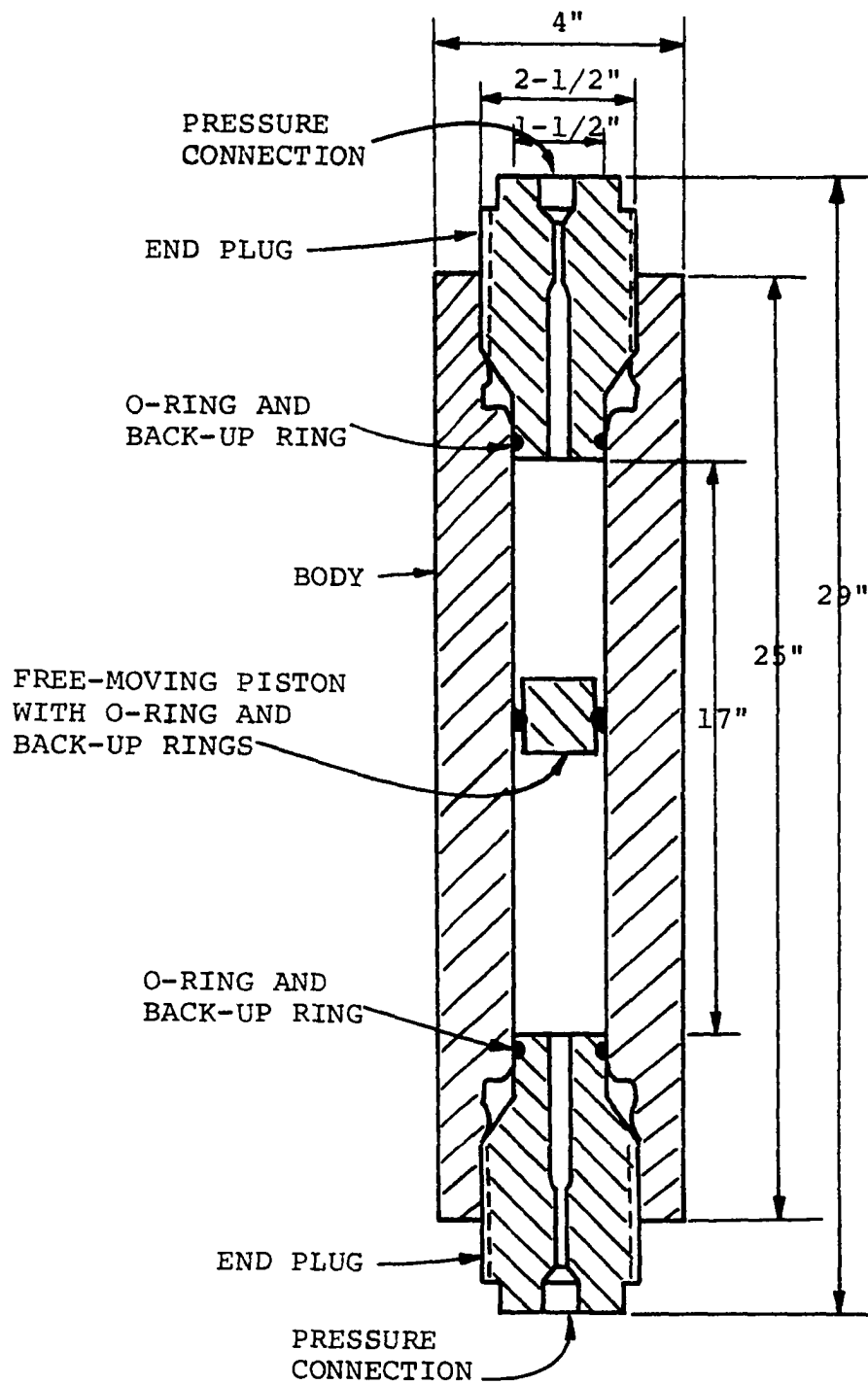


Figure 17. The Assembly Diagram of the Liquid Separator.

of the intensifier) was a 1/4-inch pipe connection which was used to vent the cylinder cavity into a sight-glass during the pressure stroke. Piston location was determined by the displacement of oil level in a graduated polyglass vessel with 1/8-inch divisions connected to the 1/4-inch pipe connection. An assembly diagram of the intensifier is shown in Figure 18.

The 150,000 psig pressure duplex vessel with 1-1/2 inch ID by 9 inch OD by 12 inches in internal length was designed and fabricated by Autoclave Engineers Corporation. The shrink fit vessel was built from HY-140 stainless steel outer and inner shells. The seal of this two-ended cylinder was accomplished with O-rings and beryllium copper back-up rings.

Four holes, 90-degrees apart, 3/8-inch deep and tapped 10-24 on the inside end of the bottom closure were provided for the crystal holder. Electrical leads with a beryllium copper conical-shaped plug entered the pressure vessel through two holes in the bottom plug. The bottom plug is also equipped with a thermocouple well so that the fluid temperature inside of the high pressure vessel can be recorded. Details of the assembly of the high pressure vessel are given in Figure 19.

In the present design, the test fluid was pressurized in the intensifier and was transferred into the high pressure vessel containing the viscometer through a transfer line having an internal diameter of 0.025 inches. The operating pressure was limited to the level where the test fluid became

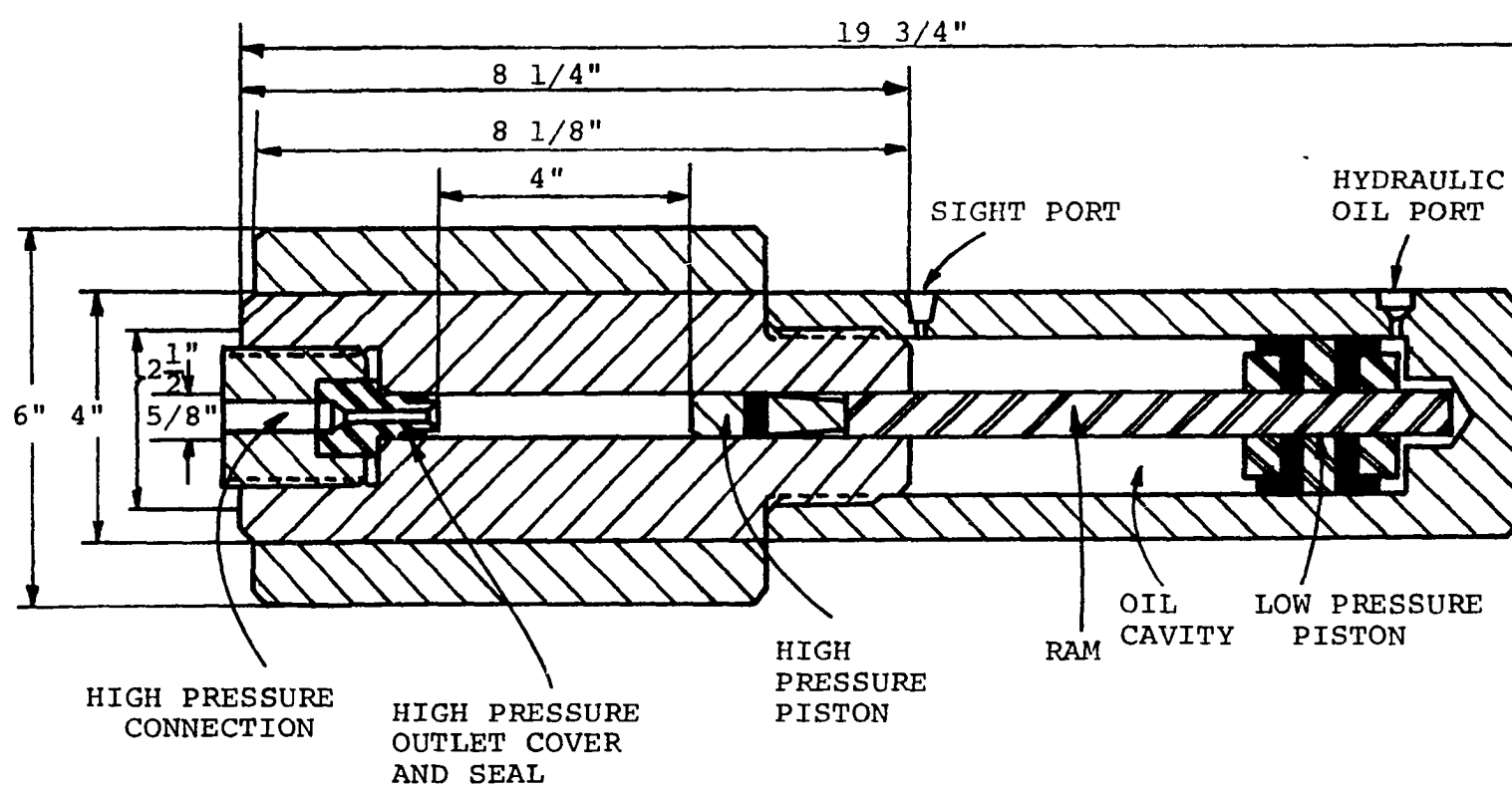


Figure 18. The Assembly Diagram of High Pressure Intensifier.

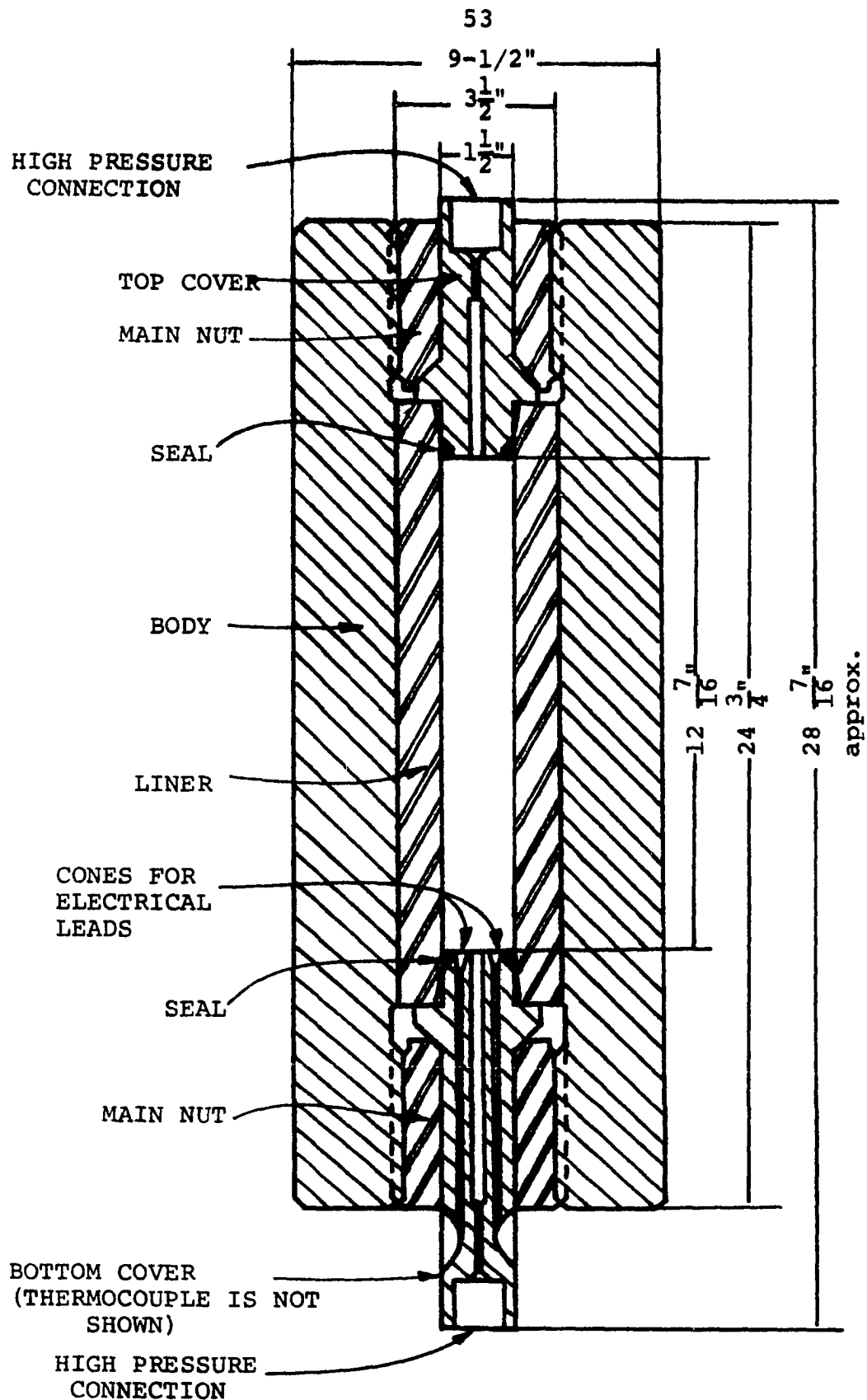


Figure 19. The Assembly Diagram of the 150,000 psi High Pressure Vessel.

so viscous that it virtually solidified in the transfer line. This problem might be circumvented by using a low-viscosity fluid to transmit pressure across a bellows (33) or by a free-moving piston which separates the transmitting fluid from the test fluid. Thus, the test fluid would be charged to the crystal viscometer at atmospheric pressure.

The free-moving piston technique for avoiding freezing in the lines was attempted in this experiment using normal pentane as the pressure-transfer fluid. Unfortunately, since no provision was made to prevent the piston from hitting the quartz crystal, the latter was damaged and had to be replaced. In a future modification of the design of the viscometer, a stop or wedge will be incorporated midway in the bore. Another alternative would be to incorporate a tracer in the piston so that the exact location of the free-moving piston can always be detected while the vessel is being pressurized.

Pressure Measurement

System pressures below 20,000 psig were read directly from conventional pressure gauges. Pressures over 20,000 psig were measured with a manganin gauge accompanied with a Carey-Forster Bridge. Both instruments were purchased from Harwood Engineering Company, Incorporated.

The manganin gauge contained two, non-conductive, wound resistance coils. One is the active coil and the other is a compensating coil. These two coils were wired in series

to form adjacent arms of a Wheatstone bridge. The active coil is subjected to hydrostatic pressure to be measured, while the compensating coil compensates for gross ambient temperature changes.

The essential characteristic of a manganin coil is that under pressure the coil resistance increases by a small amount, which is a well-known function for manganin coils. Increases in the resistance can be measured by connecting the active and the compensating wires onto the respective binding posts of a pressure measuring bridge. The bridge, Carey-Forster Type S, used in this experiment, is a direct current, battery-operated unit; therefore, the capacitive and inductive effects are eliminated. Direct pressure reading was obtained by manually turning the pressure-indicating dial on the bridge to a null deflection as shown on a high sensitivity millivoltmeter.

A pressure measurement correction chart is plotted in Figure 20. Calibration of this particular set-up of manganin gauge and bridge was made based upon the manganin gauge factor at 100,000 psig, supplied by the manufacturer. The manufacturer claimed that this bridge-gauge combination measured pressures with an accuracy of better than $\pm 1/2$ percent.

Auxiliaries

Originally an oil bath was used to maintain the high pressure vessel at constant temperature levels. However, this method of heating was unacceptable because of fumes from

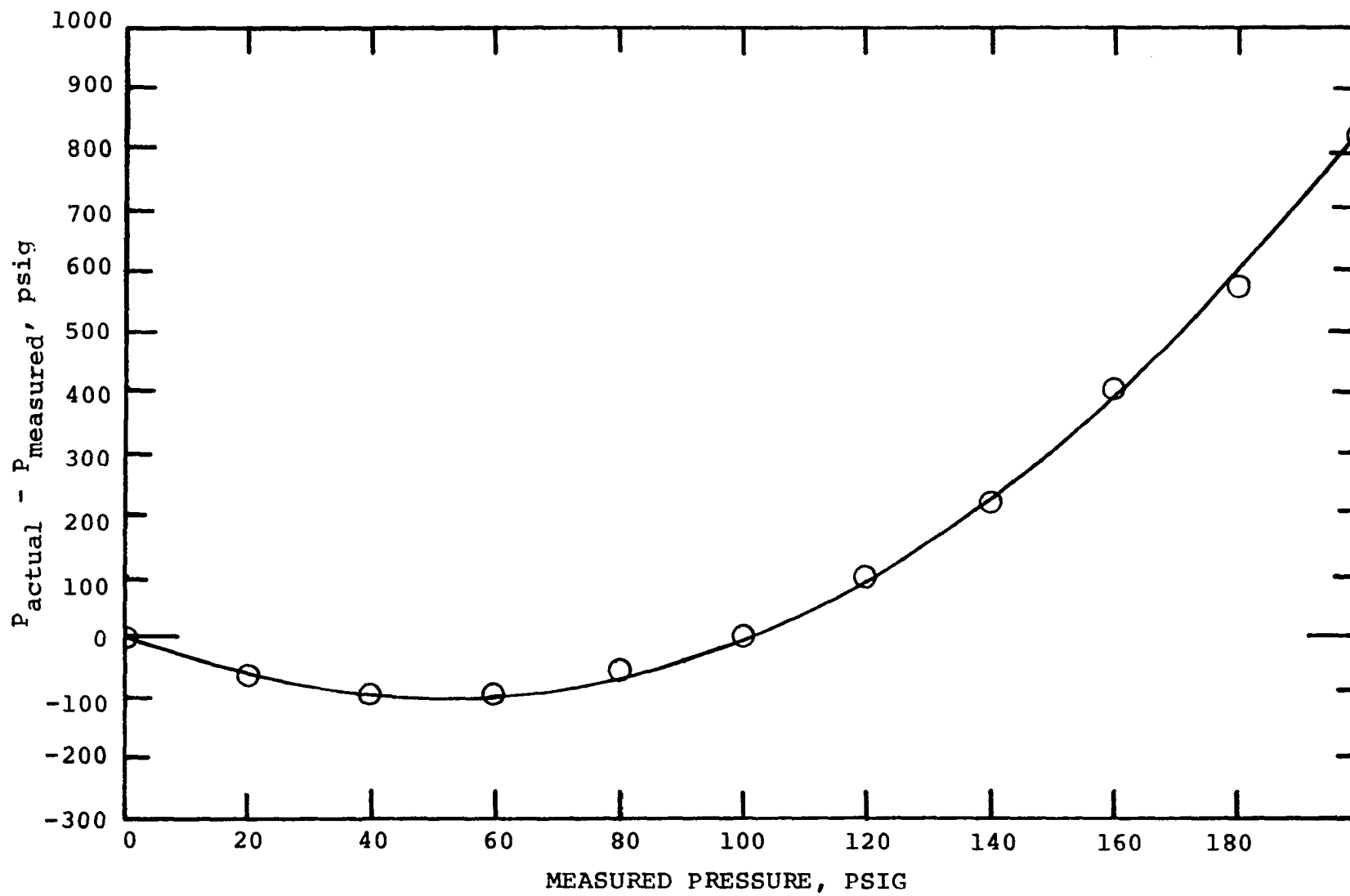


Figure 20. Pressure Measurement Correction Chart.

the hot oil since it was difficult to achieve a completely closed system. Consequently, the oil bath was eventually replaced by direct electric heaters. Four strip heaters were attached on the outer surface of the high pressure vessel and were covered with fiberglass insulation material. A constant temperature level was maintained with a temperature controller manufactured by Thermo Electric Company.

In addition to the thermocouple well built in the high pressure vessel, a second thermocouple was bonded in the middle of the outside cylindrical surface of the vessel to detect the temperature profile across the vessel wall. Monitoring the outer surface temperature also helped to keep the vessel temperature within the designated temperature limits during the heating-up period.

CHAPTER IV

EXPERIMENT PROCEDURES

Experiments were carried out by first installing the crystal viscometer in the pressure vessel. The viscometer constants were then determined by obtaining frequency and resistance data with the crystal immersed in several calibration fluids for which the Newtonian viscosity and density were known as functions of temperature and pressure. Viscosities and viscoelasticities of the test fluids were then calculated from the frequencies and resistances of the crystal when immersed in test fluids and from the predetermined viscometer constants. Densities of the test fluids were also measured in the course of viscosity measurements. Details on the experimental procedures are described in the following sections.

Pressure Generation

Fluid was transferred from a liquid reservoir into the system (Figure 16) by compressed air. Pressures below 20,000 psig were generated in the liquid separator with an air-driven hydraulic pump after closing the appropriate valves. For pressures above 20,000 psig the low pressure side of the

system was isolated by closing the frozen valve No. 1, shown in Figure 16. Further pressurization of the high pressure vessel was accomplished by driving the intensifier piston forward with the hydraulic pump. As could be expected, an additional amount of liquid was required for building up higher pressure. Provision for recycling the intensifier was made possible by means of manipulating frozen valves No. 1 and No. 2. Adjustment of internal pressure of the high pressure vessel could be attained simply by driving the intensifier piston further forward with the hydraulic pump, or driving the intensifier piston backward by the liquid pressure accumulated inside of the vessel.

For density measurements, pressurization of the high pressure vessel was carried out with the intensifier alone right after the pressure vessel was filled with liquid.

Calibration of Viscometer

Determination of the crystal constants, K_f , f_o , K_r , and R_{EO} required prior to making viscosity measurements was a time-consuming calibration procedure. A series of fluids with known viscosities and densities as functions of temperatures and pressures were selected as calibration liquids such as normal pentane, normal octane, toluene, methylcyclohexane, and di-(2-ethylhexyl) sebacate.

After the crystal was prepared, as described in Chapter III, it was mounted in the crystal holder which had been

installed on the bottom plug of the high pressure vessel. Satisfactory operation of the crystal viscometer was checked with a number of fluids, air, normal pentane, toluene, di-(2-ethylhexyl) sebacate, and viscosity standards S-3, S-20, and S-60 from the National Bureau of Standards, in a glass container outside the pressure vessel. The measurements on resistance versus frequency for each fluid were subjected to a second order least squares curve fit to derive an equation which was then differentiated to obtain the minimum point of the resistance. The frequency at which the resistance was found to be a minimum was taken to be the resonant frequency of the crystal. The calculated values of resonant frequency and resistance were plotted as f versus $(\omega\rho\eta/2)^{1/2}$ and R_E versus $(\omega\rho\eta/2)^{1/2}$. The linear dependence of Equations 43 and 44 was validated with these plots. A non-linear relation indicated that the torsional oscillation was accompanied by other types of motion resulting from an improper mounting.

A typical plot of the rough calibration of the crystal viscometer is shown in Figure 21. The crystal viscometer was placed in the high pressure vessel until the calibration curves were found to be linear. Satisfactory functioning of the viscometer was confirmed by taking a measurement while the crystal was immersed in an inviscid fluid such as air. Agreement between measurements of the minimum resistance and resonant frequency in this inviscid fluid and the previous rough calibration indicated that the crystal had remained

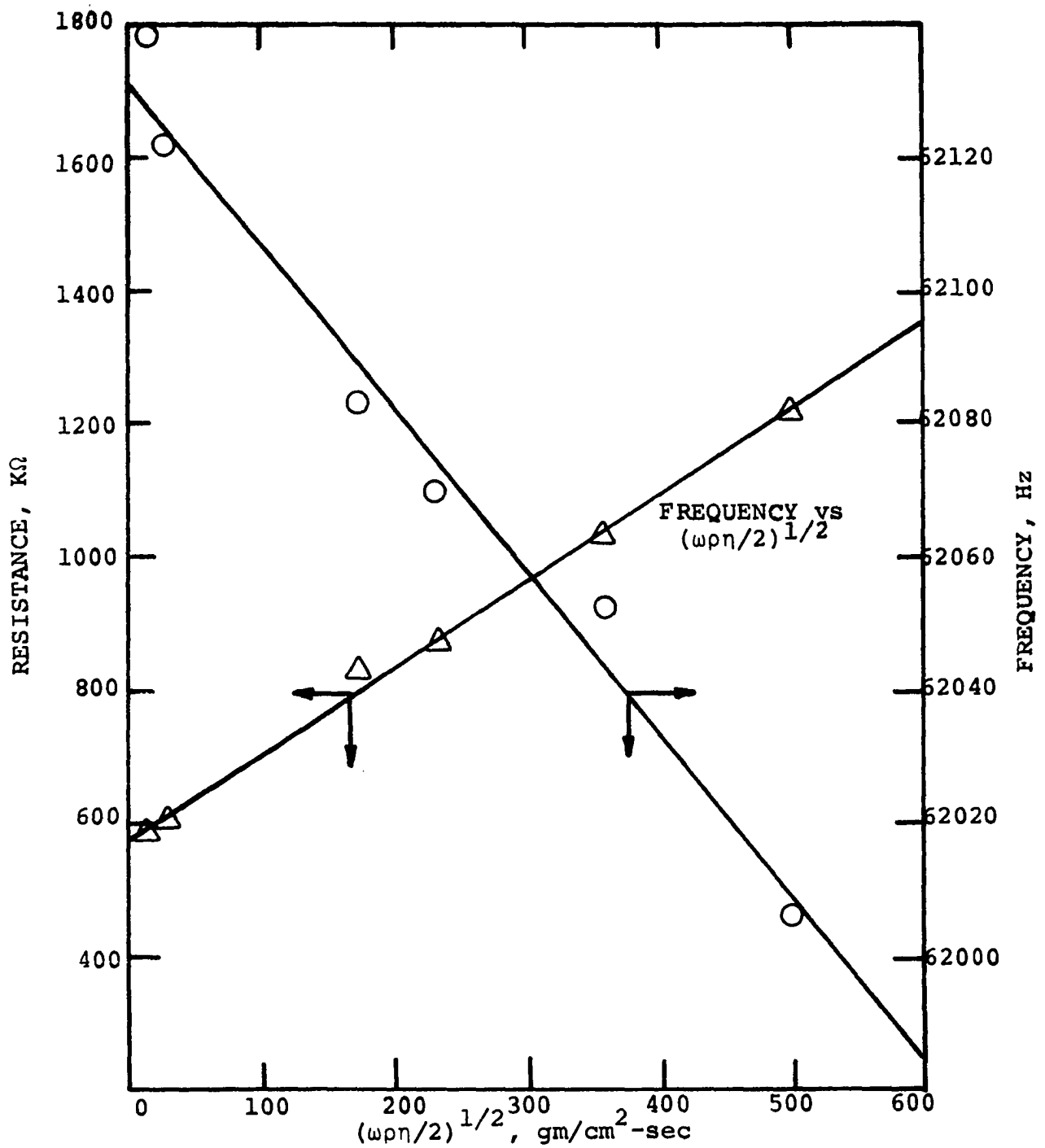


Figure 21. Typical Out-side Pressure Vessel Calibration Data (60-I kHz Crystal).

intact in its mounting during the subsequent assembling of the closure and sealing of the pressure vessel. If agreement were not obtained, the crystal had to be examined, corrective steps had to be taken and the calibration procedures had to be repeated.

Calibration of the viscometer was begun only after the proper operation of the crystal was assured. The calibration consisted of measuring the resistance as function of frequency of the crystal when immersed in a calibration fluid at desired levels of temperature and pressure. A series of measurements for each fluid were carried out through the entire range of temperature and pressure.

The data on resistance versus frequency for each fluid at each temperature and pressure were also subjected to a least squares quadratic (or cubic where necessary) fit to obtain the resonant frequency and the minimum resistance as prescribed in the rough calibration. A typical plot is shown in Figure 22 for one of the test liquids, Humble FN-3158 at 210°F and 20,200 psig, which is quite representative of the data obtained at all levels of temperature and pressure for both the calibration and test fluids. It should be noted that the abscissa in Figure 22 is given in terms of $(f - 19,900)$ rather than f . The only purpose in using this shift was to spread the data along the horizontal axis to facilitate visual examination.

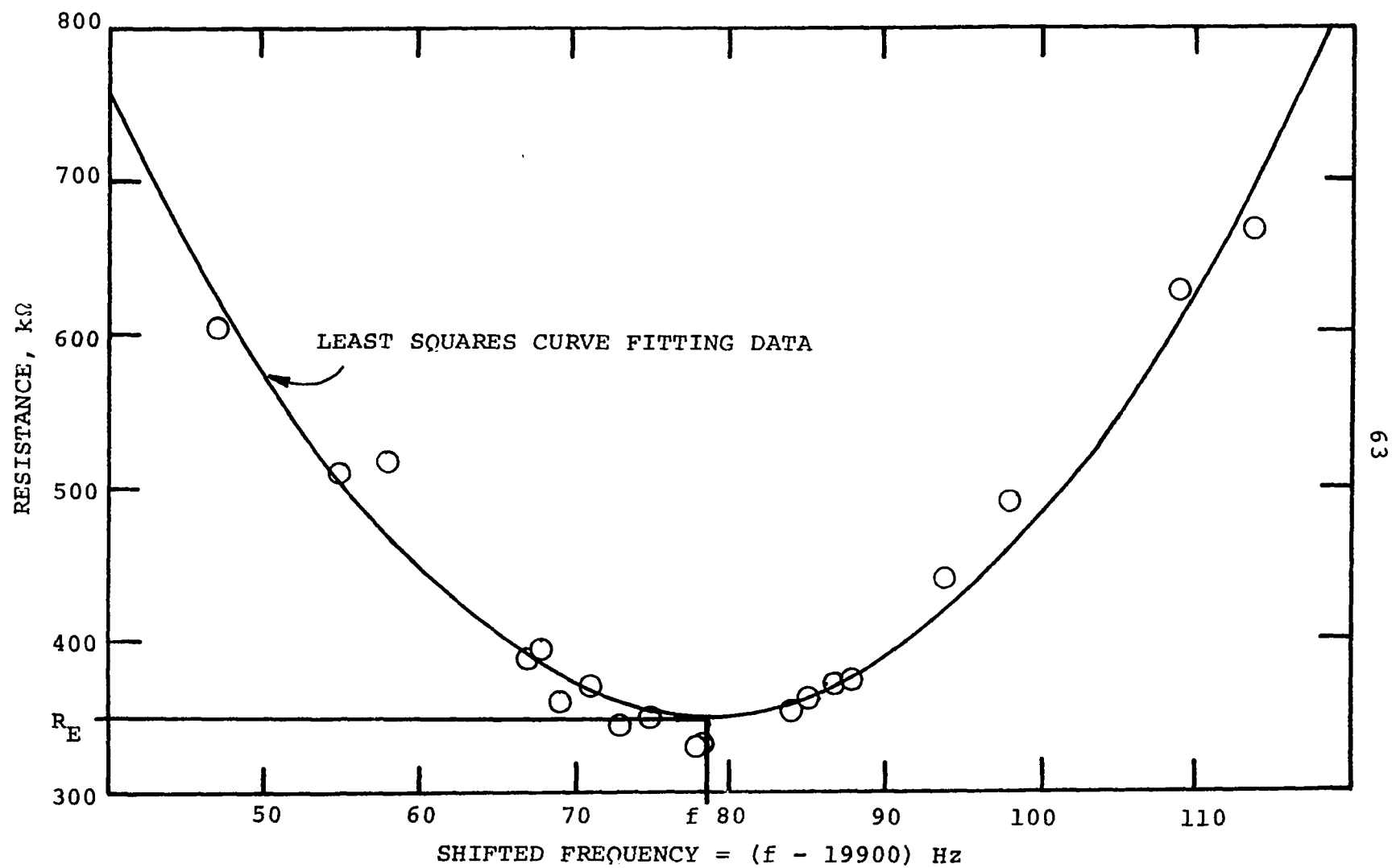


Figure 22. Typical Data for Determining Resonant Frequency (Data for FN-3158 at 210°F and 20,200 psi).

After all the necessary data were obtained with one fluid, it was discharged from the system. Cleaning of the pressure vessels and lines was accomplished without opening the vessel closures to eliminate the need for replacing the seals, and re-calibrating the crystal viscometer, as well as avoiding the possibility of scratching the bore. The system was flushed several times with petroleum ether for removal of any residual liquid. The system was then subjected to vacuum for hours, usually overnight. Subsequently the clearness of the crystal was checked by measuring the values of resonant frequency and resistance before the next liquid was introduced into the viscometer and comparing the values of f and R_E with those obtained in air before the run was started. If the value of resonant frequency or resistance deviated significantly from the values obtained from previous runs, the system was again flushed with petroleum ether, and the test for crystal clearness was repeated. The pressure vessel was then filled with the next liquid to be investigated, and the measurements were begun only if it was obvious that the system was clean.

A run was terminated if a defect either on the pressure equipment or on the quartz crystal was observed. In the latter case, the crystal viscometer was removed from the high pressure vessel and was examined carefully on the mounting and electrical contacts. Once the viscometer was taken out of the pressure vessel, the whole procedure of calibration had to be repeated from the very beginning.

In this study the calibration runs were repeated between sets of measurements on the test liquids to insure that the quartz crystal viscometer was performing properly.

Viscosity and Viscoelasticity Determination

Viscosity measurements on test liquids were carried out by the same procedures as calibrating the viscometer with calibration fluids. At different experimental conditions, R_M and X_M were calculated by Equations 41 and 42, using the measured values for the resonant frequency and the minimum resistance along with the predetermined set of viscometer parameters.

Newtonian fluids have equal values of mechanical reactance and mechanical resistance. Since the mechanical reactance, X_M , is subjected to more experimental errors than the mechanical resistance, R_M , for less viscous fluids, the viscosity of a Newtonian fluid is calculated from Equation 63 rather than Equation 40.

$$\eta = \eta' = 2R_M^2/\omega\rho ; \quad \eta'' = 0 \quad (63)$$

The viscoelastic properties G' and η' were calculated by Equations 39 and 40, respectively. For a given value of $(\omega\rho\eta/2)^{1/2}$, a viscoelastic fluid should have a resonant frequency significantly higher than would be expected for a Newtonian fluid. On the other hand, the resistance at resonant frequency for a viscoelastic fluid should be significantly

lower than would be expected for a Newtonian fluid. Therefore, the characteristic impedance resistance calculated by Equation 41 would be appreciably larger than the characteristic impedance reactance calculated by Equation 42 for a viscoelastic fluid. Viscoelastic behavior of a fluid is present only if both criteria are satisfied.

Density Determination

Density information for the test liquids must be known in order to make viscosity calculations with Equations 39 and 40. If density data at various temperatures and pressures were not previously available for test liquids, the following procedure allowed densities to be measured concurrently with the viscosity measurements.

When density measurements were made only the intensifier was used to pressurize the high pressure vessel, i.e., the liquid separator shown in Figure 16 was not used for pressurizing. The temperature of the high pressure vessel was maintained constant at a desired level. The mass of fluid introduced to the high pressure vessel could be deduced by measuring the movement of the intensifier piston. Movement of the intensifier piston was determined by the amount of oil displaced from the oil cavity into the sight-glass (see Figure 16). When the intensifier was recycled, frozen valve No. 2 was not opened until the pressures on both sides of the valve were equal.

Because of the above technique the following reasoning and equations could be used to calculate densities from measurements of intensifier piston movements during pressurization.

The mass of fluid introduced into the high pressure vessel, dm_{ves} , is equal to the mass of fluid displaced by the intensifier piston, $-dm_{inten}$. Thus,

$$dm_{ves} = -dm_{inten} = \rho_{inten} A d\ell \quad (64)$$

where A is the cross section area of the high pressure piston of the intensifier, ρ_{inten} is the density of fluid in the intensifier at the existing pressure and temperature of the intensifier, and $d\ell$ is the piston displacement during the pressurization. The total mass in the high pressure vessel at any pressure is equal to the mass that was present at atmospheric pressure, m_o , plus the amount added during the pressurization. Therefore,

$$m_{ves} = m_o + \int dm_{ves} = m_o + \int \rho_{inten} A d\ell \quad (65)$$

Dividing Equation 66 by the volume occupied by the liquid gives

$$\begin{aligned} \rho = \rho_{ves} &= \rho_o + \frac{A}{V} \int \rho_{inten} d\ell \\ &= \rho_o + \frac{A}{V} \int \rho_{inten} \left(\frac{\partial \ell}{\partial P} \right)_T dP \end{aligned} \quad (66)$$

where ρ = fluid density at a given temperature and elevated pressure

ρ_o = fluid density at a given temperature and atmospheric pressure

A = cross section area of the high pressure piston of the intensifier

V = volume occupied by the test fluid. This volume was approximated by (internal volume of the high pressure vessel - the volume occupied by the quartz crystal - the volume occupied by the crystal holder)

$(\frac{\partial \ell}{\partial P})_T$ = slope of the piston stroke-pressure curve

It is necessary to know ρ_{inten} as a function of pressure at the intensifier temperature. Based on the mass balance of Equation 64, and restricted to the case of equal temperatures in the pressure vessel and the intensifier, the following finite difference equation was used to determine the required intensifier density information as a function of pressure,

$$\rho_{n+1}/\rho_n = [1 + \frac{A}{2V} \Delta \ell_T] / [1 - (\frac{A}{2V}) \Delta \ell_T] \quad (67)$$

where $\Delta \ell$ represents the piston displacements during a given pressure change and the subscript T indicates that the intensifier and pressure vessel must be at the same temperature level. Densities of the test fluids were measured at temperatures above room temperature, whereas the intensifier was always at room temperature. Thus, no measurements were made in which the pressure vessel and intensifier were actually at

the same temperature. Values of the piston stroke of the intensifier at room temperature were measured as a function of pressure in the viscometer at several temperature levels (100°, 210° and 300°F). The resulting curves were cross-plotted at several pressure levels, from which the piston stroke at the intensifier (room) temperature could be obtained by extrapolation.

CHAPTER V

RESULTS AND DISCUSSION OF RESULTS

Results on the densities of four lubrication fluids and one solution of polystyrene in toluene are given in this chapter. Determination of the calibration parameters for the viscometers follow, along with data on the viscosities. Finally, viscoelastic properties of the test fluids are presented in subsequent sections.

Density Measurement

Densities of the test fluids were determined by the technique described in Chapter IV and calculated according to Equation 66,

$$\rho = \rho_0 + \frac{A}{V} \int \rho_{\text{inten}} \left(\frac{\partial \rho}{\partial P} \right)_T dP \quad (66)$$

The volume V , in Equation 66, was approximated closely by subtracting the volume occupied by the quartz rod and the volume occupied by the crystal holder from the total internal volume of the high pressure vessel. For the measured dimensions of the high pressure vessel, the quartz crystal, and the crystal holder, the volume available to the test liquid was calculated to be 19.5 cubic inches with the 20 kHz crystal

and 19.98 cubic inches with the 60 kHz crystal. The high-pressure piston of the intensifier had a cross sectional area of 0.307 square inches for all the density measurements except the measurements on Humble FN-3158. The densities of Humble FN-3158 were measured with an over-sized piston having a cross sectional area of 0.342 square inches. Thus, A in Equation 66 was 0.307 square inches for all runs except the Humble FN-3158 run, for which A was equal to 0.342 square inches. The compression as a function of pressure, $d\ell(p)$, was read from the level of oil in the sight-glass connected to the high pressure intensifier. The ratio of full stroke of the intensifier high-pressure piston to oil level displacement in the sight-glass was determined to be 0.41. Therefore, the actual strokes of the intensifier high-pressure piston were obtained as 0.41 times the sight-glass readings.

This density-determination technique was validated by comparing densities calculated by Equation 66 for one of the calibration liquids, di-(2-ethylhexyl) sebacate with reported values. As shown in Table I, the calculated densities of di-(2-ethylhexyl) sebacate demonstrates an agreement with ± 2 percent of reported values (3).

The densities of the four tested lubricants as functions of pressure at different constant temperature levels are shown in Figures 23, 24 and 25. The densities of these lubricants at atmospheric pressure and at various temperatures are plotted in Figure 26. The values in Figure 26 were obtained

TABLE I

A COMPARISON OF DENSITY VALUES FOR
DI-(2-ETHYLHEXYL) SEBACATE

Temp (°F)	Pressure (1000 psig)	ρ^* , g/cc (this study)	ρ , g/cc (Ref. 3)	% Error (Abs.)
77	0.0	--	0.912	--
	10.0	0.956	0.949	0.738
	20.0	0.988	0.974	1.440
	30.0	1.013	0.994	1.91
	40.0	1.035	1.014	2.11
	50.0	1.053	1.029	1.61
	58.5	1.066	1.045	2.01
100	0.0	--	0.903	--
	10.0	0.939	0.941	0.213
	20.0	0.968	0.965	0.311
	40.0	1.008	1.007	0.099
	60.0	1.034	1.037	0.289
	80.0	1.057	1.064	0.658
210	0.0	--	0.860	--
	10.0	0.903	0.906	0.331
	20.0	0.938	0.934	0.428
	40.0	0.985	0.982	0.305
	60.0	1.014	1.013	0.099
	80.0	1.037	1.034	0.290
	100.0	1.067	1.064	0.282
300**	0.0	--	0.824	--
	10.0	0.870	0.879	1.024
	20.0	0.908	0.913	0.548
	40.0	0.960	0.963	0.312
	60.0	0.989	0.997	0.602

*Densities were measured with 20 kHz crystal in use except densities at 77°F which were measured with 60 kHz crystal in use.

**Densities for Reference 3 were obtained by interpolation of known $\rho(T)$ data at each pressure.

TABLE I--Continued

Temp (°F)	Pressure (1000 psig)	ρ^* , g/cc (this study)	ρ , g/cc (Ref. 3)	% Error (Abs.)
482***	0.0	--	0.750	--
	10.0	0.813	0.832	2.280
	20.0	0.866	0.874	0.915
	40.0	0.935	0.928	0.754
	60.0	0.968	0.965	0.311
	80.0	0.986	0.996	1.004
	100.0	1.013	1.023	0.987
	115.0	1.054	1.039	<u>1.444</u>
				Average = 0.613

*Densities were measured with 20 kHz crystal in use except densities at 77°F which were measured with 60 kHz crystal in use.

***Densities for Reference 3 were obtained by extrapolation of known $\rho(T)$ to 482°F at each pressure.

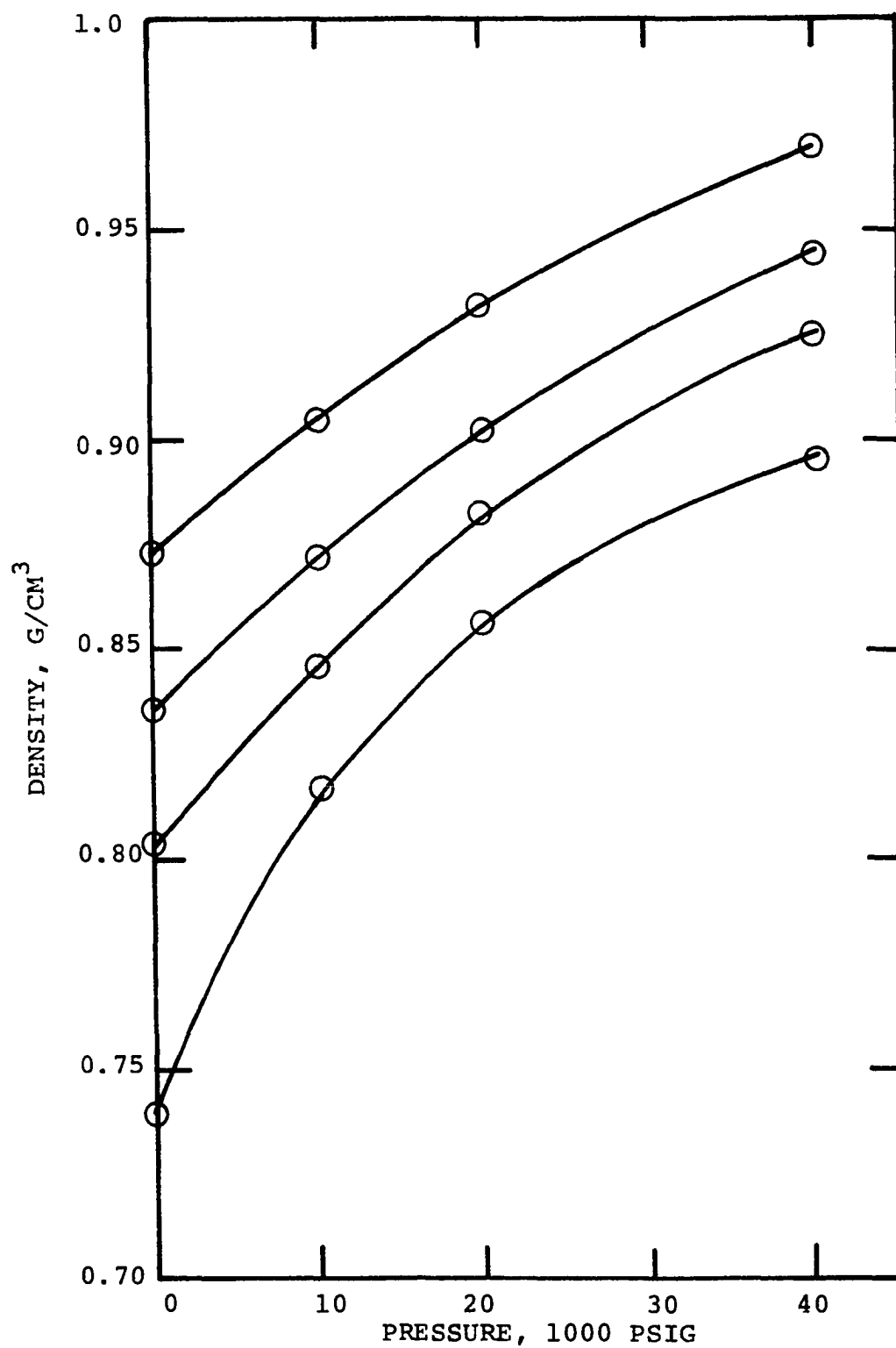


Figure 23. The Effects of Pressure and Temperature on the Density of Humble FN-3158 and Humble FN-3158 + 10vol.% Kendall 0839.

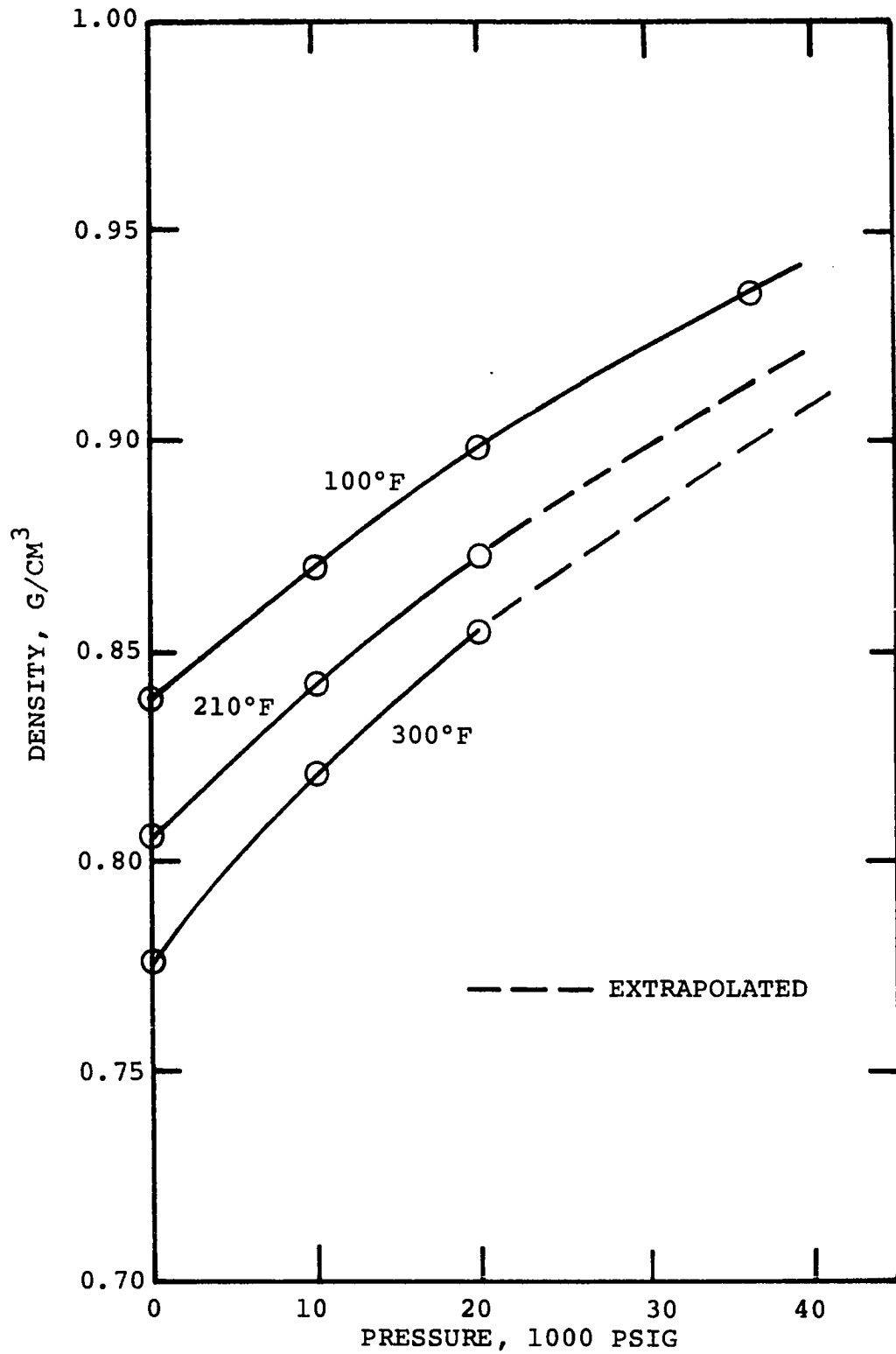


Figure 24. The Effects of Pressure and Temperature on the Density of Mobil XRM-109.

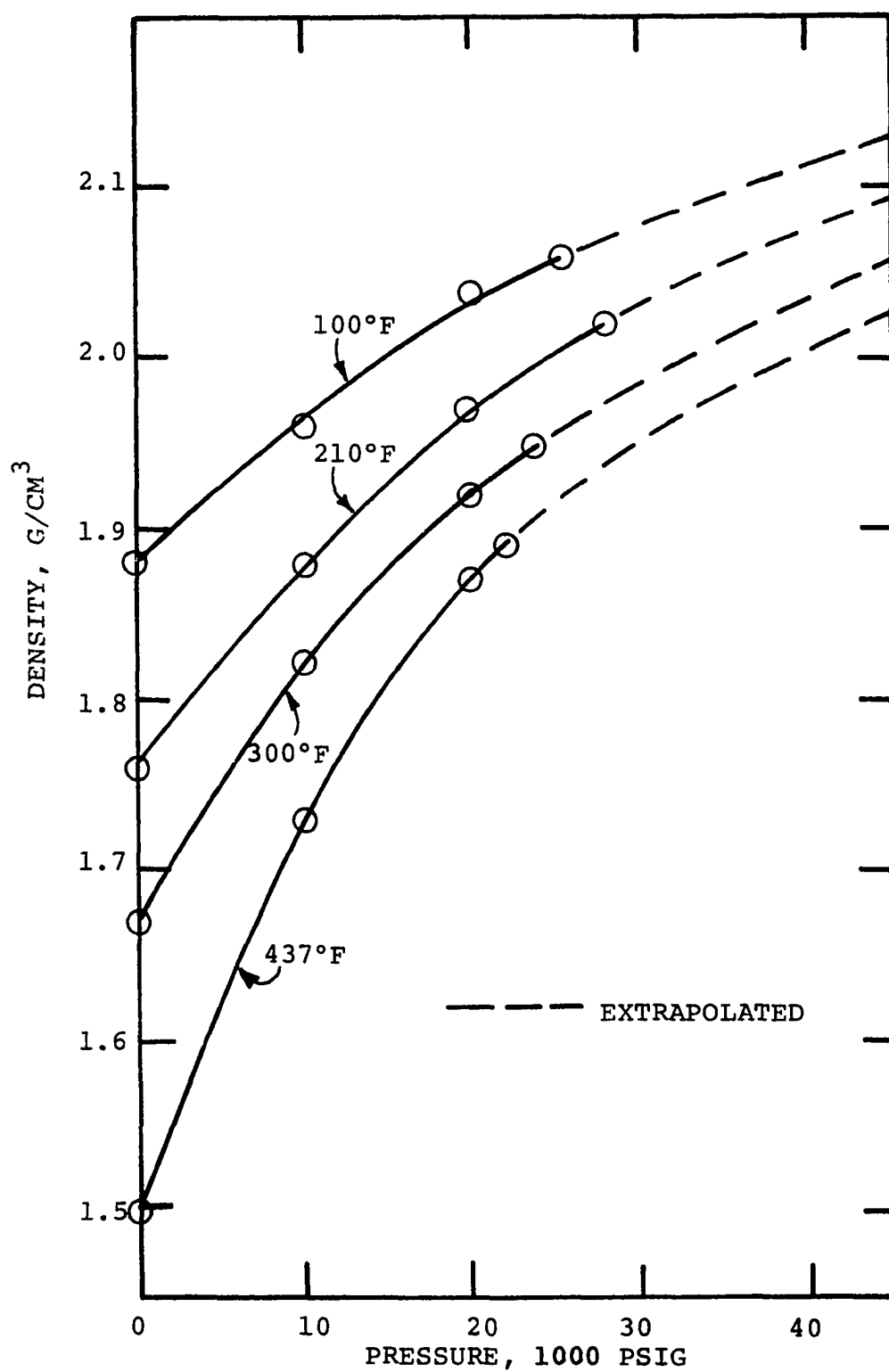


Figure 25. The Effects of Pressure and Temperature on the Density of DuPont Krytox 143-AB.

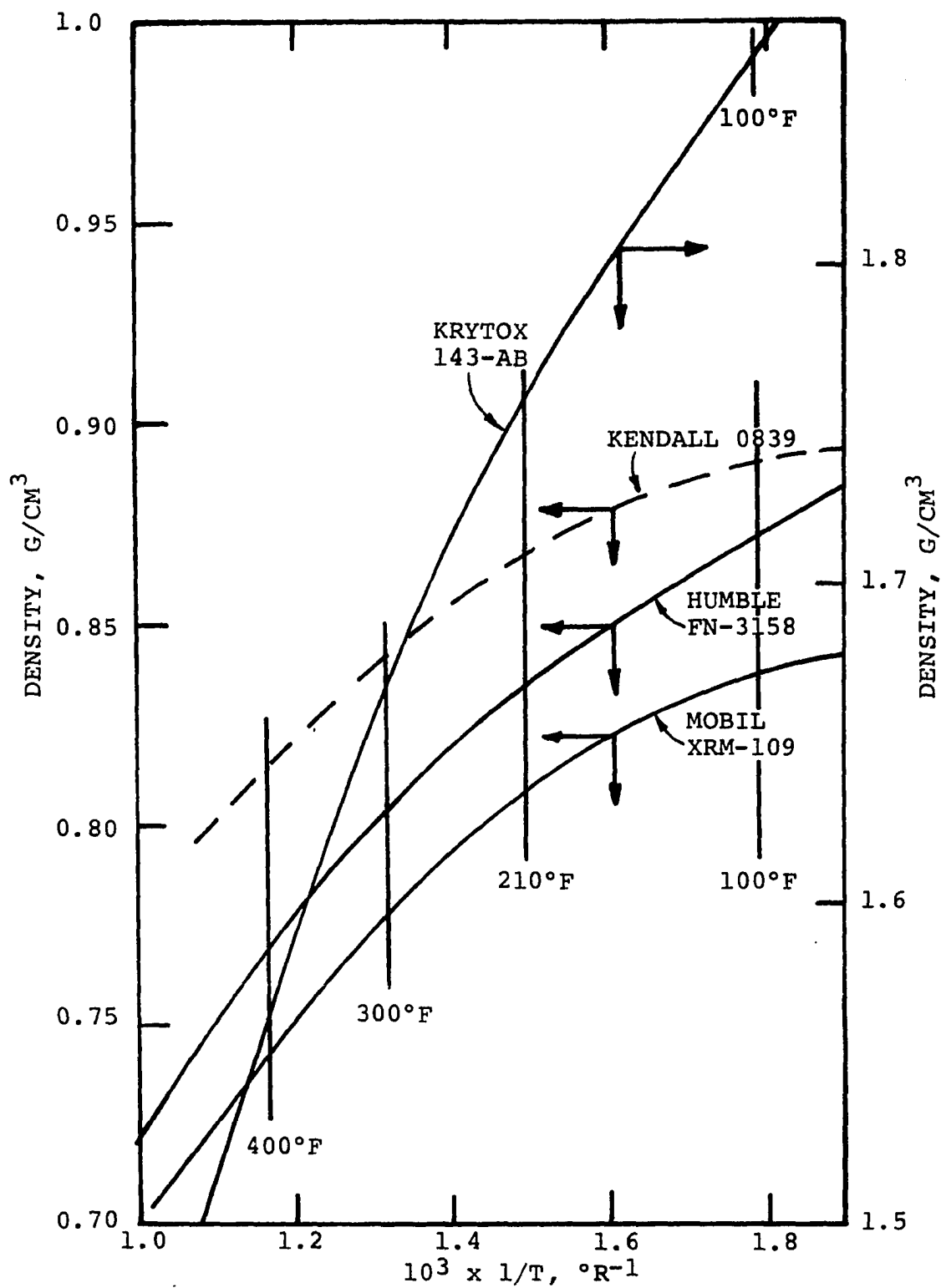


Figure 26. Density of Lubricants at Atmospheric Pressure (Data from Reference 19).

by interpolation and extrapolation of data supplied by NASA (19).

As could be expected, the density-pressure curve for Humble FN-3158 and the mixture of Humble FN-3158 plus ten volume percent Kendall 0839 were found to be essentially identical. The density of each of these components was similar at atmospheric pressure, and apparently the presence of ten volume percent of Kendall 0839 did not introduce any deviations from additive volume behavior (33).

Density of the solution of three weight percent S-109 polystyrene in toluene at atmospheric pressure and 77°F was determined by means of an hydrometer and was found to be the same as the density of toluene at this condition. The solution densities shown in Figure 27 were calculated from Equation 66 and from measurements of the oil displaced into the sight-glass connected to the intensifier. Calculations by Equation 66 were started with density values at 10,000 psig instead of atmospheric pressure to avoid the effects of leakage across the high-pressure piston of the intensifier at atmospheric pressure. The density of the solution at 10,000 psig was assumed to be identical with the density of toluene at this pressure.

Densities of the polymer solution at 77°F and 100°F as functions of pressure are plotted in Figure 27. It was found that the dissolved polymers did not introduce significant density deviations between the solution and the solvent

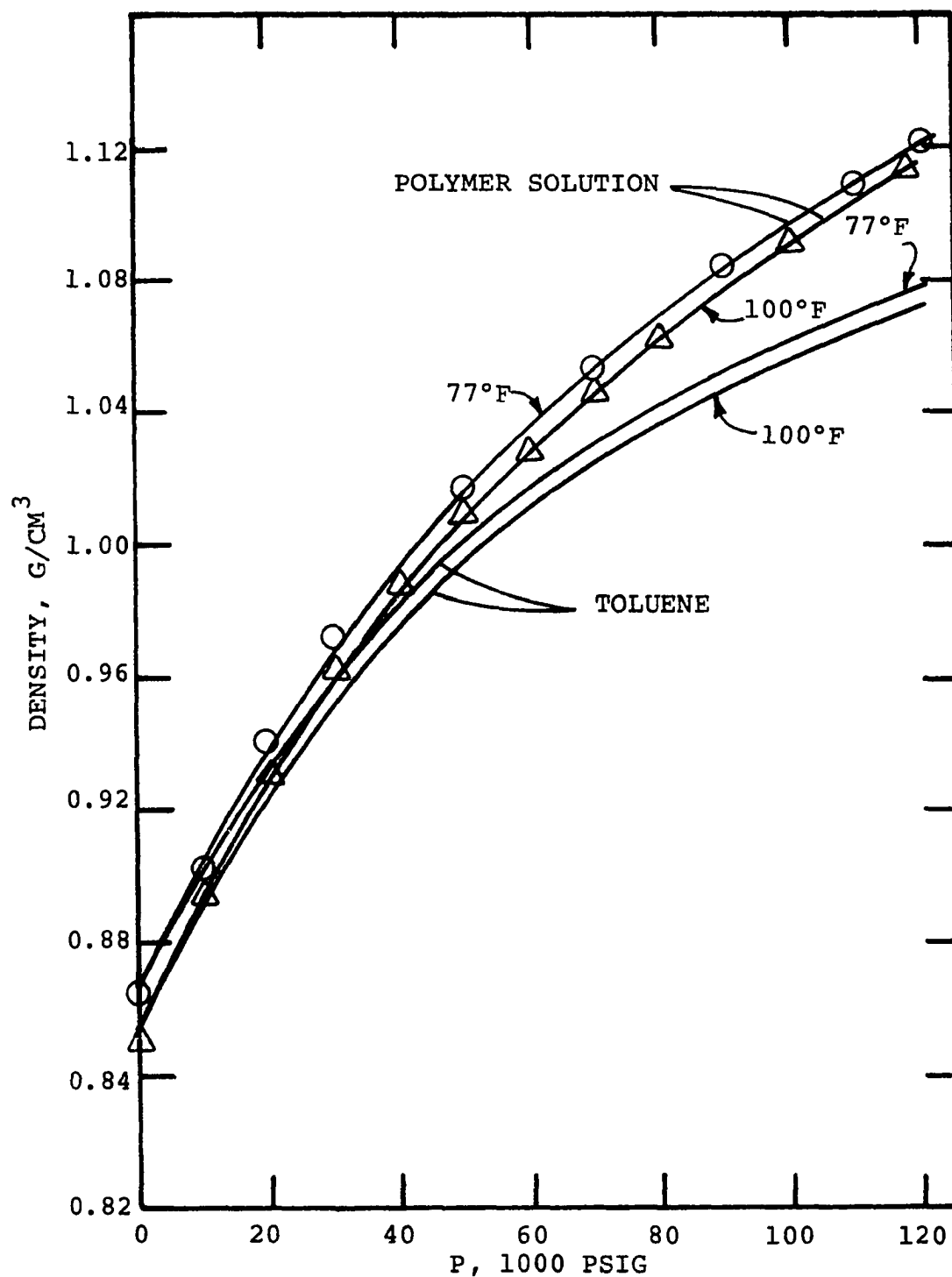


Figure 27. The Effects of Pressure and Temperature on the Density of the Solution of 3 wt.% of S-109 Polystyrene in Toluene.

until the pressure exceeded 80,000 psig. The maximum deviation between densities of the polymer solution and the solvent is four percent which was observed for both temperatures and 120,000 psig as shown in Figure 27.

Measured density data for all test liquids are tabulated in Appendix D.

Calibration Parameters

Details of the crystal viscometer preparations were given in Chapter III. Two different techniques for making contact between the electrical leads and the conducting surfaces of the quartz crystal were employed in this experiment. Electric contact was made with set screws to hold the leads on the crystal surface of the 20 kHz-I and 60 kHz-I viscometers. A silver epoxy was used to bond leads onto the crystal surface for the 60 kHz-II viscometer. The designations -I and -II refer to these two different means for obtaining electrical contact. In addition to the difference in crystal mounting, the 60 kHz-II crystal was coated with gold film instead of the silver film used on the -I viscometers.

Fluids with known viscosity-pressure-temperature and density-pressure-temperature properties were used to calibrate the crystal viscometers according to the techniques described in Chapter IV. Calibration fluids of known viscosity and density were used to determine the parameters K_f , f_o , K_r , and R_{Eo} from linear relations between the resonant frequency of

the crystal and $(\omega\eta/2)^{1/2}$, and the resistance at resonant frequency and $(\omega\eta/2)^{1/2}$. According to Equation 43,

$$f = f_o - K_f (\omega\eta/2)^{1/2} \quad (43)$$

Thus, a plot of f versus $(\omega\eta/2)^{1/2}$ should yield straight line with slope of $-K_f$ and intercept of f_o . According to Equation 44,

$$R_E = R_{Eo} + K_r (\omega\eta/2)^{1/2} \quad (44)$$

and a plot of R_E versus $(\omega\eta/2)^{1/2}$ should yield a straight line with slope of K_r and intercept of R_{Eo} . Normal pentane, toluene, methylcyclohexane, and di-(2-ethylhexyl) sebacate were used as calibration liquids for both the 20 kHz-I and 60 kHz-I viscometers. The same calibration liquids plus normal octane were used in calibrating the 60 kHz-II viscometer.

The required data on viscosities as functions of pressure at 86°F (30°C) and 167°F (75°C) in Reference 6 were interpolated to obtain viscosity-pressure information at 100°F for normal pentane, normal octane, toluene, and methylcyclohexane. These reported viscosity-pressure data were also extrapolated at 77°, 210° and 300°F to obtain the required viscoeity-pressure information at those temperatures.

Densities of normal pentane and normal octane as functions of pressure at 77°, 100°, 210° and 300°F were obtained by interpolation and extrapolation of the data in Reference 7. Density-pressure information for methylcyclohexane was

calculated by interpolation and extrapolation from Reference 8. Published density-pressure data for toluene at 30°C (9) were used to estimate the density-pressure relations at other temperatures by use of a corresponding-state correlation (29).

Information on viscosities and densities as functions of pressure and temperature for di-(2-ethylhexyl) sebacate were obtained from the ASME Pressure-Viscosity Report (3).

Uncertainties in predicting the viscometer calibration parameters were attributed to surface roughness of a 60 kHz crystal (31, 33, 36). A discontinuity in crystal resonant frequency versus $(\omega\rho\eta/2)^{1/2}$ was observed for measured values of $(\omega\rho\eta/2)^{1/2}$ less than seventy (31). With the above limit on $(\omega\rho\eta/2)^{1/2}$, most of the calibration liquids were not suitable until the system pressure was greater than 40,000 psig for which $(\omega\rho\eta/2)^{1/2}$ exceeded seventy. Because of this limitation sufficient calibration information could not be obtained for the 60 kHz-I crystal viscometer. The viscometer parameters were then determined in accordance with the correlation suggested in Reference 33.

However, the crystal surface roughness apparently did not introduce any difficulty in calibrating the 60 kHz-II crystal. Straight calibration lines for both f and R_E versus $(\omega\rho\eta/2)^{1/2}$ were obtained over the entire experimental range. This improved calibration might be explained by a better conductive coating or better mounting of the crystal.

Calibration on the 60 kHz-II crystal viscometer at 210°F was also attempted. Scatter in the calibration data at 210°F was much greater than the calibration measurements taken at lower temperature levels. No correlation could be established for this set of calibration data. The inferior measurements were thought to be the result of a loose electrical contact between the electrical lead and the crystal conductive surface, which interfered with the functioning of the viscometer. Therefore, the viscometer was cooled back to 100°F. Behavior of the viscometer was then checked with di-(2-ethylhexyl) sebacate. The measurements were found to be satisfactory, compared with the previous set of measured values. The question on the effects of high temperature accompanying the high pressure on the 60 kHz-II viscometer is still not resolved.

All the liquids except di-(2-ethylhexyl) sebacate were suitable for calibration of both the 20 kHz-I and 60 kHz-II viscometers. Di-(2-ethylhexyl) sebacate could be used only over a limited range of pressures and temperatures because data for this fluid deviated from the linear relations given by Equations 43 and 44 and thus precluded its use for calibrations. The possibility of viscoelastic behavior causing this deviation was speculated, but it was not sufficiently conclusive to be reported as such.

Figures 28 and 29 present typical calibration data used to obtain K_f and f_o for the 20 kHz-I and 60 kHz-II

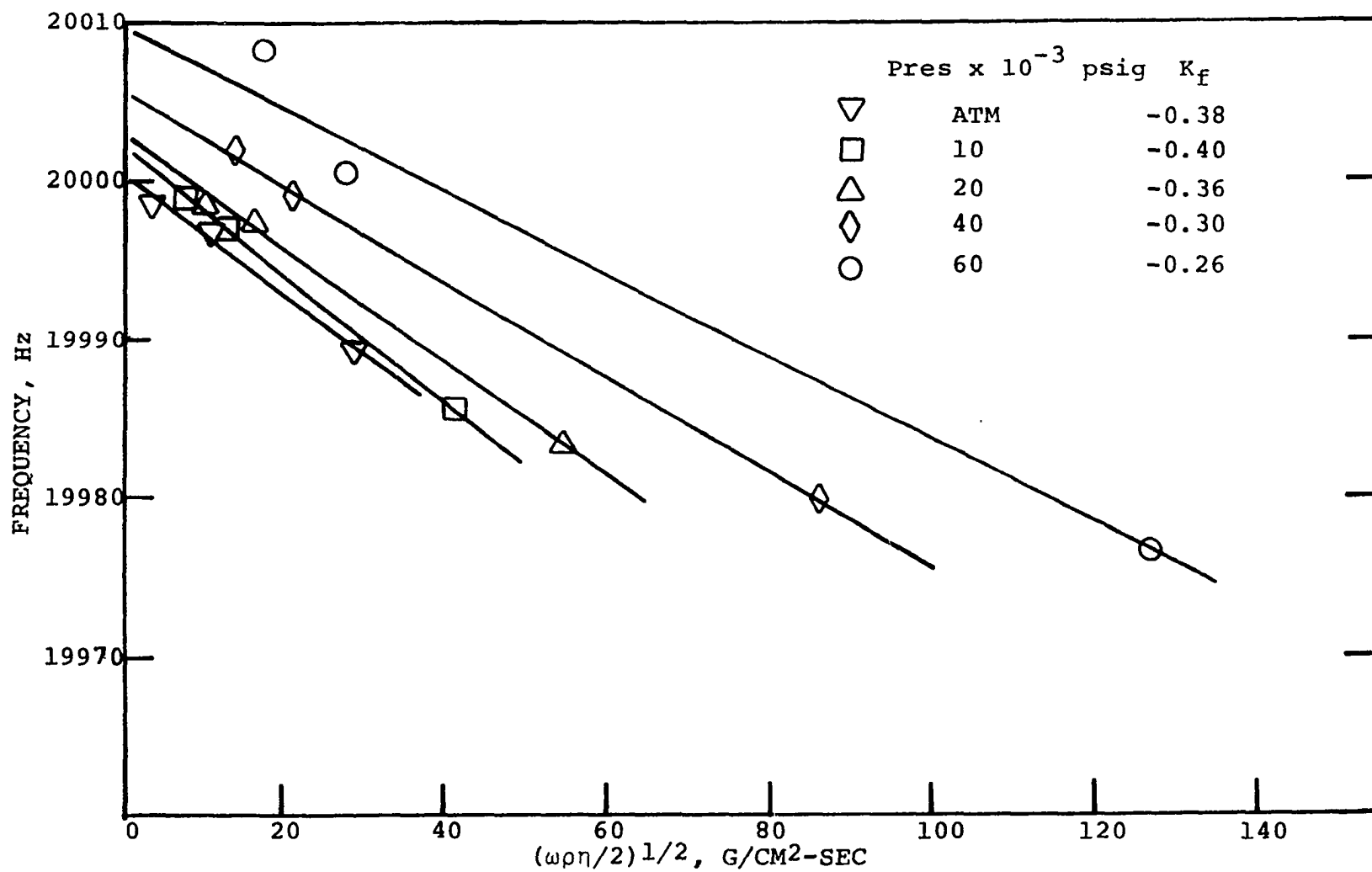


Figure 28. Typical Frequency Calibration Data for 20 kHz-I Crystal Viscometer.

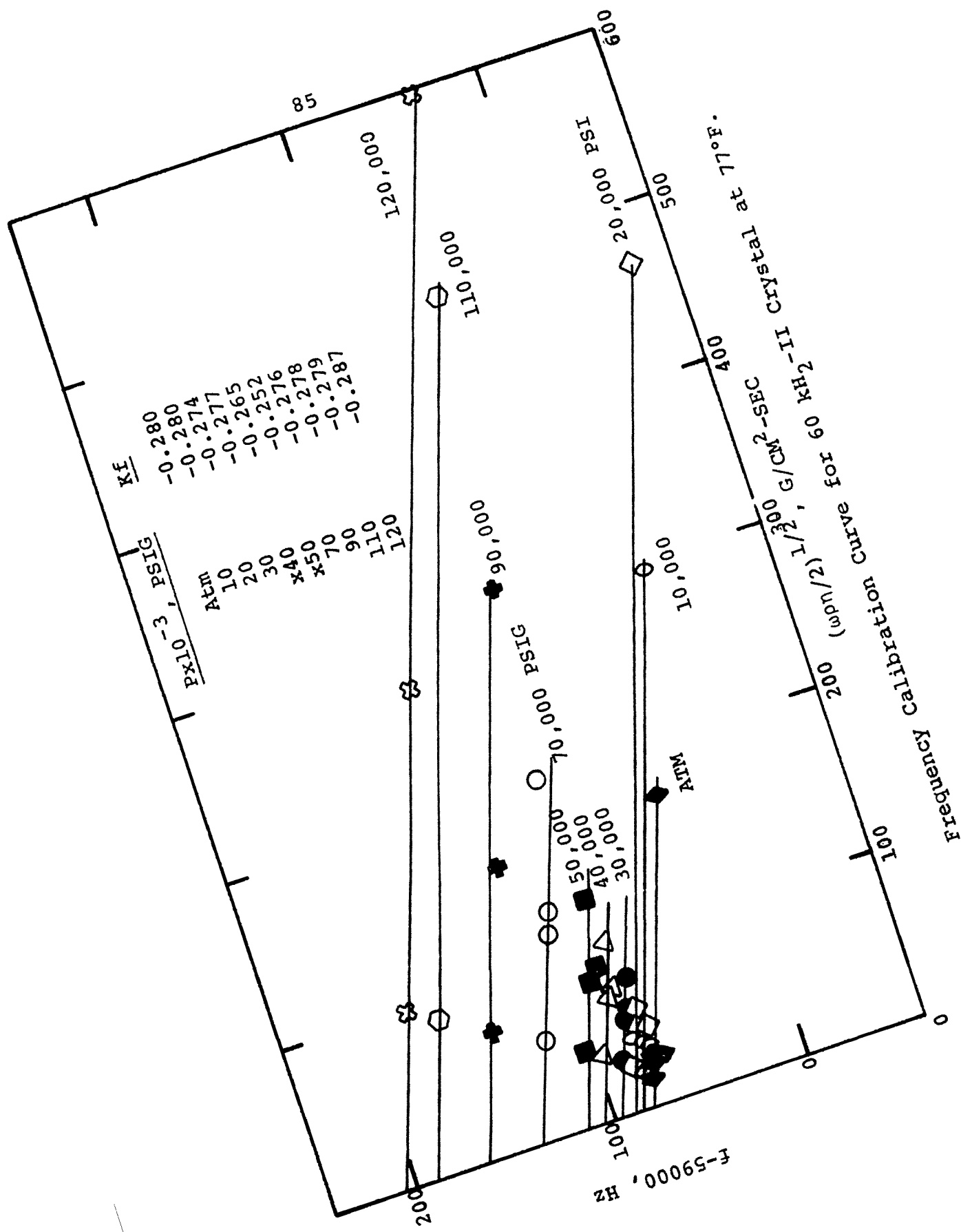


Figure 29.

viscometers, respectively. Because of the random variation in K_f with pressure, as shown on these figures, K_f was assumed to be independent of pressure over this range of pressures. This conclusion is consistent with previous observations (2, 31, 33). In agreement with previous observations (2, 33), K_f was also found to be independent of temperature. The mean and standard deviation for K_f values for all temperatures and pressures are summarized in Table II. Values for the 60 kHz-II viscometer were obtained with combined data at 77° and 100°F.

TABLE II
MEANS AND STANDARD DEVIATIONS OF K_f

Viscometer	No. of Points	Mean	Standard Deviation
20 kHz-I	12	0.314	7.62×10^{-3}
60 kHz-II	18	0.285	3.36×10^{-3}

Values for f_0 were found to vary with both pressure and temperature. Therefore, f_0 had to be determined at every temperature and pressure for which viscosity measurements were to be made. The temperature and pressure dependences of Δf_0 , the difference between f_0 at elevated pressure and f_0 at atmospheric pressure are plotted in Figures 30 and 31 for 20 kHz-I and 60 kHz-II crystal viscometers, respectively. The pressure dependence of Δf_0 for both crystals agreed with reported data (31). The temperature dependence of Δf_0 for the

20 kHz-I crystal (Figure 30) was also determined. However, measurements with the 60 kHz-II crystal were only made at 77° and 100°F, and this temperature range is too small to allow determination of a temperature effect on Δf_0 for the 60 kHz-II crystal.

Results of least squares fit of Δf_0 data of the form $\Delta f_0 = a_0 + a_1P + a_2P^2$ are summarized in Table III. Because a temperature effect on Δf_0 could not be obtained for the 60 kHz-II crystal were combined in the least squares analysis.

Attempts to obtain a master curve which would take care of both temperature and pressure effects on Δf_0 were unsuccessful. However, correlations for $\Delta f_0/f_0$ as functions of pressure at constant temperatures were obtained. The coefficients from least squares fit of $\Delta f_0/f_0$ as functions of pressure are listed in Table IV.

Constants obtained from this investigation and from Reference 31 for the change in $\Delta f_0/f_0$ at 100°F with pressure are compared in Table V. Data from Reference 31 have been converted to psig to provide a common basis for comparison. The least-squares parabolas for $\Delta f_0/f_0$ as a function of pressure are in good agreement. The slight numerical deviation is within the range of experimental error.

Figures 32 and 33 present typical data used to obtain K_r and R_{EO} for the 20 kHz-I and 60 kHz-II viscometers, respectively.

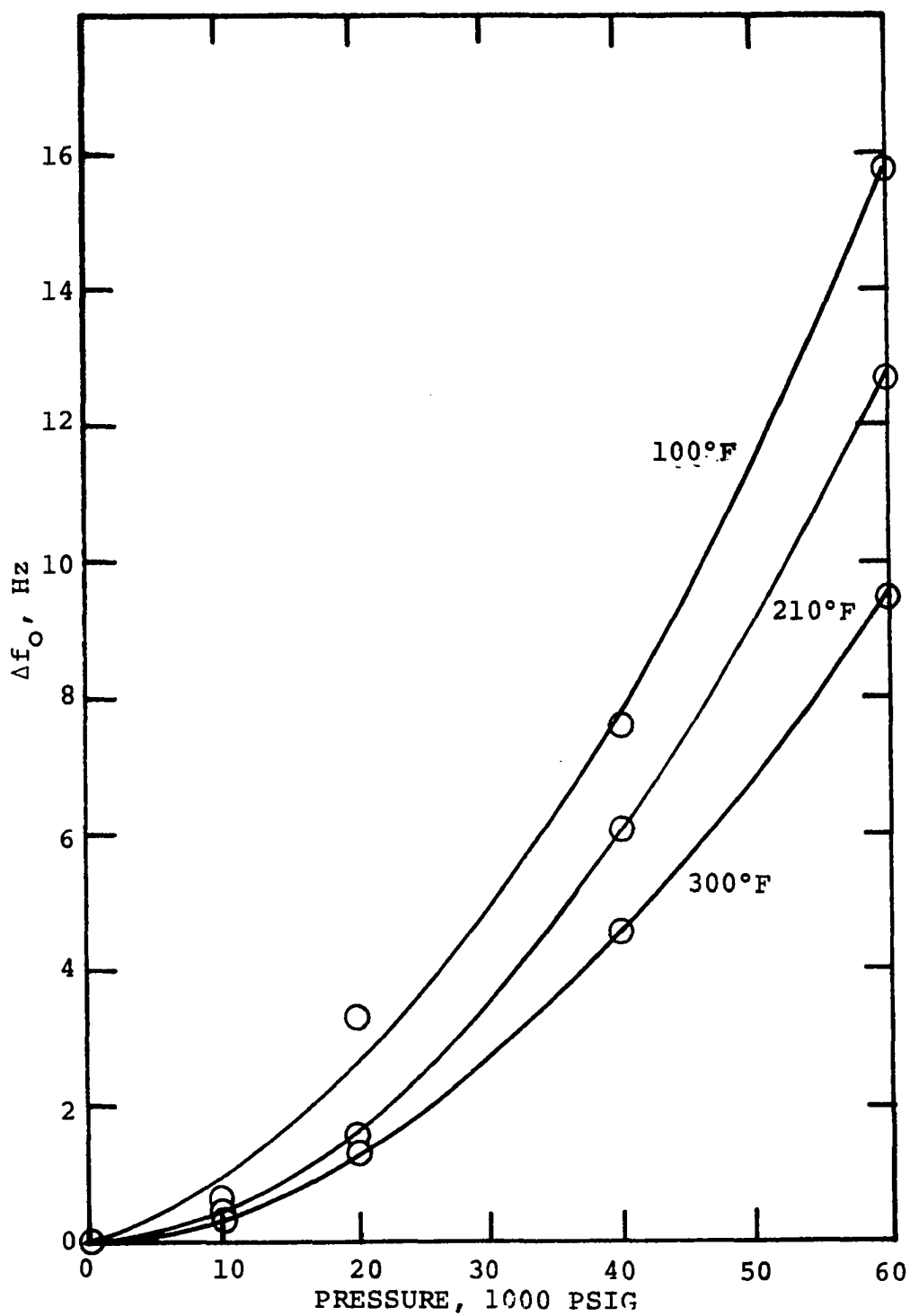


Figure 30. The Effects of Pressure and Temperature on Δf_0 for 20 kHz-I Crystal.

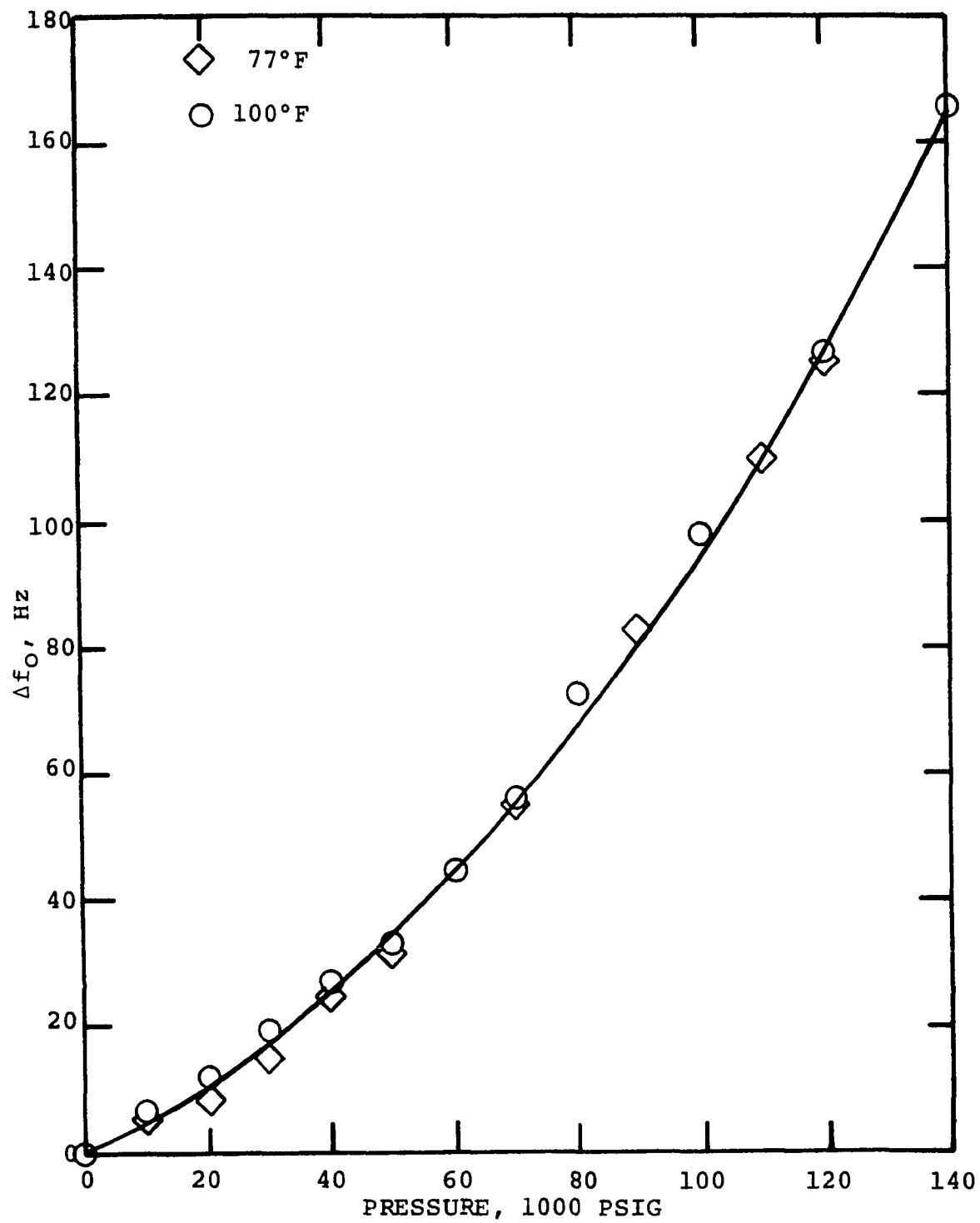


Figure 31. The Effects of Pressure on Δf_0 for 60 kHz-II Crystal.

TABLE III
LEAST SQUARES FIT ON THE CHANGE IN Δf_o WITH PRESSURE*

$$\Delta f_o = a_o + a_1 P + a_2 P^2$$

Viscometer	Temp °F	a_o	$a_1 \times 10^5$	$a_2 \times 10^9$	Mean of Δf_o	Standard Error of Estimation	Coefficient of Correlation
20 kHz-I	100	-0.169	3.54	3.86	5.93	0.368	0.9976
	210	-0.0159	2.55	3.12	4.20	0.133	0.9997
	300	-0.0350	2.40	2.25	3.16	0.0685	0.9999
60 kHz-II**		-0.111	4.32	5.31	54.90	2.04	0.9991

*P has units of pounds per square inch gauge pressure.

**60 kHz-I crystal parameters were calculated from the correlation in Reference 31. No correlation on 60 kHz-I viscometer as explained in the text, page 86. Correlation was made with data at 77°F and 100°F combined.

TABLE IV
LEAST SQUARES FIT ON THE CHANGE IN $\Delta f_o/f_o$ WITH PRESSURE*

$$\Delta f_o/f_o = a_o + a_1 P + a_2 P^2$$

Temp °F	$a_o \times 10^6$	$a_1 \times 10^9$	$a_2 \times 10^{13}$	Mean of $\Delta f_o/f_o$ $\times 10^4$	Standard Error of Estimation	Coefficient of Correlation
100**	-7.99	7.57	0.876	7.71	3.39	0.9988
210	-0.794	1.27	1.56	2.10	0.667	0.9998
300	-2.08	1.20	1.13	1.58	0.369	0.9998

*Pressure is in pounds per square inch gauge.

**Statistics were determined from data taken at 100°F with 20 kHz-I and 77°F and 100°F with 60 kHz-II crystals.

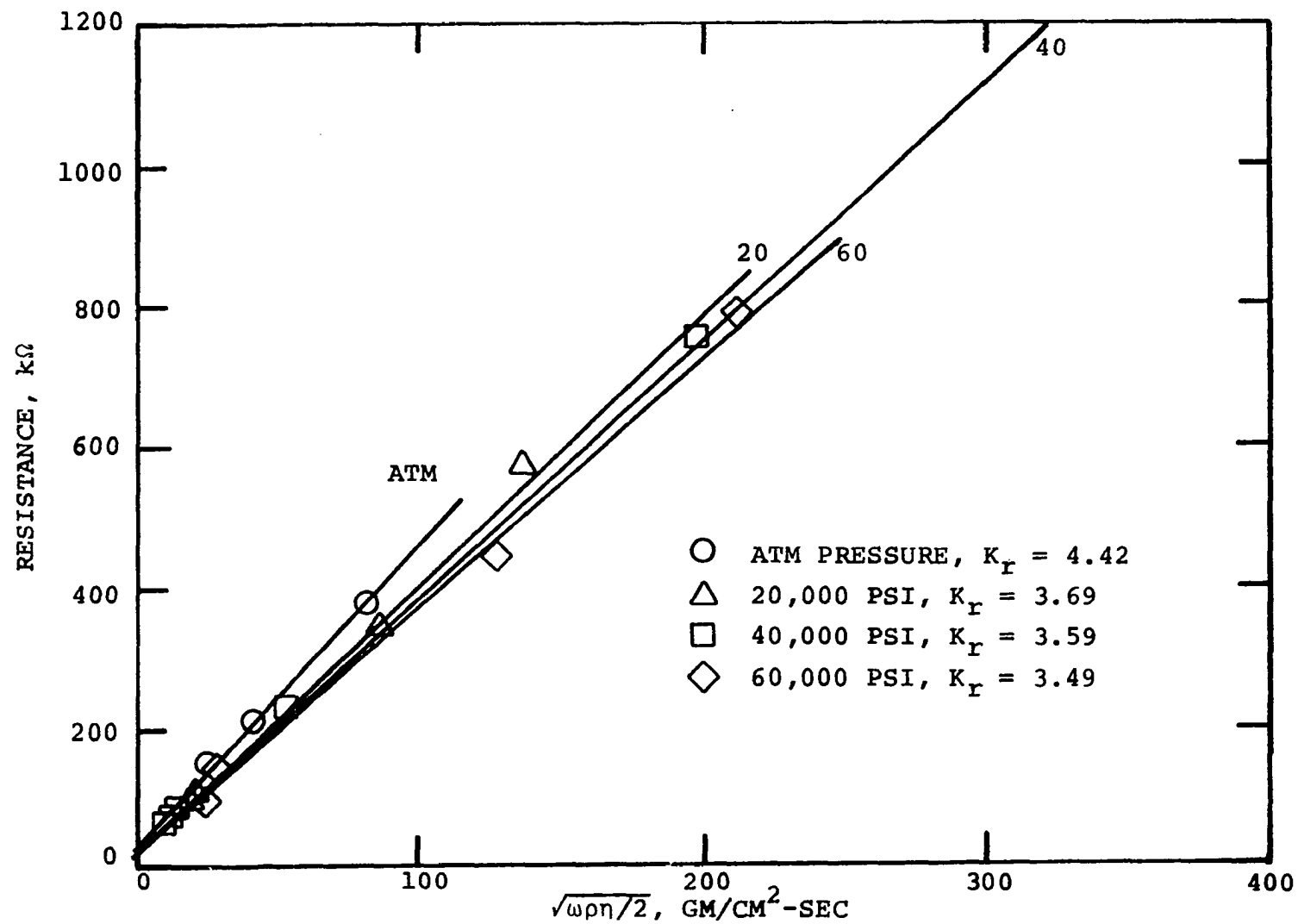


Figure 32. Typical Resistance Calibration Data. (Data from Run 20 kHz-I).

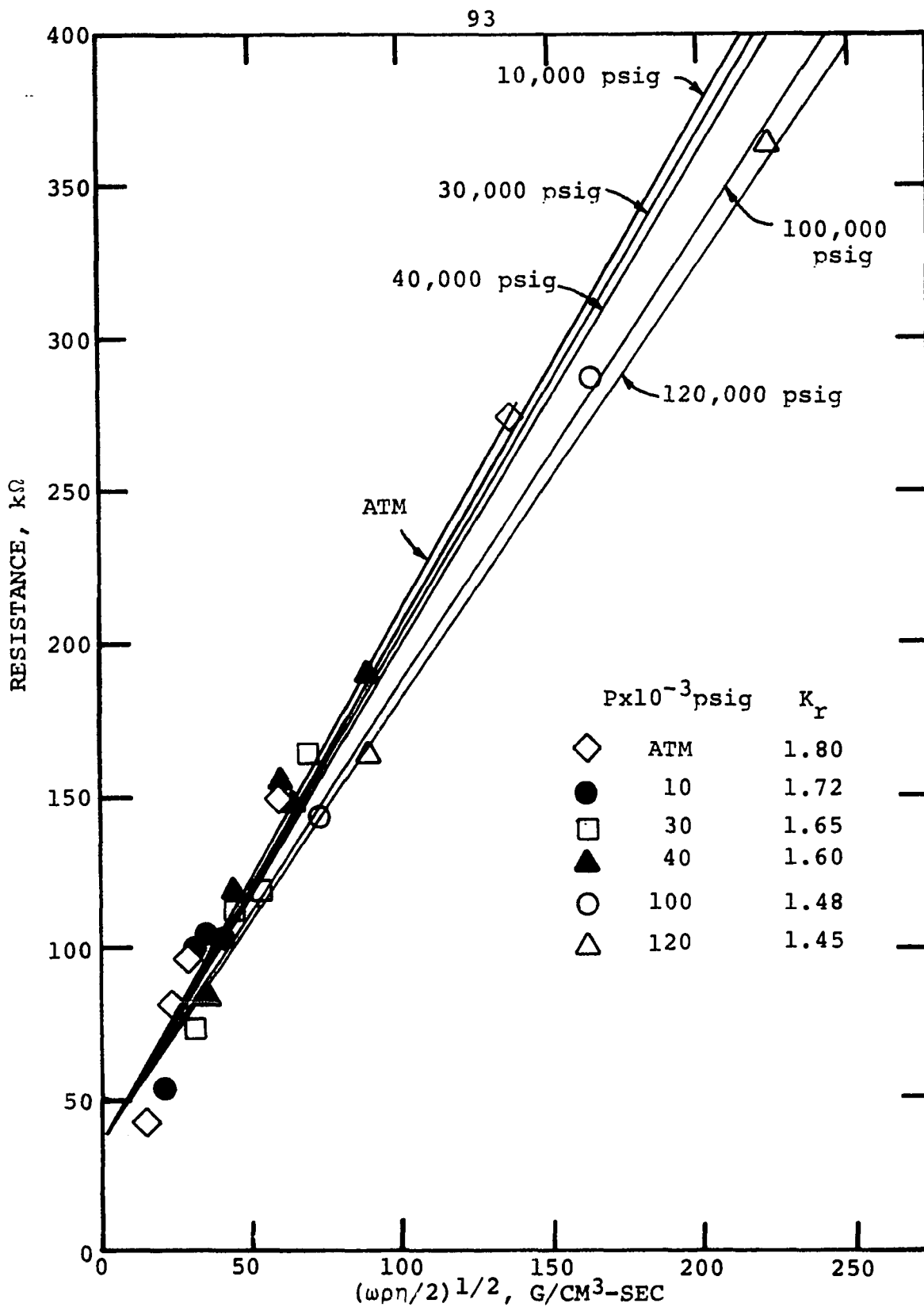


Figure 33. Typical Resistance Calibration Data
(Data from 60 kHz-II at 100°F).

TABLE V

COMPARISON OF PARABOLIC CONSTANTS OF
 $\Delta f_O/f_O = a_O/10^{-6} + a_1 \times 10^{-9}P + a_2 \times 10^{-14}P^2$

Constants	This Investigation	Reference 35	Abs. %
a_O	-7.99	-0.690	91.5
a_1	7.57	7.63	0.815
a_2	8.76	9.47	7.74

In contrast to the results reported by other investigators (2, 32), K_r was found to depend on pressure as indicated in Figure 34. A close inspection of the data in Reference 2 indicated a small change in K_r with pressure. However, because the change in K_r with pressure is very small and, because that investigation (Reference 2) only covered a relatively small pressure range (atmospheric pressure to 15,000 psig), the variation in K_r with pressure would not have been obvious. Because the change in K_r with pressure is small, this change would have a negligible effect on their results. Uncertainties in data might have masked any changes in K_r with pressure in Reference 32. The values of K_r were found independent of temperature, in accordance with previous investigations (2, 33).

A random variation in the values of R_{EO} with temperature and pressure led to the conclusion that R_{EO} is independent of pressure and temperature within the precision of the measurements. This observation agrees with previous results (2, 32,

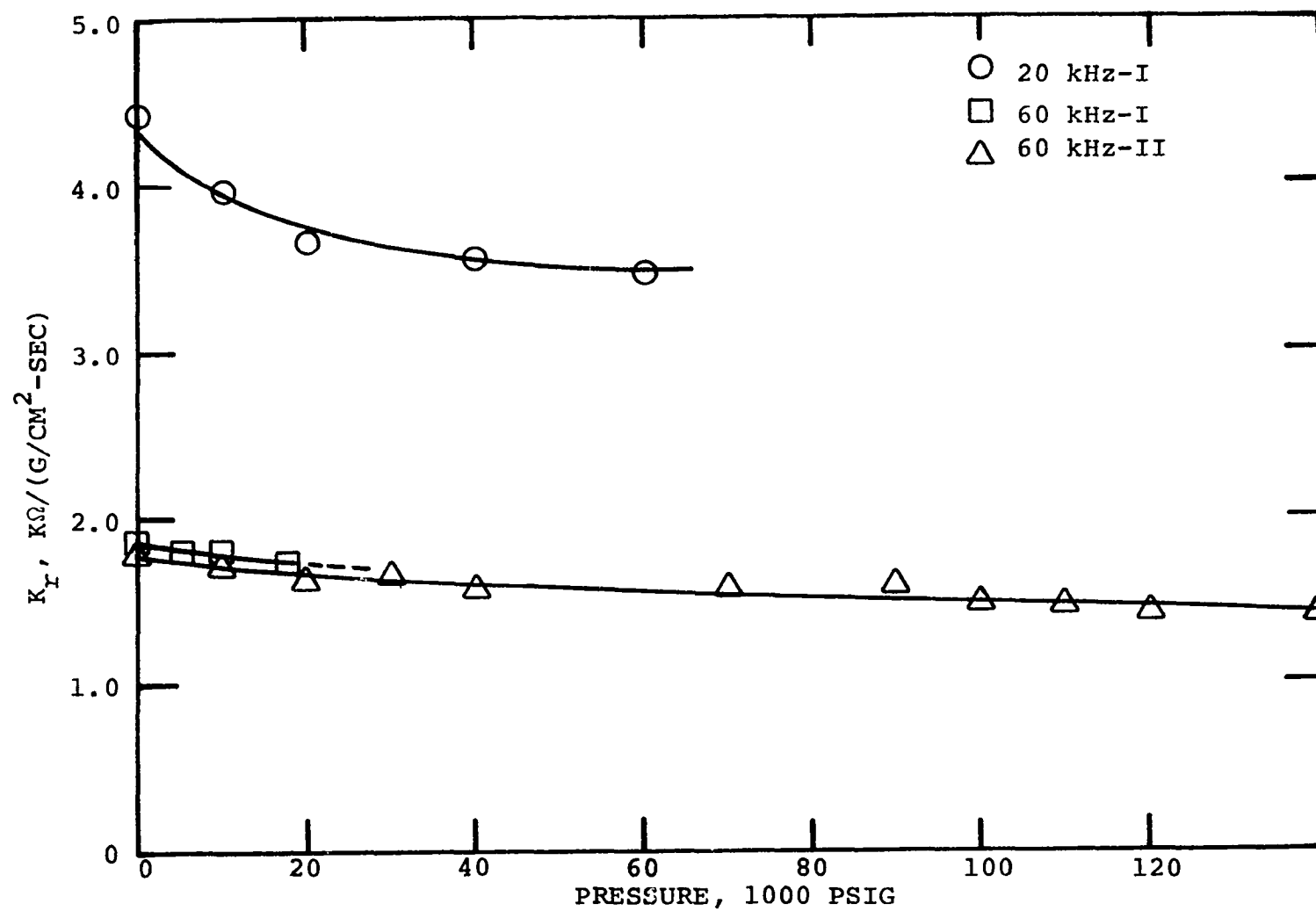


Figure 34. The Effects of Pressure on the Calibration Parameter, K_r .

33). Table VI lists the means and standard deviations of R_{EO} for all temperatures and pressures. Statistics were not obtained for the 60 kHz-I viscometer as explained on page 82.

TABLE VI
MEANS AND STANDARD DEVIATIONS OF R_{EO}

Viscometer	No. of Points	Mean	Standard Deviation
20 kHz-I	12	41.2	8.16
60 kHz-II	18	44.6	2.04

The principal results of the calibration runs are summarized in Table VII.

Viscosity Measurement

Viscosities of test liquids were measured by the same technique as the calibration of viscometer. Components of complex viscosity, or complex shear modulus, were calculated according to

$$\eta'' = G'/\omega = (R_M^2 - X_M^2)/\omega\rho \quad (39)$$

and

$$\eta' = G''/\omega = 2 R_M X_M/\omega\rho \quad (40)$$

The mechanical reactance, X_M , and resistance, R_M , are related to the resonant frequency and the resistance of the oscillating crystal by

TABLE VII
CALIBRATION PARAMETERS FOR EACH DATA RUN

Viscometer*	Parameter	Value	Comments
20 kHz-I	K_f	0.314	Independent of temperature and pressure
	K_r		Independent of temperature, dependent on pressure as shown in Figure 34
	f_o		Empirically determined for each temperature and pressure of measurement**
	R_{EO}	41.1 k Ω	Independent of temperature and pressure
60 kHz-I	K_f	0.32	Independent of temperature and pressure
	K_r		Independent of temperature, dependent on pressure as shown in Figure 34
	f_o		Determined from correlation in Reference 31
	R_{EO}	0.0 k Ω	Independent of temperature and pressure
60 kHz-II***	K_f	0.285	Independent of temperature and pressure
	K_r		Independent of temperature, dependent on pressure as shown in Figure 34
	f_o		Empirically determined for each temperature and pressure of measurement**
	R_{EO}	44.6 k Ω	Independent of temperature and pressure

*The -I and -II designate different mounting of the crystal.

**Values of f_o are tabulated in Appendix C.

***Values on 60 kHz-II crystal were determined by combining measurements obtained at 77°F and 100°F.

$$R_M = (R_E - R_{EO})/K_r \quad (41)$$

and

$$X_M = (f_O - f)/K_f \quad (42)$$

The parameters R_{EO} , K_r , f_O and K_f are calibration constants.

A characteristic of the oscillating quartz crystal viscometer is that the difference $(R_E - R_{EO})$ in Equation 41 is much larger than the difference $(f_O - f)$ in Equation 42. Thus, as viscosity decreases, f approaches f_O much faster than R_E approaches R_{EO} . A loss in significant figures for the difference $(f_O - f)$ results for measurements on low viscosity liquids (fluids with viscosities less than one centipoise). For this reason, errors in measurements of frequency are more serious than errors in measurements of resistance for computing viscosities according to Equations 39 through 42. Because of this uncertainty, whenever the calculated values of R_M differed significantly from X_M for measurements at a particular temperature and pressure, whereas measurements on this liquid consistently result in R_M being equal to X_M at other pressures and temperatures (for which a difference in R_M and X_M would have been more plausible) the calculation of viscosity η' was based entirely on the more reliable resistance measurements. In this case Equation 64 is more favorable than Equation 40.

$$\eta' = 2 R_M^2 / \omega \rho \quad (64)$$

Viscosities of the fluids showing no elastic effects ($\eta'' = 0$) were calculated by the above equation. Tabulated viscosity data on the test fluids are summarized in Appendix E.

Results for the viscosity measurements of the lubricants as functions of pressure at different temperatures are given in Figures 35 through 38. It will be noted in Figure 38 that viscosity data for DuPont Krytox 143-AB are given only at 100°F. Although data were taken at higher temperatures, they were not considered sufficiently reliable to report. Upon completion of the higher temperature runs, the pressure vessel was opened. Examination of the crystal mounting revealed that the measurements were not true. One of the four electric leads to the crystal was found to be broken.

The zero-shear viscosities of the polymer solution at 77°, 100° and 210°F and those of the lubricants at 74.3°, 112°, 130° and 190°F (from Reference 33) were determined by means of a Canon-Fenske capillary viscometer. These capillary viscosities are plotted in Figures 39 and 40 for the polymer solution and the four lubricants, respectively. The same values of zero-shear viscosities are also shown on the zero pressure ordinate in Figures 35 through 38 and Figure 42 in the next section. The discrepancies between the two methods of measurement are within the estimated accuracy of the oscillating quartz crystal viscometers.

The high viscosity of some tested lubricants at elevated pressures caused very high measured values of electrical

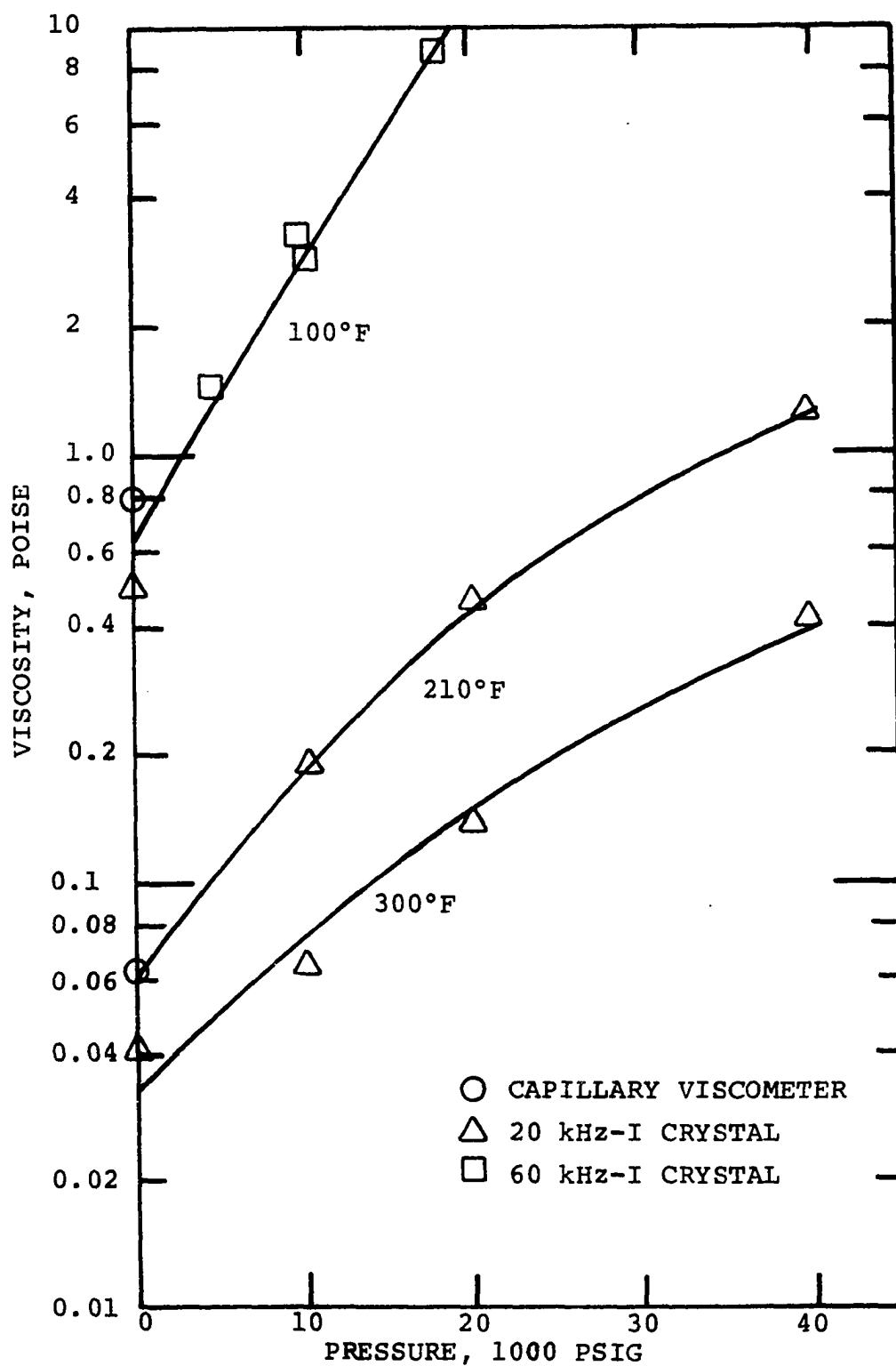


Figure 35. The Effects of Pressure and Temperature on the Viscosity of Humble FN-3158.

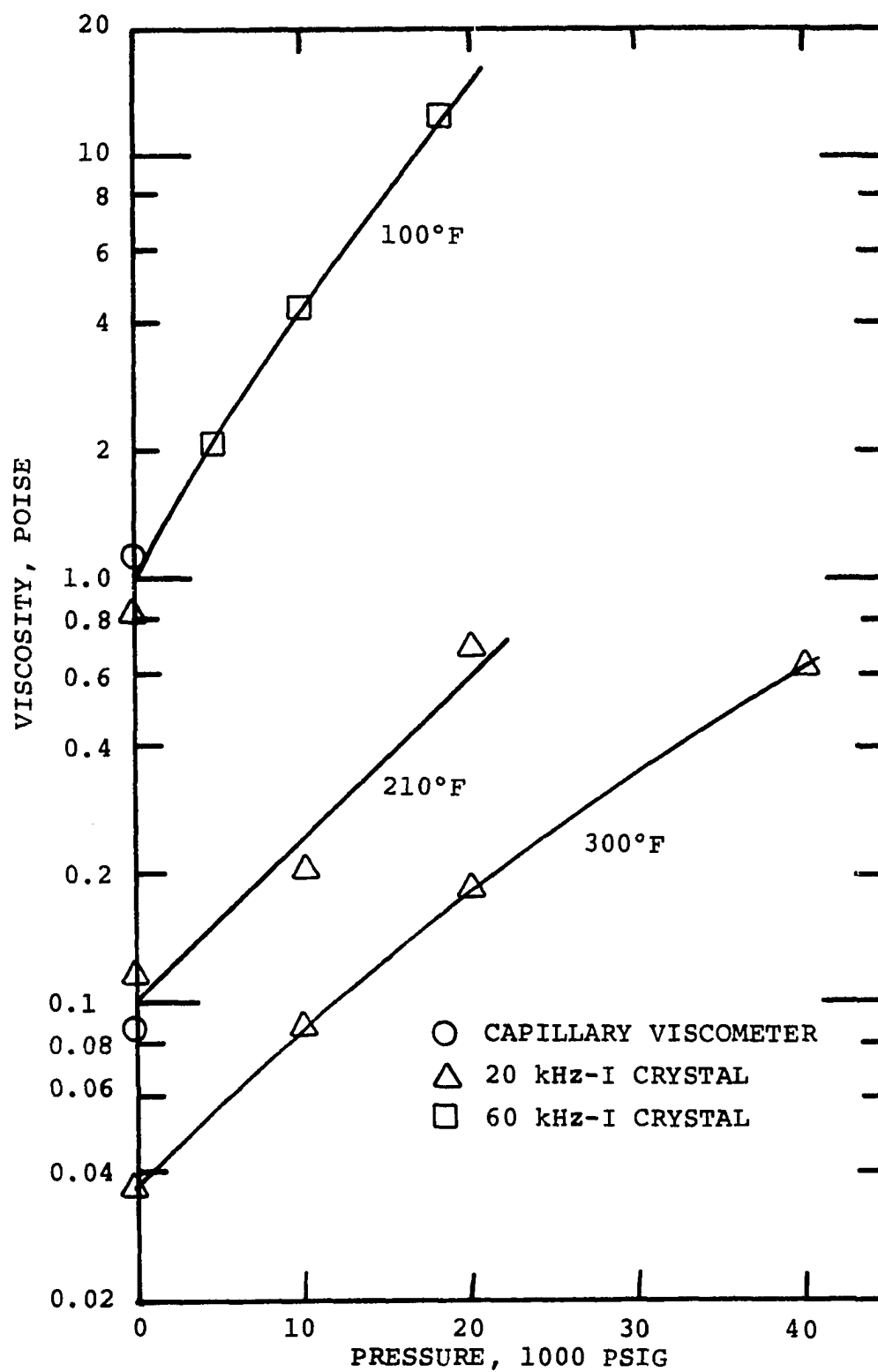


Figure 36. The Effects of Pressure and Temperature on the Viscosity of the Mixture of Humble FN-3158 + 10 vol.% Kendall 0839.

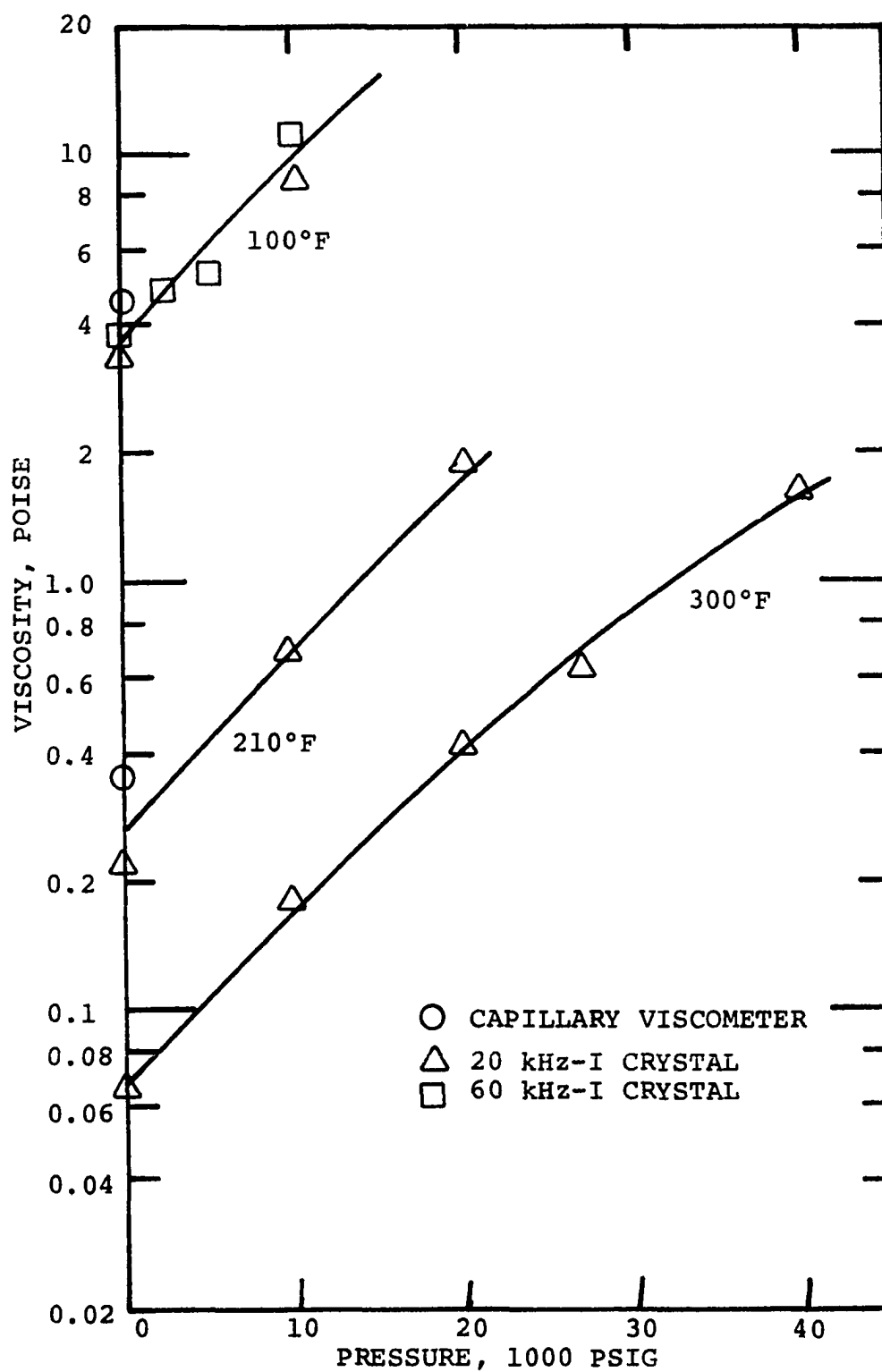


Figure 37. The Effects of Pressure and Temperature on the Viscosity of Mobil XRM-109.

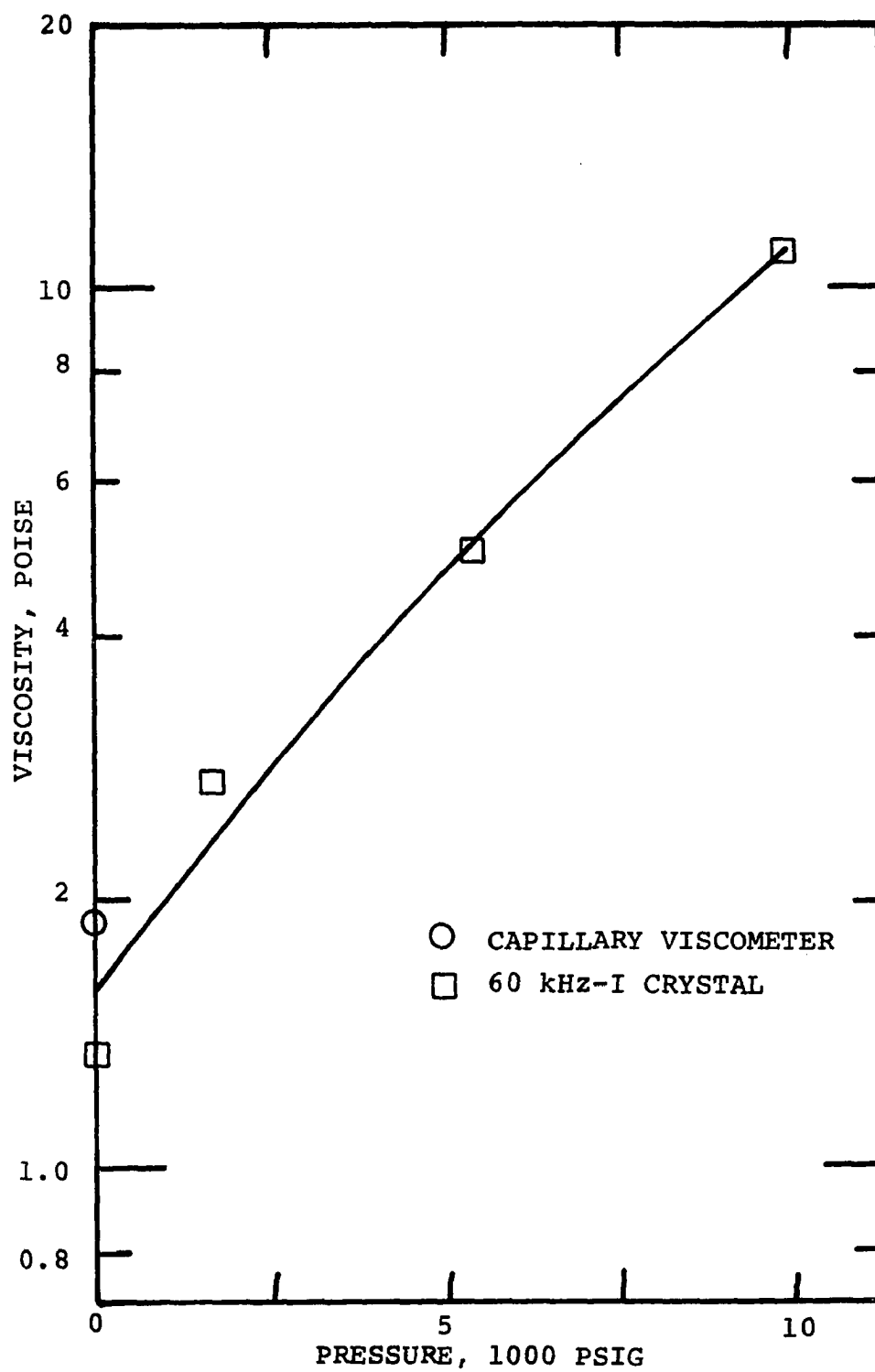


Figure 38. The Effects of Pressure on the Viscosity of DuPont Krytox 143-AB at 100°F.

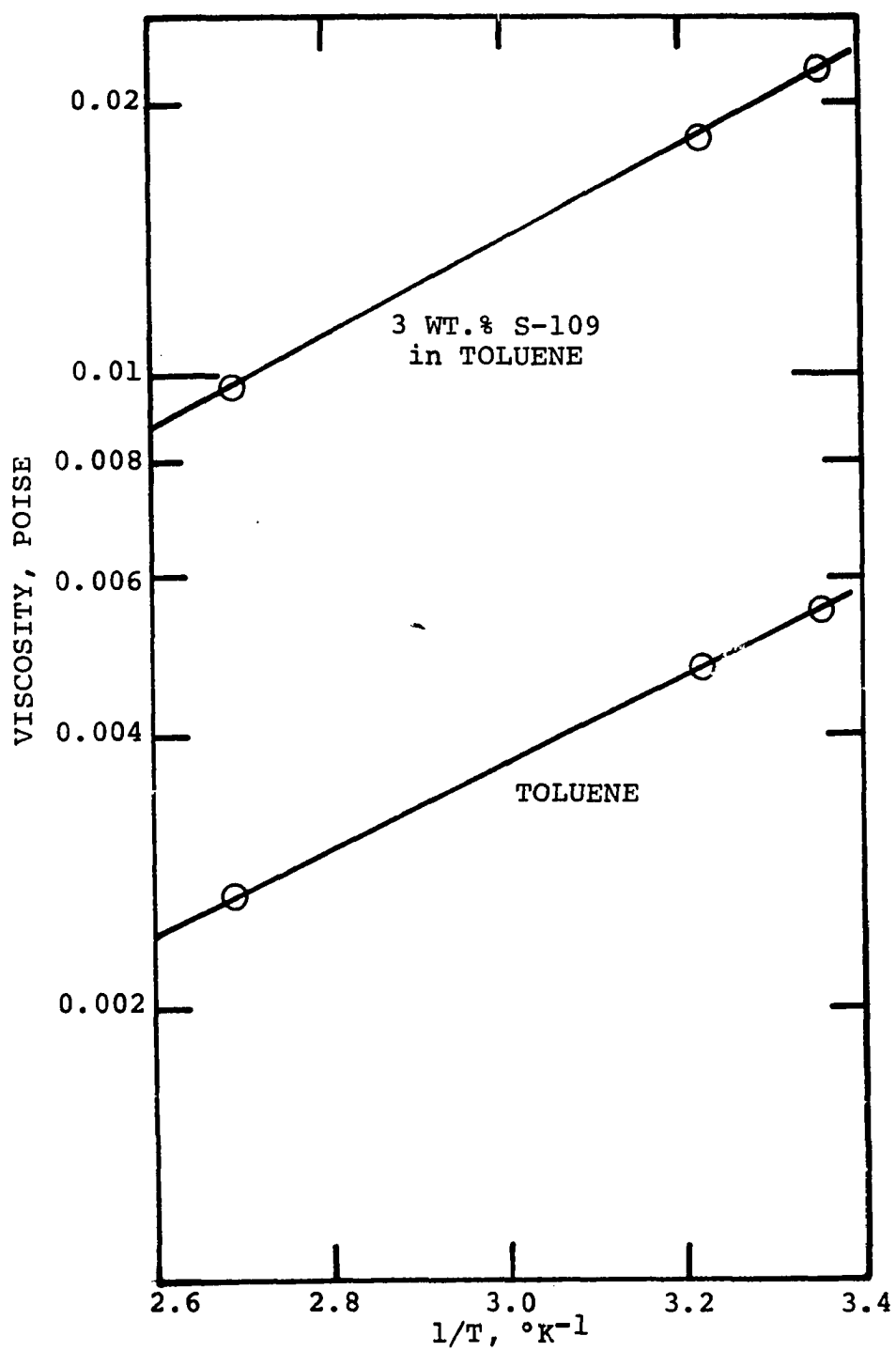


Figure 39. Viscosity of Solution of 3 wt.% S-109 Polystyrene in Toluene as Determined from Capillary Viscometer at Atmospheric Pressure.

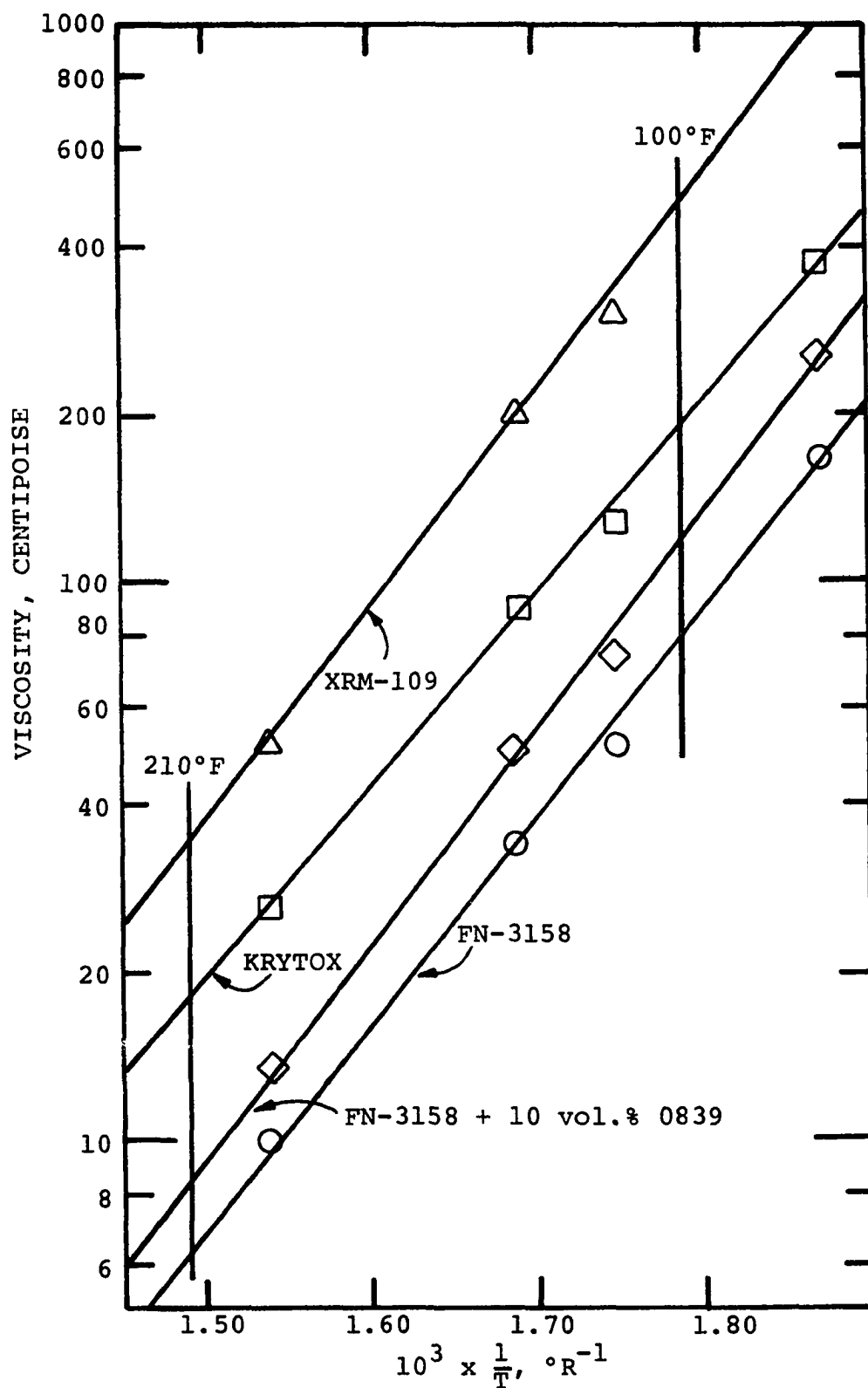


Figure 40. Viscosity of Lubricants as Determined from Capillary Viscometer at Atmospheric Pressure (Data from Reference 33).

resistances. Often, measured resistances were greater than two megohms. At these high resistances, locating the minimum resistance, R_E , was very difficult because of flattening of the resistance versus frequency curve. The sharpness of R versus f curve is determined by the quality factor $Q = \omega L_C / R_E$. The larger R_E results in a lower Q value. Figure 41 is an illustration of the effects of liquid viscosity on measured values of resistances and frequencies. Data were taken with 20 kHz-I crystal at 100°F on di-(2-ethylhexyl) sebacate at atmospheric pressure ($\eta = 0.107$ poises), and Mobil XRM-109 at atmospheric pressure ($\eta = 3.39$ poises) and at 10,200 psig ($\eta = 8.80$ poises). As the liquid viscosity went higher, the sharpness of the resistance-frequency curve became worse as shown in Figure 41. And finally, the measured data showed nothing but a linear relation between the resistances and frequencies. It was thought that the flatness of the resistance-frequency curve was caused by the liquids becoming electrically conductive. This idea was found to be false by plotting the data points. If the liquid was becoming conductive, the measured resistances should have much lower values.

The uncertainty of finding the minimum value of resistances is summarized in Tables VIII and IX for the lubricants and polymer solution, respectively. The uncertainties were determined to be ± 7.34 percent on lubricants and ± 2.00 percent on the solution of polystyrene in toluene. It was assumed that errors in finding resonant frequency values were

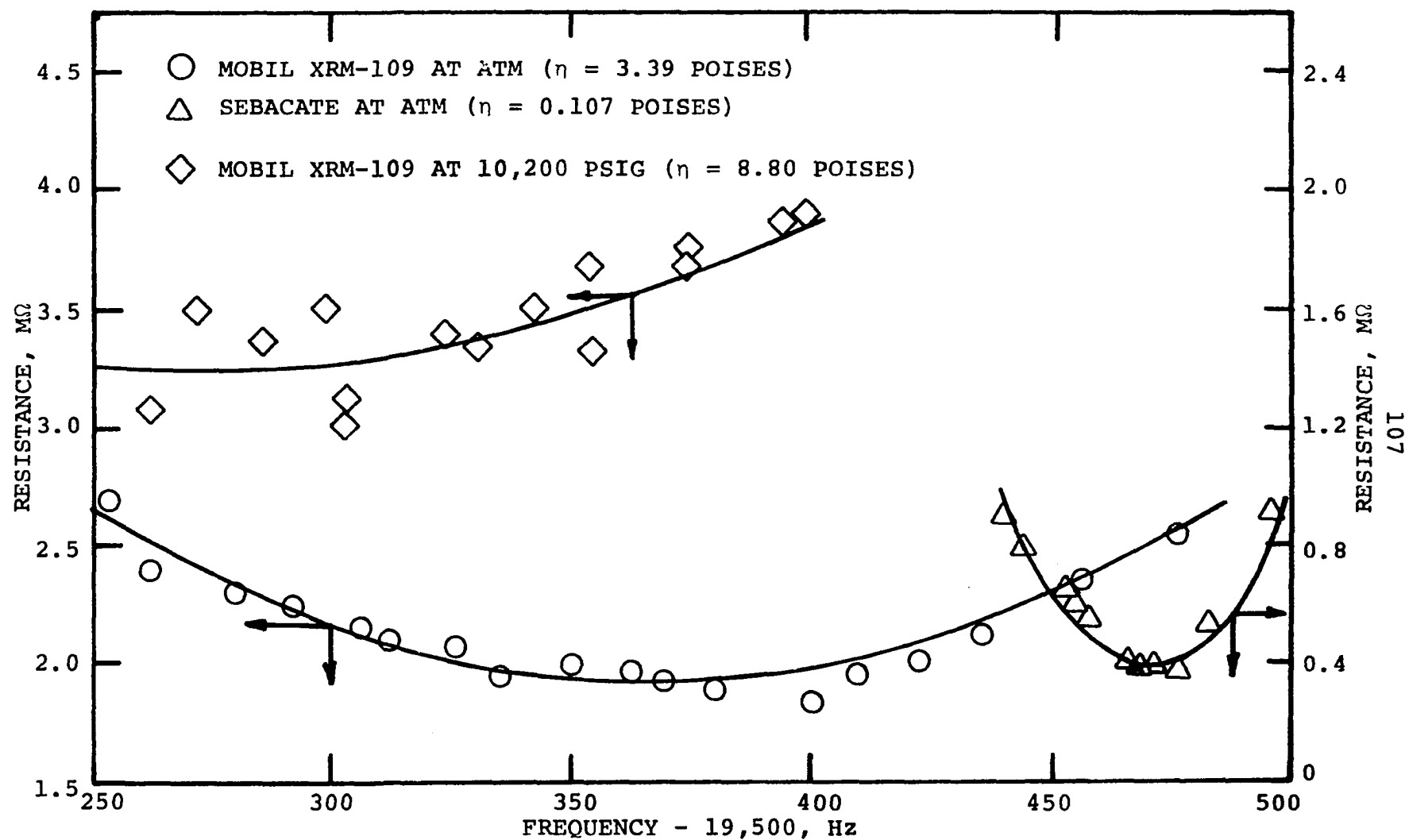


Figure 41. High Electrical Resistance from Excessive Viscosity of Test Fluid Measured with 20 kHz-I Crystal at 100°F.

TABLE VIII

ESTIMATION OF ERRORS ON R_E (LUBRICANTS)

Fluid	Temp °F	Px1000 (psig)	R_E , k Ω	S.E.E.	$\frac{S.E.E.}{R_E} \times 100$
FN-3158	100	0.0*	649	20	3.01
		0.0	790	96	12.2
		4.92*	967	62	6.41
		9.94*	1376	141	10.2
		10.0	1336	305	22.8
		10.1*	1333	50	3.75
		18.1*	2298	613	26.7
	210	0.0	290	32	11.0
		10.2	443	35	7.90
		20.1	567	19	3.35
		39.9	968	53	5.48
	300	0.0	186	14	7.53
		10.2	758	13	1.72
		20.1	354	21	5.93
		40.5	548	29	5.29
FN-3158 + 10vol% 0839	100	0.0	1107	49	4.43
		0.0*	741	84	11.3
		5.3*	1161	60	5.17
		10.2*	1641	69	4.20
		18.4*	2827	177	6.26
	210	0.0	383	52	13.6
		10.1	486	36	7.41
		20.0	714	43	6.02
	300	0.0	198	19	9.60
		10.1	297	16	5.39
		20.0	386	34	8.82
		40.5	638	13	2.04
XRM-109	100	0.0	1894	109	5.76
		0.0*	1489	118	7.92
		2.24*	1718	202	11.8
		5.00*	1736	63	3.63
		9.64*	2622	308	11.7
		10.2	3234	200	6.18

*Data run from the 60 kHz-I viscometer.

TABLE VIII--Continued

Fluid	Temp °F	Px1000 (psig)	R _E , kΩ	S.E.E.	$\frac{S.E.E.}{R_E} \times 100$
XRM-109	210	0.0	505	17	3.37
		9.86	766	34	4.44
		20.0	1058	95	8.98
	300	0.0	281	14	4.98
		9.96	439	23	5.24
		19.9	509	16	3.14
		26.9	564	51	9.04
		40.1	941	55	5.84
	100	0.0*	1291	101	7.82
		2.42*	1721	26	1.51
		5.38*	2324	99	4.26
		9.80*	3257	241	7.40

Number of Observations = 45

Sum of Percent Deviation = 330.5

Mean Deviation = 7.34

*Data run from the 60 kHz-I viscometer.

TABLE IX

ESTIMATION OF ERRORS ON R_E (POLYMER SOLUTION)

Fluid*	Temp °F	Px1000 (psig)	R_E , k Ω	S.E.E.	$\frac{S.E.E.}{R_E} \times 100$
3 wt.% S-109 Polystyrene in toluene	77-b	0.0	166	3.00	1.80
		9.96	177	2.79	1.58
		19.9	192	1.53	0.799
		29.9	213	2.28	1.07
		49.9	269	4.15	1.54
		69.9	346	3.70	1.07
		90.0	444	8.68	1.96
		110	562	12.6	2.24
		120	628	13.4	2.13
	100-a	0.0	168	1.69	1.01
		9.96	178	6.27	3.52
		20.0	192	7.85	4.08
		30.0	210	8.20	3.90
		40.0	231	9.24	3.60
		50.0	255	2.97	1.17
		59.9	284	19.9	7.02
		69.9	315	4.54	1.44
		79.9	350	3.36	0.961
		100	431	6.98	1.62
		120	525	9.90	1.89
	100-b	0.0	152	3.26	2.15
		9.96	164	1.09	0.667
		20.0	179	1.46	0.815
		29.9	197	3.08	1.56
		49.9	242	4.18	1.73
		69.9	299	3.47	1.16
		90.0	368	4.45	1.21
		110	449	7.39	1.65
		120	494	13.0	2.64

Number of Observation = 29

Sum of Percent Deviation = 58.0

Mean Deviation = 2.00

*Data run from the 6- kHz-II viscometer.

of the same order as those for R_E . Thus, the total errors: explained errors plus inherent errors of the equipment set-up, are believed to be ± 20 percent for the measurements on lubricants and ± 9 percent for the measurements on the polymer solution.

Viscoelastic Behavior

Viscoelastic behavior was observed for the solution of three weight percent S-109 polystyrene in toluene at all pressures and at 77°F and 100°F with the 60 kHz-II viscometer. The measured dynamic viscosity and storage modulus are shown as functions of pressure at 77°F and 100°F in Figures 42 and 43. Data from the 77-a run are not reported because the sample was found to be contaminated by the pressure transferring fluid. Data were also taken at 210°F, but viscosities could not be determined for these data because of the inability of obtaining calibration parameters at 210°F.

In agreement with other investigations (2, 27), the solution viscosity increased less rapidly with pressure than the viscosity of the solvent did, as shown in Figure 42. The slope of the pressure-viscosity curve of the solution and the solvent were approaching each other as pressure increased.

In contrast to the reported observations, the elastic component of the solution was more influenced by pressure at low to moderate pressures than was the viscosity of the solution. The slope of the pressure-storage modulus curve

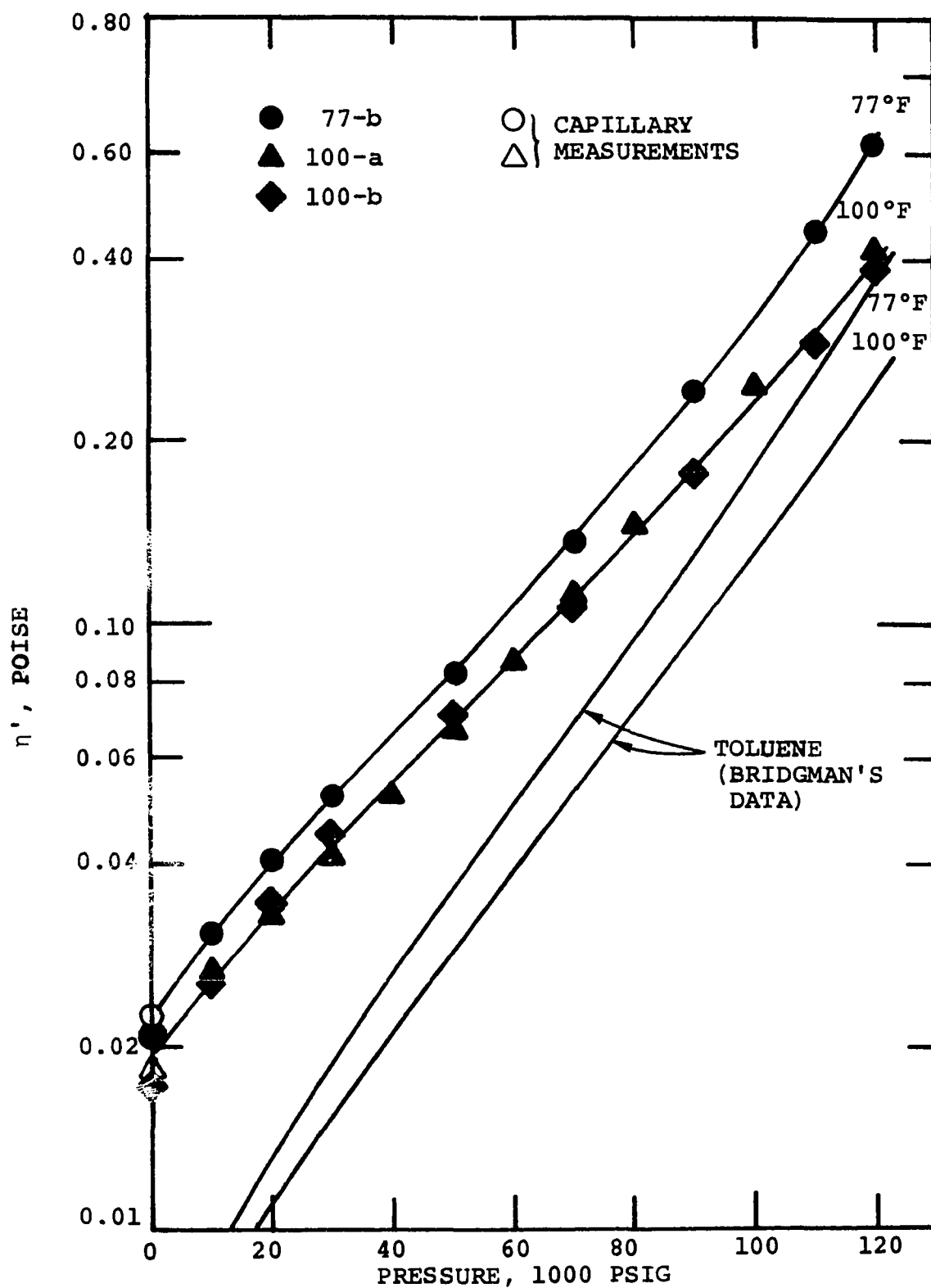


Figure 42. The Effects of Pressure and Temperature on the Viscosity of Solution of 3 wt percent S-109 Polystyrene in Toluene.

approached zero at much higher pressure as shown in Figure 43. The results were consistent on this point for all three data runs on the polymer solution.

Results from this experiment indicated that the elastic contribution of the polymer to the solution, as described by the storage modulus, was important relative to the dynamic viscosity of the solution. The importance of solution viscosity attributed to the dissolved polymer decreased as the pressure increased.

In order to study the effect of frequency on the behavior of liquids, data obtained at a single crystal frequency and different temperatures and pressures need to be transferred into a single curve at one pressure and temperature and at a series of equivalent frequencies. A set of appropriate Reduced Variables in the form as Equations 52 through 55 was used to transfer data taken at different pressures and temperatures to 77°F and atmospheric pressure.

$$a_{TP} = (T_O/T) (\rho_O/\rho) (\eta_T/\eta_O)_P (\eta_P/\eta_O)_T \quad (52)$$

$$\omega_r = a_{TP} (2\pi f) \quad (53)$$

$$G'_r = G' (T_O/T) (\rho_O/\rho) \quad (54)$$

$$\eta'_r = \eta' (\eta_O/\eta_T)_P (\eta_O/\eta_P)_T \quad (55)$$

In using Equations 52 through 55, densities for the polymer solution as functions of pressure at different constant temperature levels were determined in this experiment. The change in η_O/η with pressure of the polymer solution was assumed to

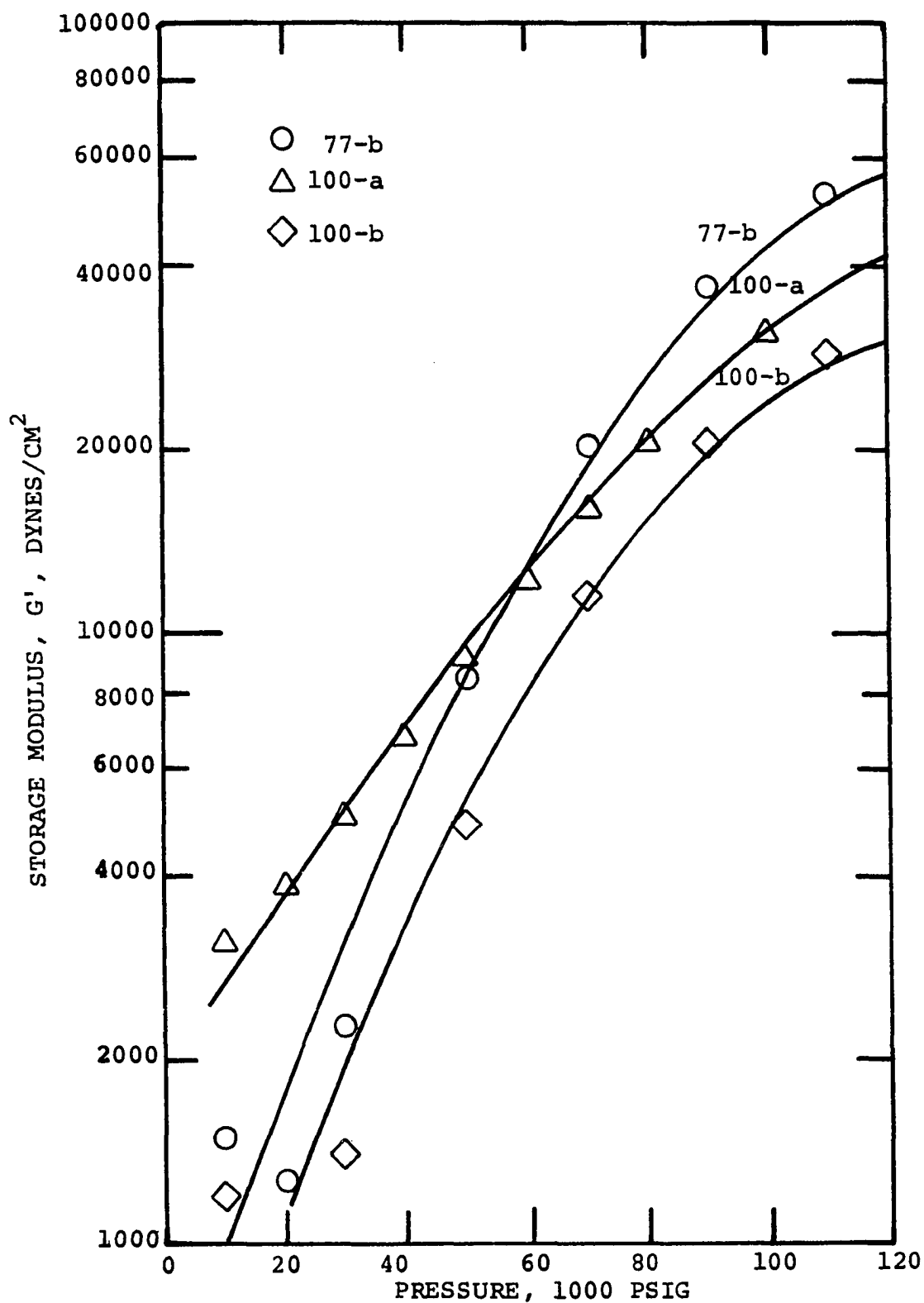


Figure 43. The Effects of Pressure and Temperature on the Storage Modulus for the Solution of 3 wt percent S-109 Polystyrene in Toluene.

be the same as that of the solvent in accordance with References 2 and 27.

Using calculated values on the shift factor, a_{TP} , the measured data were reduced to atmospheric pressure and 77°F, and the single oscillating frequency of 60 kHz was transferred to a frequency range of 3×10^5 to 2×10^7 radians per second. The contribution of the polymer to the dynamic viscosity of the solution was calculated by subtracting the static viscosity of the solvent from the reduced dynamic viscosity of the solution. The reduced viscosities and the reduced shear storage modulus are shown in Figures 44 and 45, respectively. The reduced data are given in Appendix F. Although there is some scatter of the points, the curves show a smooth transition. The plots of reduced frequency-dynamic viscosity and reduced frequency-shear storage modulus demonstrated the capability of the reduced variables for converting the effect of pressure on liquid behavior to an equivalent effect of frequency of oscillation on liquid behavior. In other words, the effect of increasing pressure is similar to that of increasing the oscillating frequency.

In order to compare the viscoelastic properties of the polymer solution obtained in this experiment with reported data and the predictions from molecular theories of Rouse and Zimm, measured data were converted to dimensionless form. The dimensionless viscosities $(\eta_r' - \eta_s)/(\eta - \eta_s)$, dimensionless shear loss modulus, $(G_r'' - \omega_r \eta_s)M/cRT$, and dimensionless shear

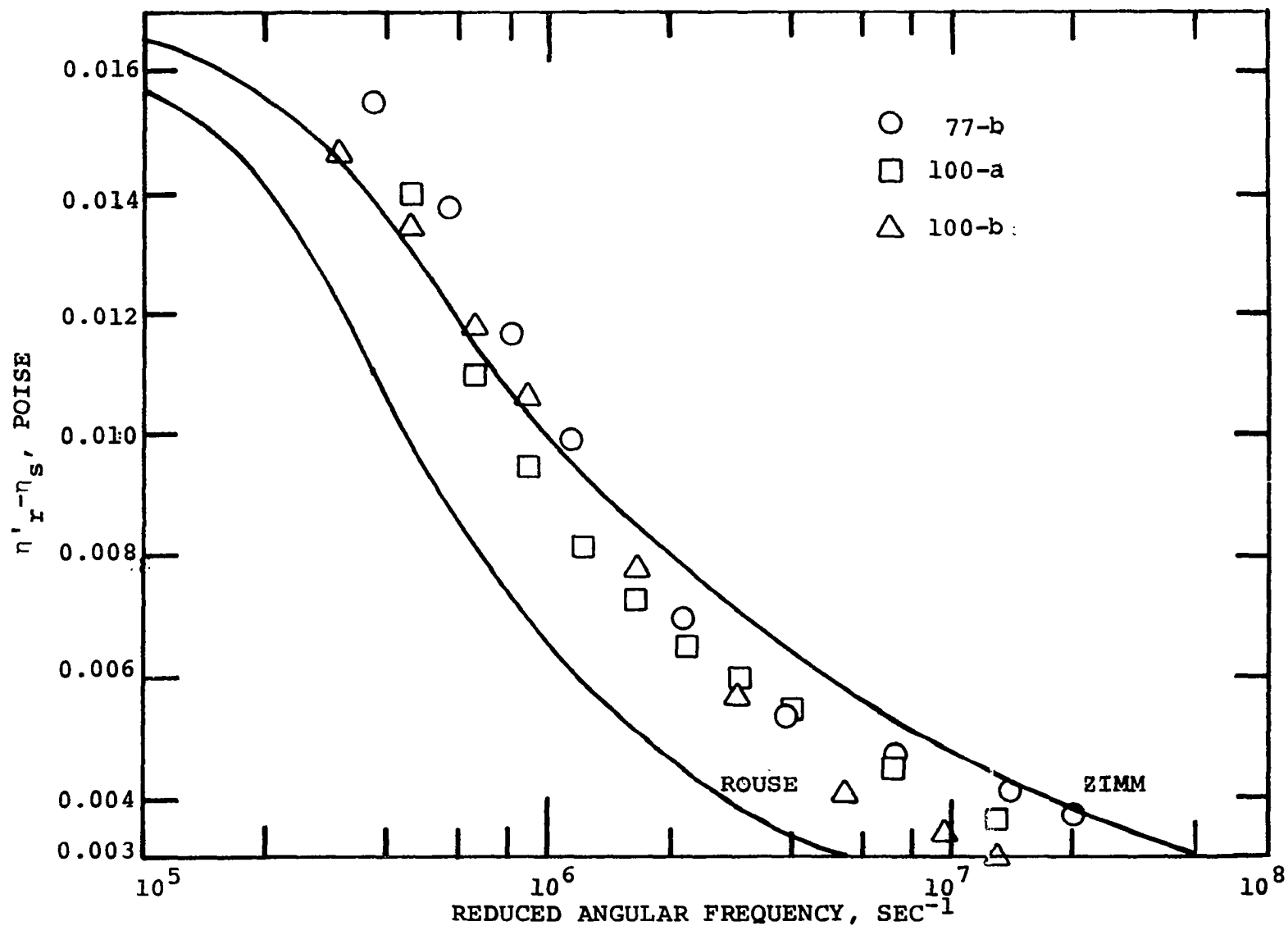


Figure 44. The Effect of Reduced Frequency on Reduced Dynamic Viscosity of Solution of 3 wt percent of S-109 Polystyrene in Toluene.

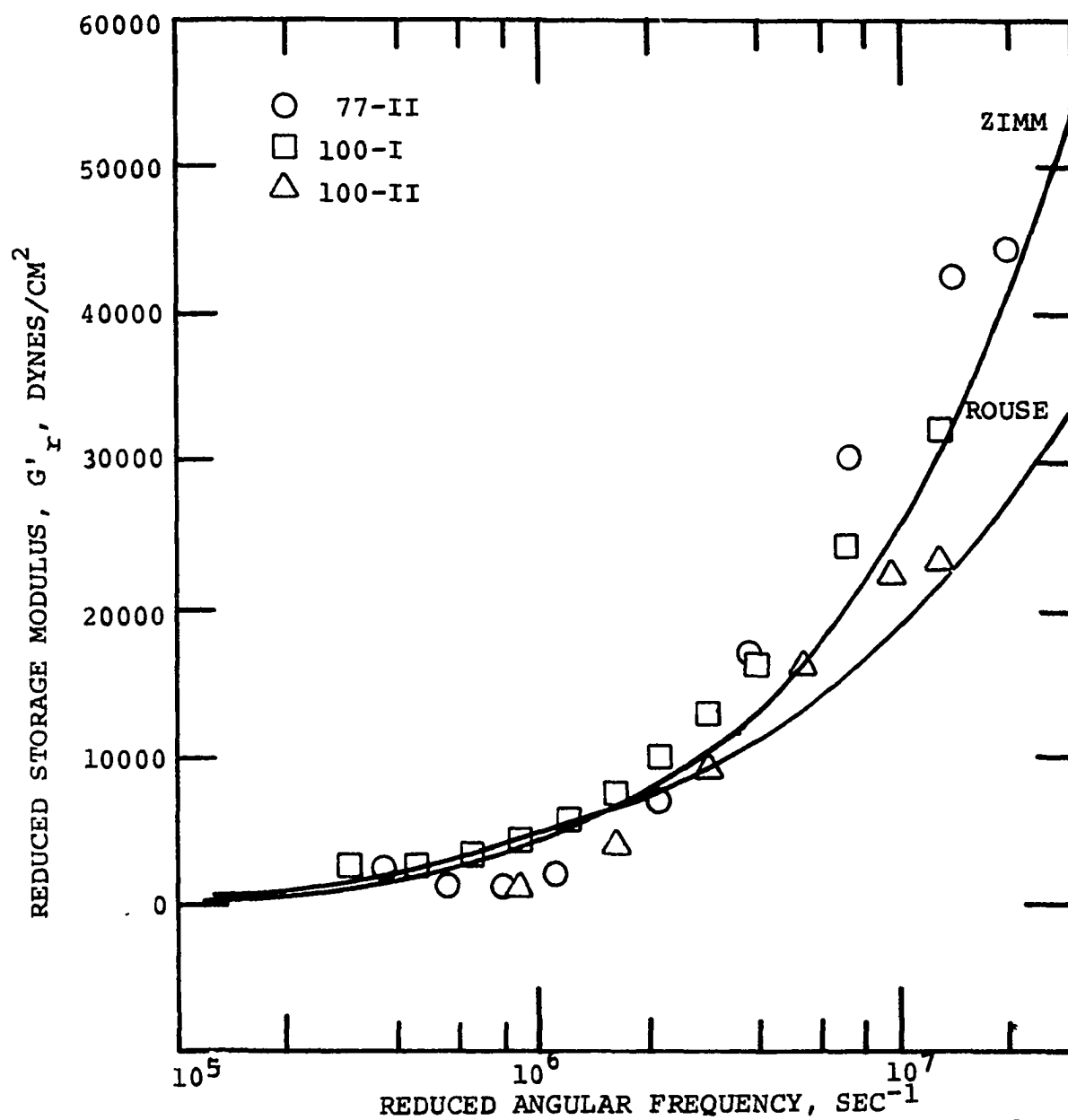


Figure 45. The Effect of Reduced Frequency on Reduced Storage Modulus of Solution of 3 wt percent S-109 Polystyrene in Toluene.

storage modulus, $G'_R M / cRT$, are plotted as functions of dimensionless angular frequency, $\omega_R = \omega_r (\eta - \eta_s) M / cRT$, in Figures 46, 47 and 48. M is the molecular weight of polymer, c is solution concentration in grams per cubic centimeter, R is gas constant, and T is absolute temperature in $^{\circ}\text{K}$. η is the zero-shear solution viscosity, and η_s is the solvent viscosity.

Data of the dynamic viscosity (Figure 46), the loss modulus (Figure 47), and the storage modulus (Figure 48) are in good agreement with the Zimm theory but do not agree with the predictions of the Rouse theory. A similar conclusion was reported by DeMallie, et al. (10) for a polystyrene of molecular weight of 2.67×10^5 in a high viscosity solvent, Aroclor 1248, and by Harrison, et al. (15) for solutions of polystyrene of molecular weights up to 2.39×10^5 in toluene.

Although the deviations of data points from the Zimm's curve were within the experimental accuracy, the dynamic viscosity data (Figure 46) and the loss modulus data (Figure 47) at frequencies, ω_R , greater than six (equivalent to $\omega_r = 10^6 \text{ sec}^{-1}$) tended to fall between the curves calculated with the Zimm and the Rouse theories. These data were all taken at pressures over 50,000 psig. A possible explanation for this behavior is based on the fact that at such high pressures the polymer molecules are squeezed closer to each other than they were under atmospheric pressure. In a close-packed mode, not all of the polymer contribution to the solution viscosity was able to relax at the very high frequencies (over 10^6 sec^{-1}).

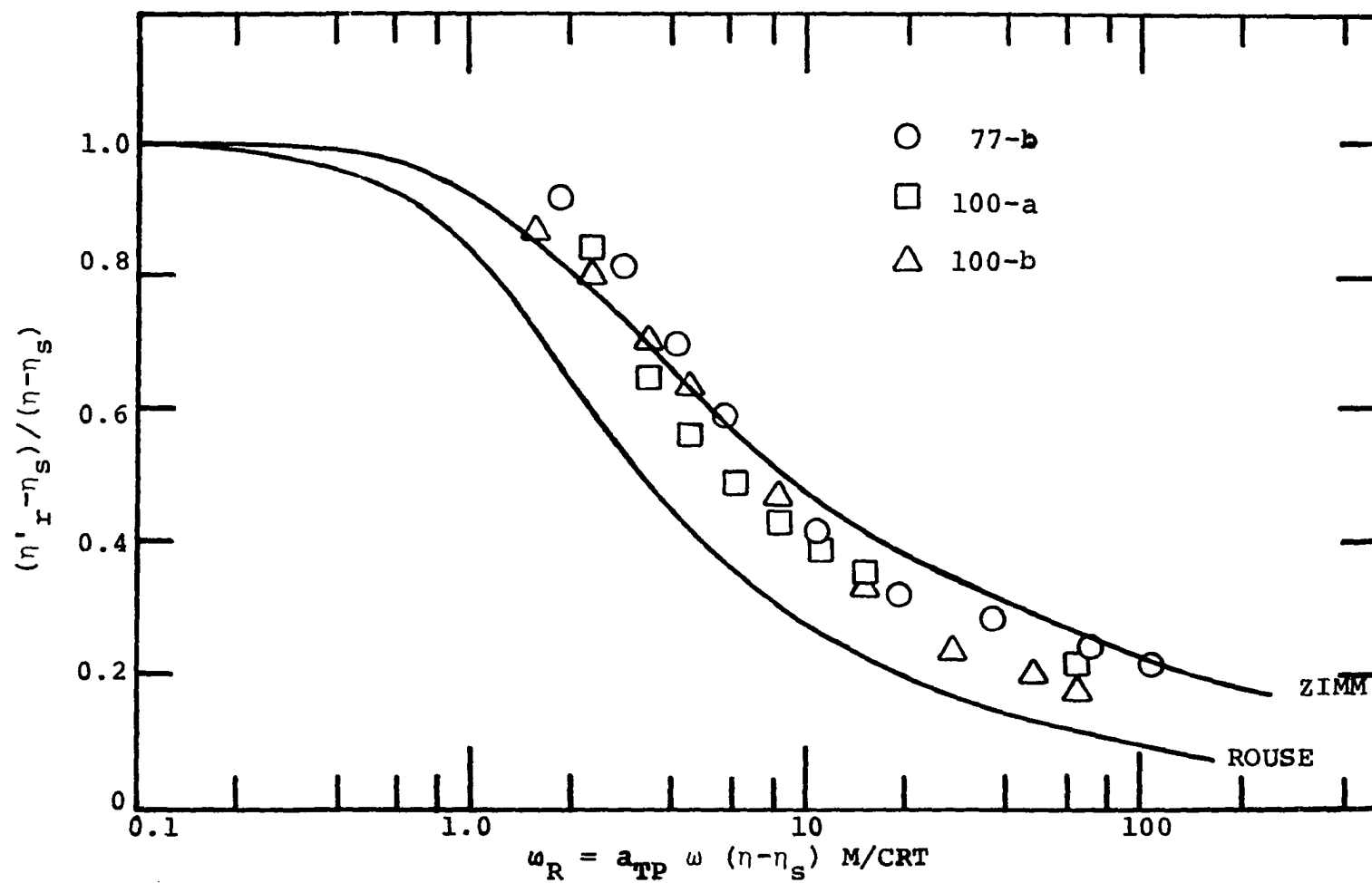


Figure 46: The Plot of Reduced Dynamic Viscosity of Solution of 3 wt% of S-109 Polystyrene in Toluene in Terms of Dimensionless Variables.

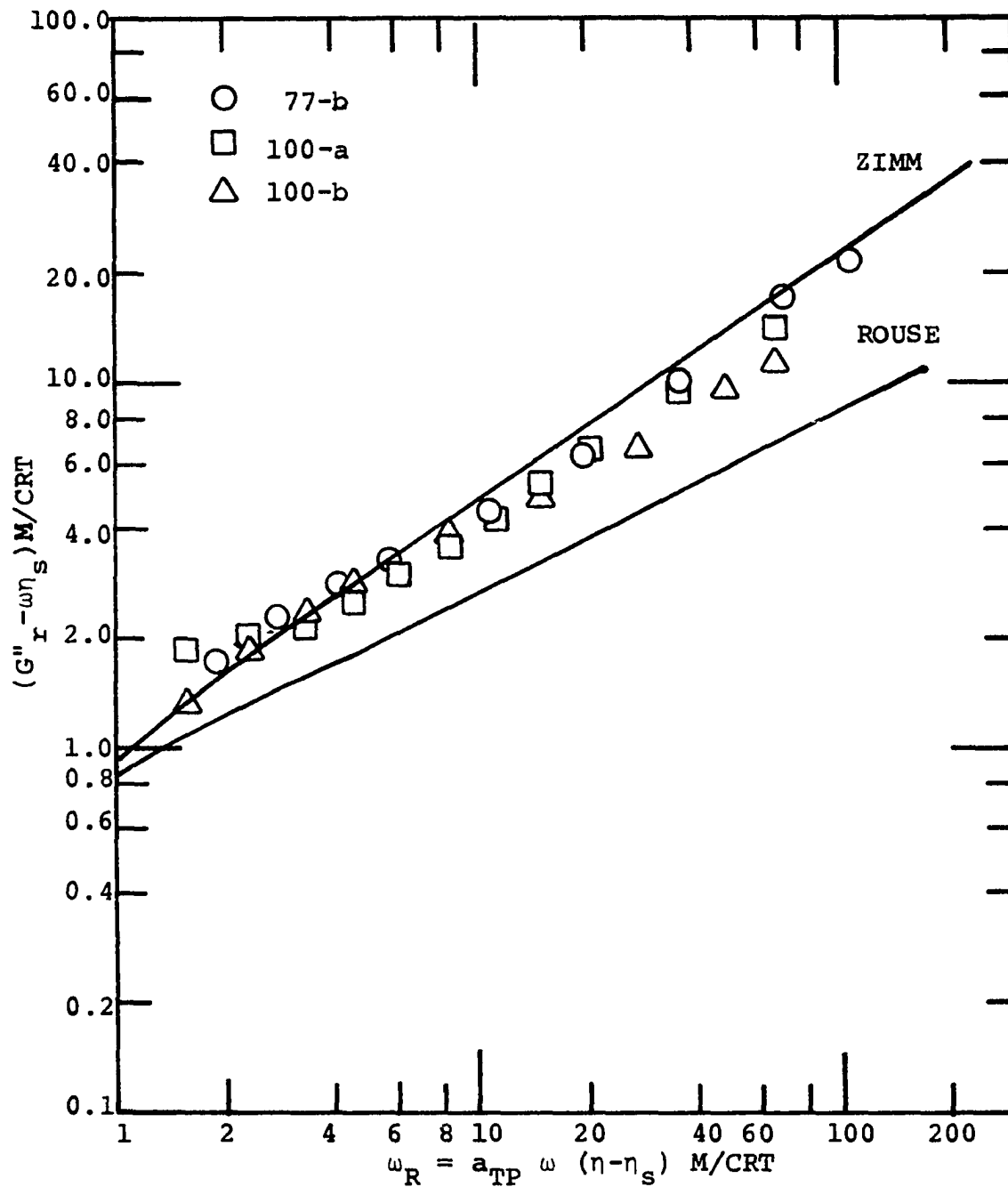


Figure 47. The Plot of Reduced Loss Modulus of Solution of 3 wt percent of S-109 Polystyrene in Toluene in Terms of Dimensionless Variables.

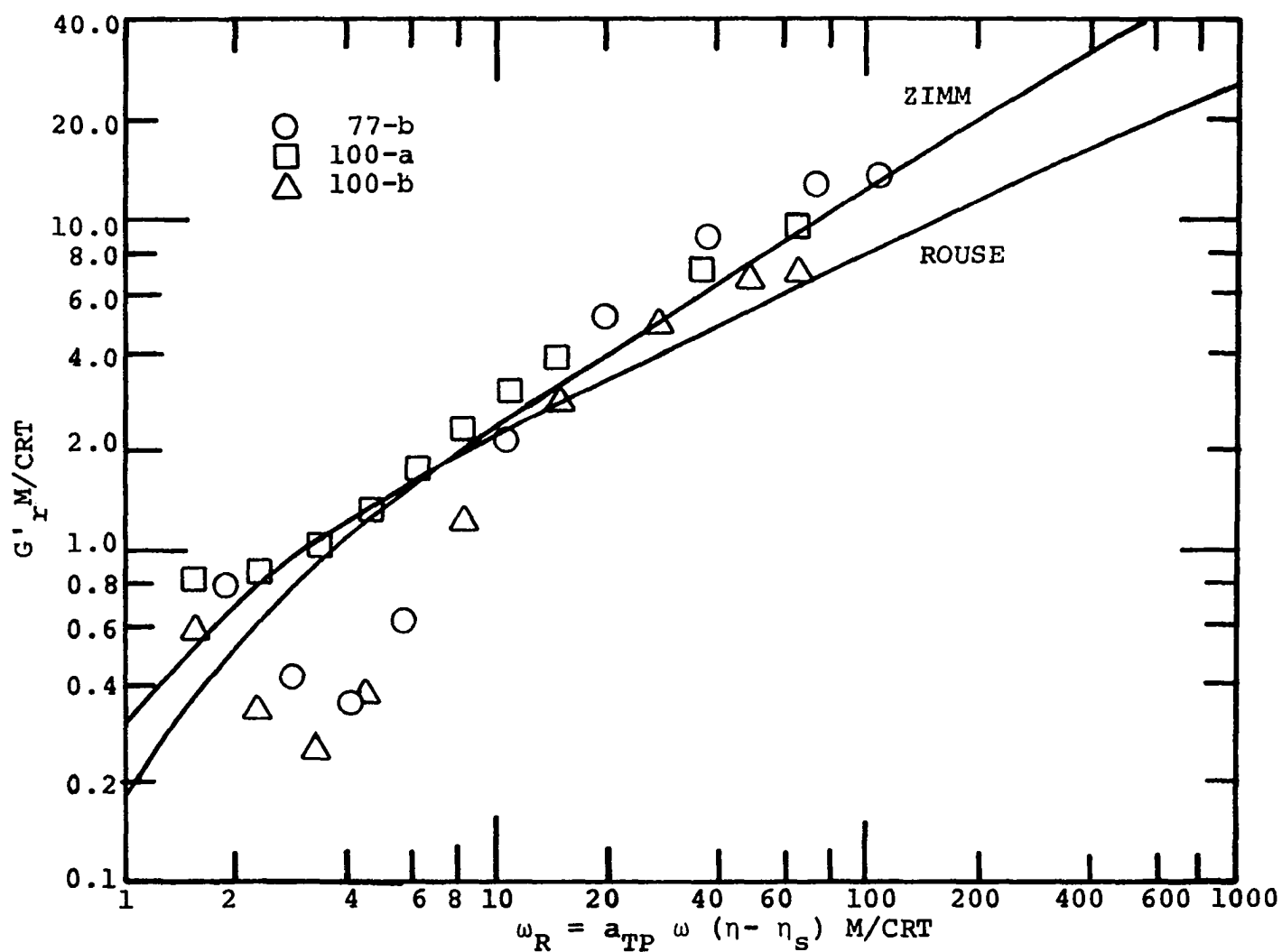


Figure 48. The Plot of Reduced Storage Modulus of Solution of 3 wt percent of S-109 Polystyrene in Toluene in Terms of Dimensionless Variables.

The polymer molecule might behave effectively as a rigid body on this short time scale. The solution thus behaved as a solvent containing a number of rigid, elastic bodies, but these suspended bodies had a porous structure through which solution could flow by virtue of the viscosity of the solvent. Therefore, the flow of the solution was not dominant, but rather it was intermediate between free draining (Rouse theory) and hydrodynamic interaction (Zimm theory).

Data on storage modulus versus dimensionless frequency in Figure 48 show a tendency of going above the Zimm's curve at ω_R larger than six. This effect could also be due to the high pressure effect upon the polymer solution. Elasticity of the hypothesis polymer chains formed by the dissolved polymer molecules became more evident as the molecular distances were decreased to an extent where the ordinary kinetic energy, as considered in both molecular theories, no longer suffices for moving the polymer molecules. In other words, more energy was stored than according to the predictions given by Rouse and Zimm.

Some data points in the low frequency range on Figure 48 fell below the theoretical curves beyond the limits of experimental error.

As shown in the preceding graphs, the Zimm theory can predict the properties of this solution better than the Rouse theory.

Measurements at higher frequencies could not be simulated with this equipment because the small crystals required would be impossible to mount. In order to obtain data in the region of frequencies greater than 10^7 sec^{-1} , it is necessary to use another quartz crystal technique reported by Barlow and Lamb (5). Their crystal provided data at frequencies at least two orders of magnitude higher than the present oscillating quartz crystal can obtain.

Pressure and frequency effects on viscoelastic behavior of dilute polymer solution were determined in this study. Data taken at steady shear under the same experimental conditions would be of great interest. A comparison between data at given frequencies and shear rates would certainly complement those correlations mentioned in Chapter II.

The measured viscoelastic properties on Humble FN-3158 plus ten volume percent Kendall 0839 and Mobil XRM-109 at different conditions are listed in Table X. Conclusions about viscoelastic properties for these two lubricants at 100°F should be regarded as tentative until more experimental data are obtained over a wider range of experimental conditions. As mentioned in Chapter III, at high pressures, the viscosity became so great that the lubricants virtually solidified in the pressure transfer lines having an internal diameter of 0.025 inches. Thus, modification on the high pressure side of present pressure systems is required to allow measurements to be made on liquids with viscosities higher than 10 poises.

TABLE X
VISCOELASTIC BEHAVIOR ON LUBRICANTS AT 100°F

Fluid	Viscometer	Px1,000 psig	poise	poise	G'x10 ⁻⁵ dynes/cm ²	G"x10 ⁻⁶ dynes/cm ²
Humble FN-3158 + 10 vol% Kendall 0839	60 kHz-I	18.40	12.40	1.94	7.50	4.09
Mobil XRM-109	20 kHz-I	10.30	8.71	2.26	2.80	1.10
	60 kHz-I	9.64	11.10	1.22	4.70	4.18

CHAPTER VI

CONCLUSION

The principal conclusions resulting from this investigation are summarized as follows:

1. The present oscillating quartz crystal viscometer can be used to measure viscosities at elevated temperatures and pressures and at discrete frequencies to an accuracy of at least ± 20 percent, and an accuracy of better than ± 10 percent if extreme care is exercised. The crystal viscometer with the present electronics is limited to liquid viscosity up to 10 poises.
2. Previous observations that the calibration parameters for the crystal viscometer, K_f and R_{EO} , are independent of both pressure and temperature are confirmed. The dependence of the calibration parameter, f_o , on both temperature and pressure is also consistent with earlier studies. The observed change in the calibration parameter, K_r , with pressure agrees with previous observations in this laboratory (33).
3. Viscoelastic behavior was observed for the solution of three weight percent S-109 polystyrene in toluene over the

entire working range of the experiments. The pressure effect on the dynamic viscosity and shear storage modulus of the polymer solution can be attributed to the dissolved polymer since the polymer contribution to the solution decreases slowly as pressure increases. The measurements on both dynamic viscosity and shear storage modulus show that the Zimm theory provides a better prediction of viscoelastic properties.

4. Use of the concept of reduced variables in combination with viscosity measurements at high pressures and temperatures to simulate high frequencies at atmospheric pressure and room temperature has been reconfirmed.
5. Measurement of density of liquids as functions of temperature and pressure can be made with the present experimental equipment.
6. A more extensive investigation of the possible viscoelastic effects in fluids would require the following additional experiments:
 - a. Determination of the effects of pressure and temperature on the viscosity of test fluids at zero (or very low) shear rates by using a technique such as the falling-weight method.
 - b. Determination of the effects of pressure, temperature, and variable frequencies up to several million Hertz by the oscillating quartz crystal technique utilized by Barlow, et al. (5).

CHAPTER VII

RECOMMENDATIONS

1. The viscoelastic behavior of Mobil XRM-109 and the mixture of Humble FN-3158 with Kendall 0839 should be investigated further at higher pressures by the quartz crystal viscometer technique, particularly with a much higher fundamental crystal frequency.
2. Additional measurements should be made on di-(2-ethylhexyl) sebacate at elevated pressures with a modified crystal viscometer to provide data for filling the gap in shear rates between 10^6 to 10^8 sec^{-1} from an earlier investigation in this laboratory (33) and the investigation by Lamb (18).
3. The combination of the crystal viscometer and high pressure should be used for measurements on more fluids for which viscoelastic behavior is expected.
4. Results on the viscoelastic properties obtained in this investigation should be compared with results obtained with a steady shear rheogoniometer. The development of a correlation between these two different experimental approaches would be of great significance.

NOMENCLATURE

a_T	ratio of relaxation times at two different temperatures
a_{Tp}	ratio of relaxation times at two different temperatures and pressures
A	cross sectional area
B	retardation spectrum
b	shifting factor along $\dot{\gamma}$ - ω axis
C, C_0	capacitance
C_j	numerical constants in Equation 60
c	concentration g/cc
e	base of natural logarithms
f	frequency, resonant frequency
f_0	resonant frequency in air at atmospheric pressure
f_r	reduced frequency
F	force
G	shear modulus, modulus of rigidity
$G(t)$	shear relaxation modulus
G_e	equilibrium modulus
G^*	complex shear modulus
G'	shear storage modulus
G'_r	reduced shear storage modulus

G''	shear loss modulus
H	relaxation spectrum
Im	imaginary part of a complex quantity
J	shear compliance
$J(t)$	shear creep compliance
J_e	instantaneous compliance
k	Boltzman constant
k_1	spring constant
k_2	damping constant of dash-pot
K_f	crystal constant pertaining to frequency measurement
K_r	crystal constant pertaining to resistance measurement
l	length
L	inductance
L_c	capacitive inductance
m	mass
n	number of polymer molecules per unit volume of solution
N	number of submolecules in a macromolecule
q	number of monomeric units in the submolecule of a macromolecule
Q	quality factor
r	radius
R	electrical resistance
R_E	electrical resistance at crystal resonant frequency
R_{Eo}	electrical resistance at crystal resonant frequency in air at atmospheric pressure

R_M	characteristic impedance resistance
t	time
T	absolute temperature
T_O	reference temperature for reduced variable
u_x	x-axis velocity component
V	volume
X	electrical reactance
X_M	characteristic impedance reactance
Z_M^*	complex characteristic impedance

Greek Symbols

α, α'	angle of deformation
σ	shear stress
σ^*	sinusoidal shear stress
σ_O	shear stress at time = 0
$\dot{\sigma}$	rate of shear stress
γ	shear strain
γ^*	sinusoidal shear strain
γ_O	shear strain at time = 0
$\dot{\gamma}$	rate of shear strain
ϵ	a small integral
η	Newtonian viscosity
η_O	viscosity of liquid at reference state to be reduced to
η_S	viscosity of solvent
η^*	complex shear dynamic viscosity
η'	real part of complex viscosity

η'_r	reduced real part of complex viscosity
η''	imaginary part of complex viscosity
δ	phase angle, or the Dirac delta
λ	retardation time
ρ	density
τ	relaxation time
ω	angular frequency
ω_r	reduced angular frequency
ω_R	dimensionless angular frequency

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APPENDICES

APPENDIX A

DENSITY DATA ON CALIBRATION FLUIDS

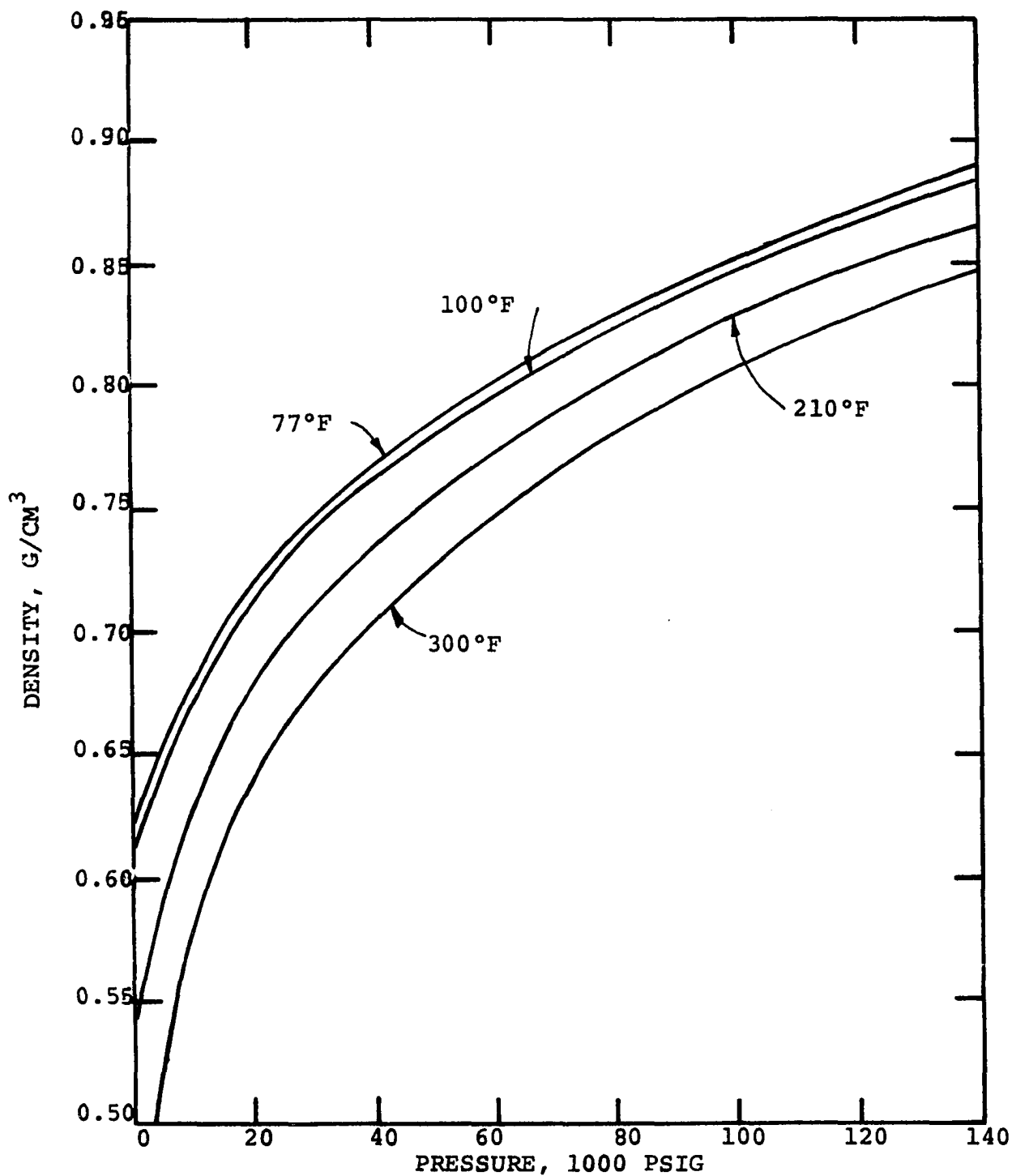


Figure 49. The Effects of Pressure and Temperature on the Density of Normal Pentane.

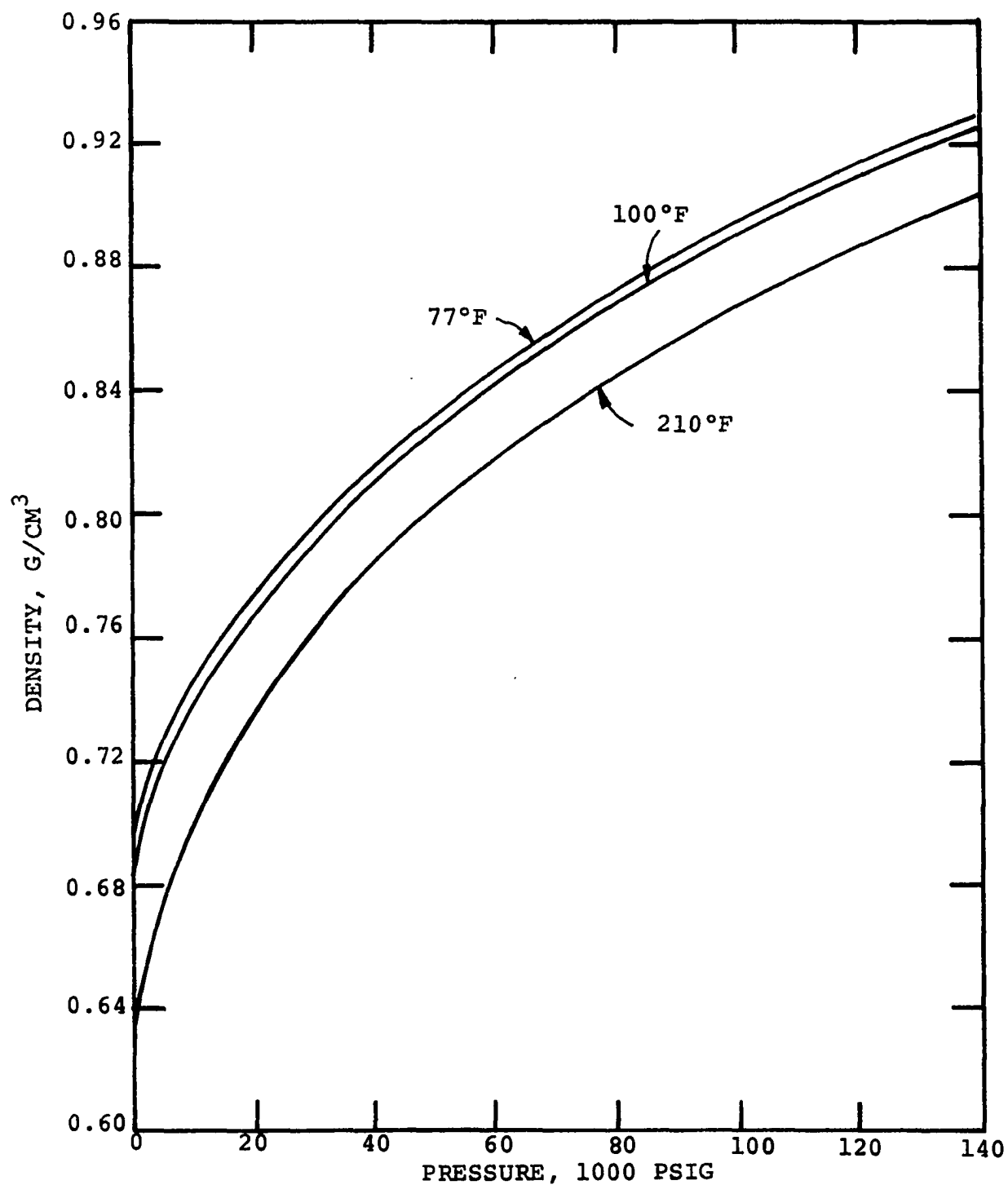


Figure 50. The Effects of Pressure and Temperature on the Density of Normal Octane.

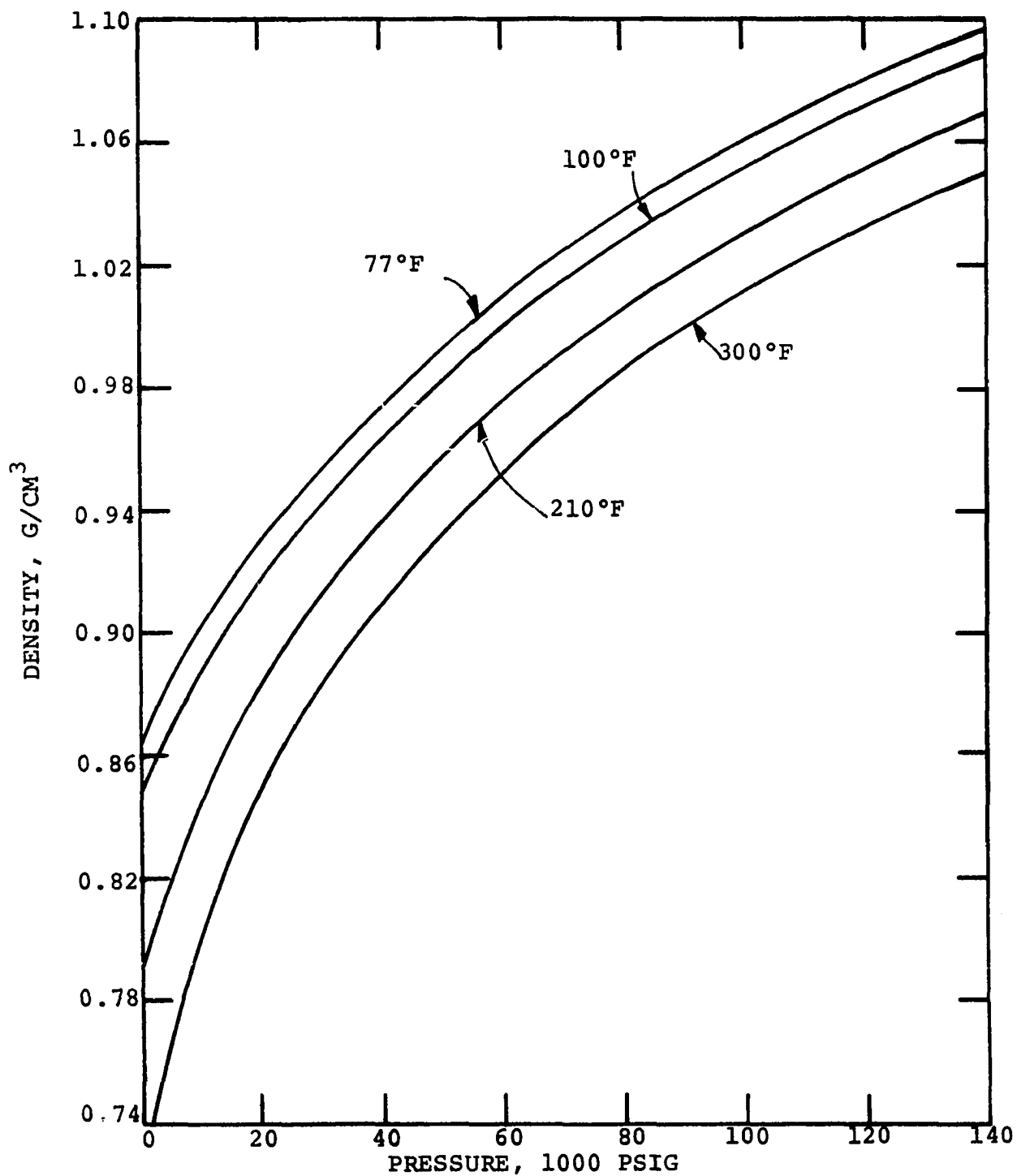


Figure 51. The Effects of Pressure and Temperature on the Density of Toluene.

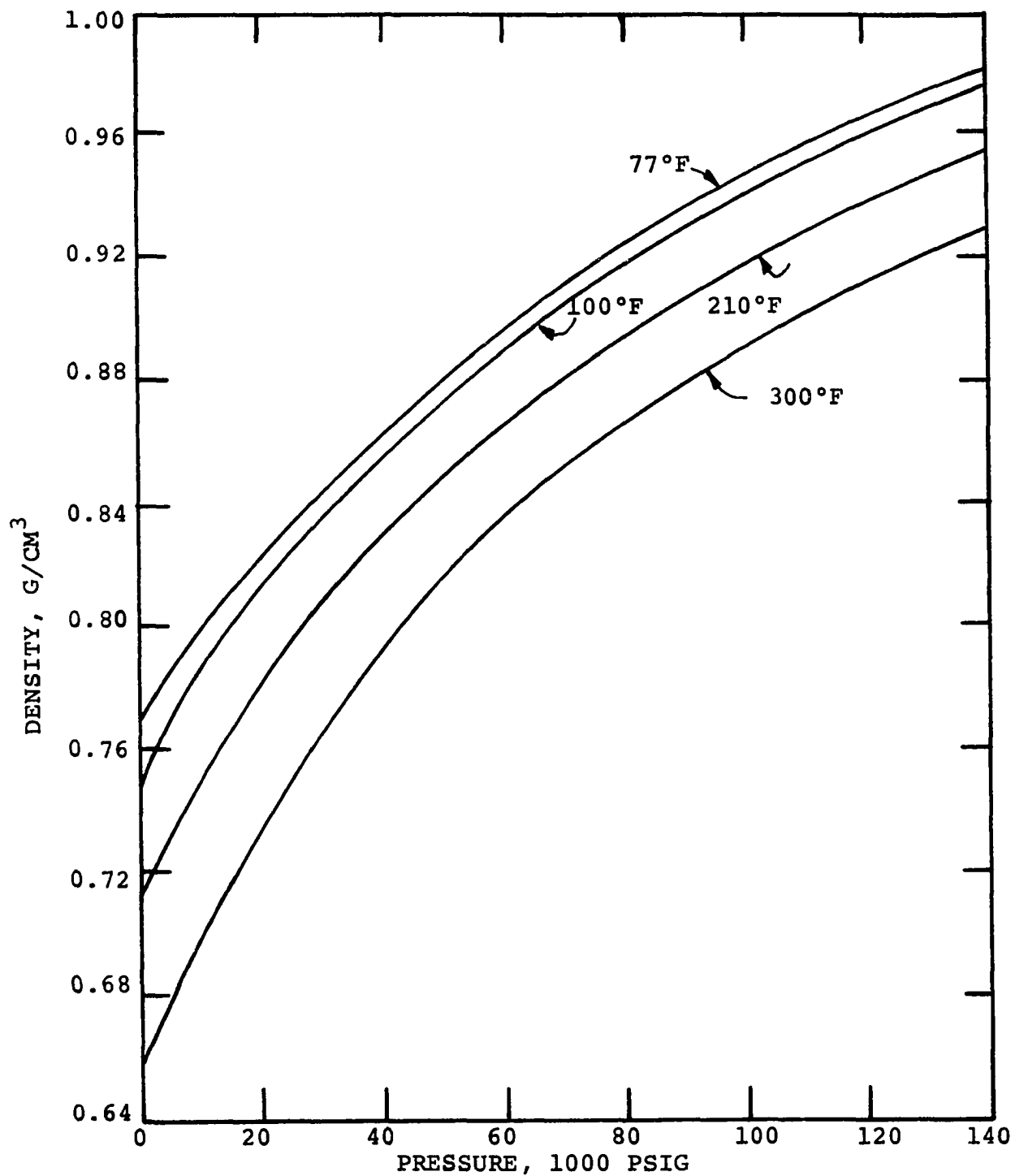


Figure 52. The Effects of Pressure and Temperature on the Density of Methylcyclohexane.

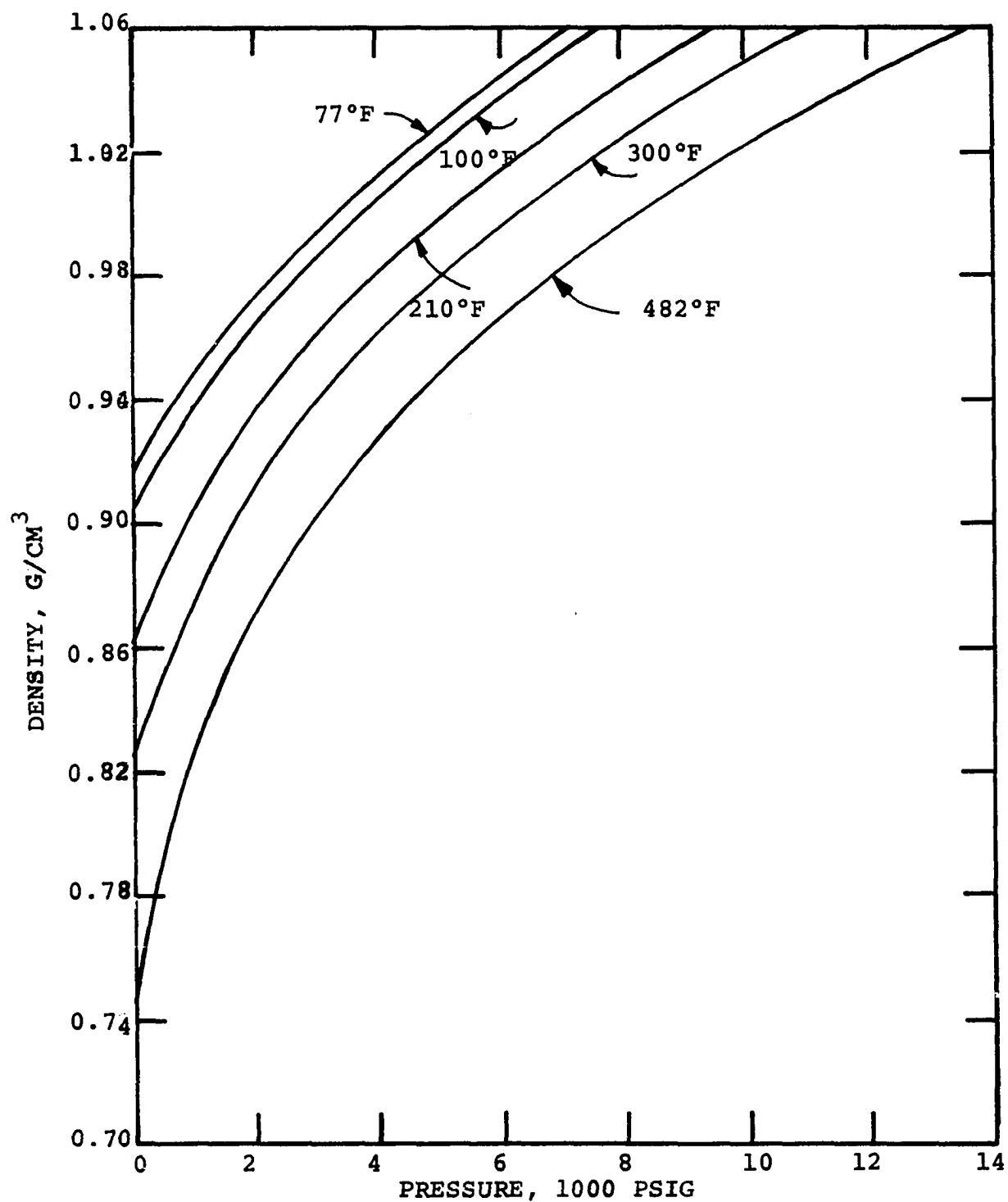


Figure 53. The Effects of Pressure and Temperature on the Density of Di-(2-ethylhexyl) Sebacate.

APPENDIX B

VISCOSITY DATA ON CALIBRATION FLUIDS

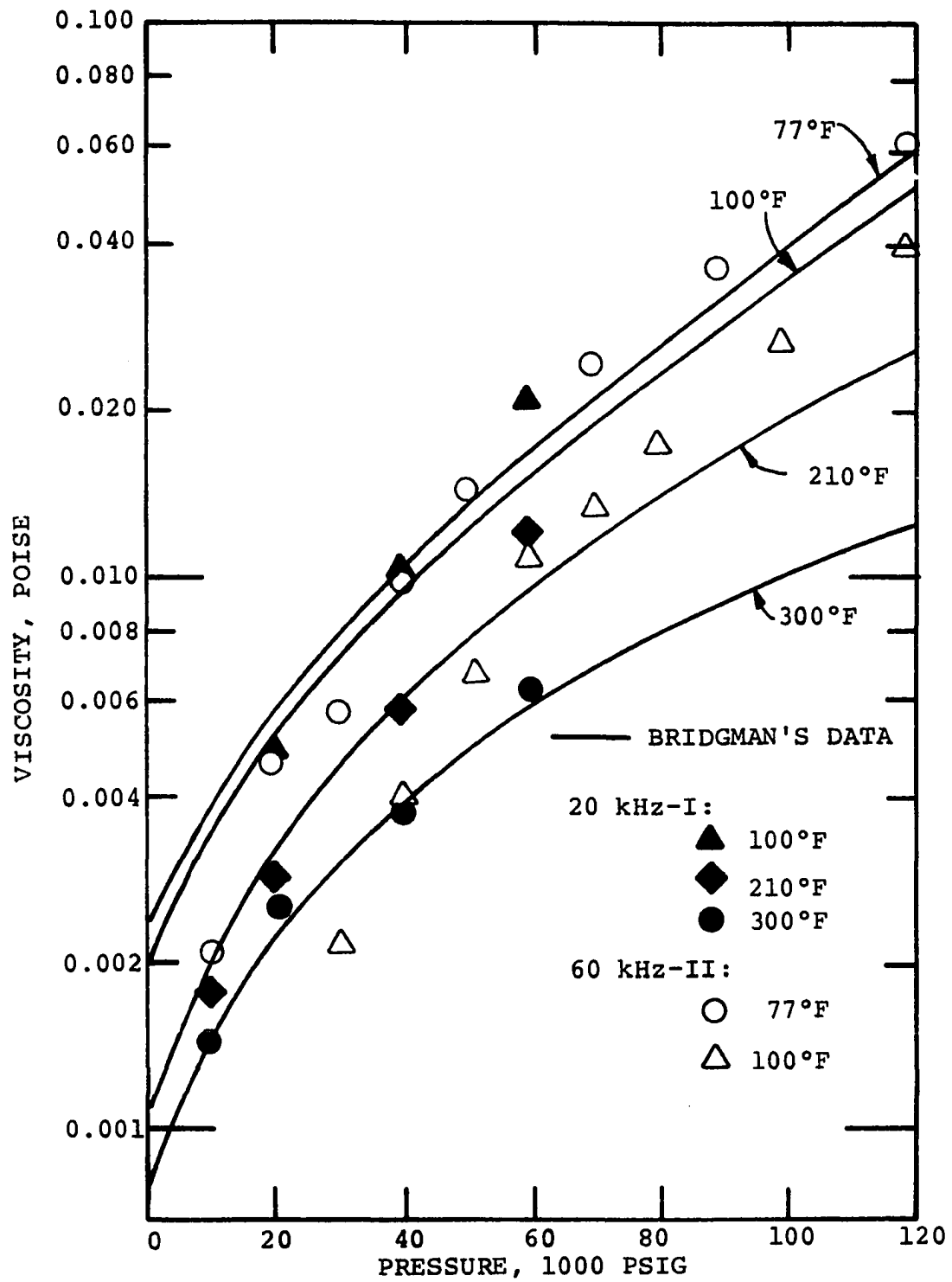


Figure 54. The Effects of Pressure and Temperature on the Viscosity of Normal Pentane.

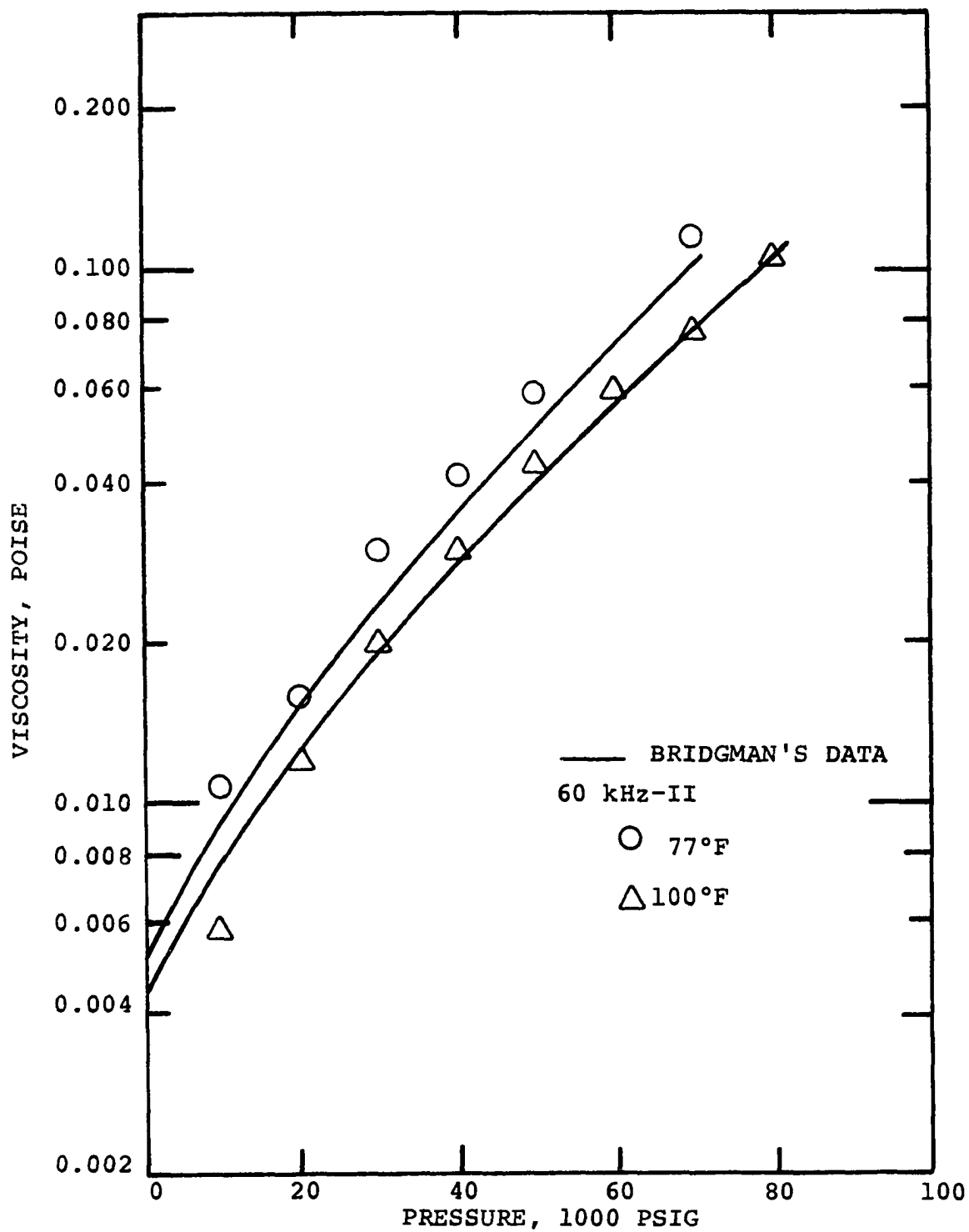


Figure 55. The Effects of Pressure and Temperature on the Viscosity of Normal Octane.

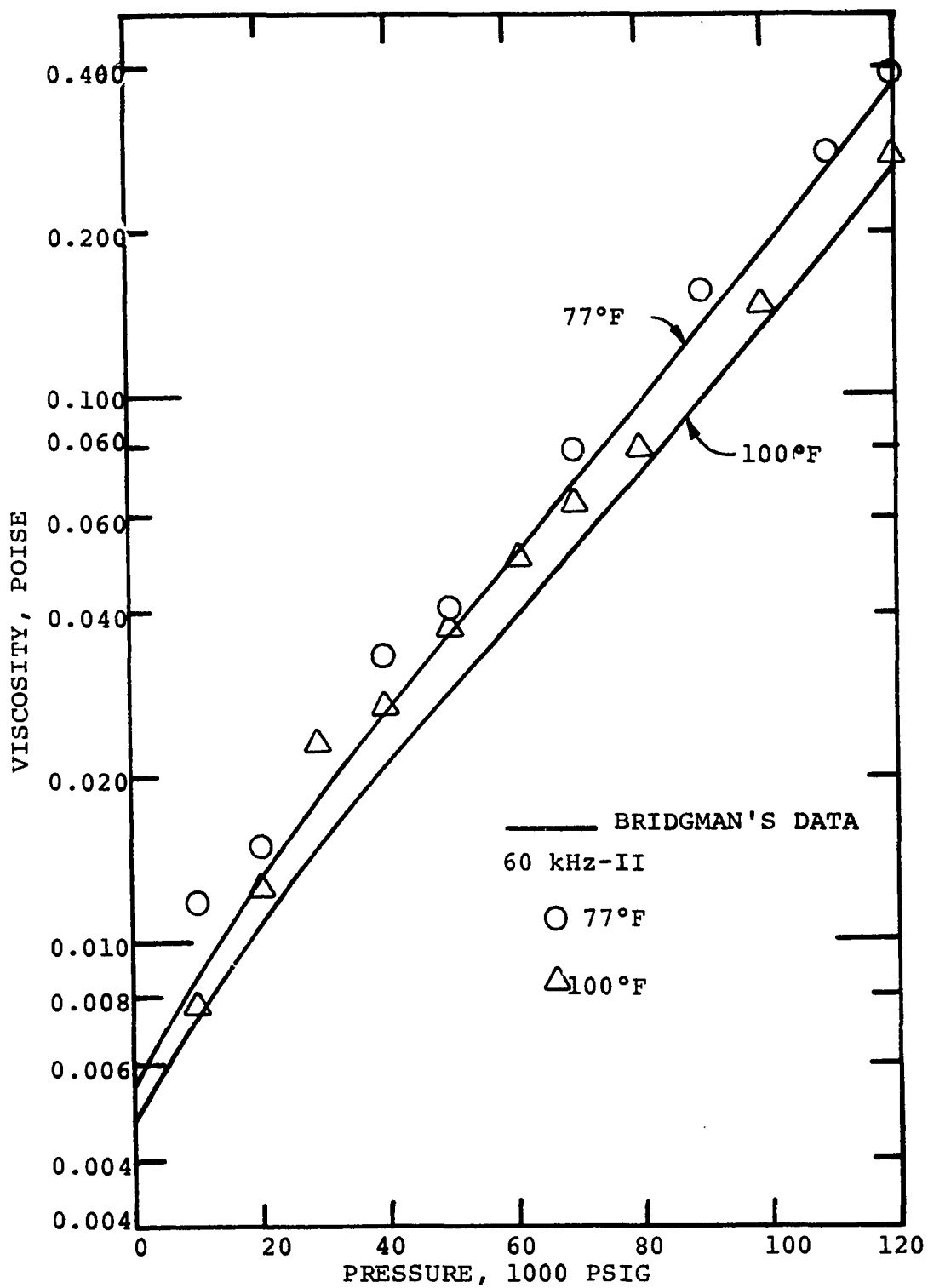


Figure 56. The Effects of Pressure and Temperature on the Viscosity of Toluene.

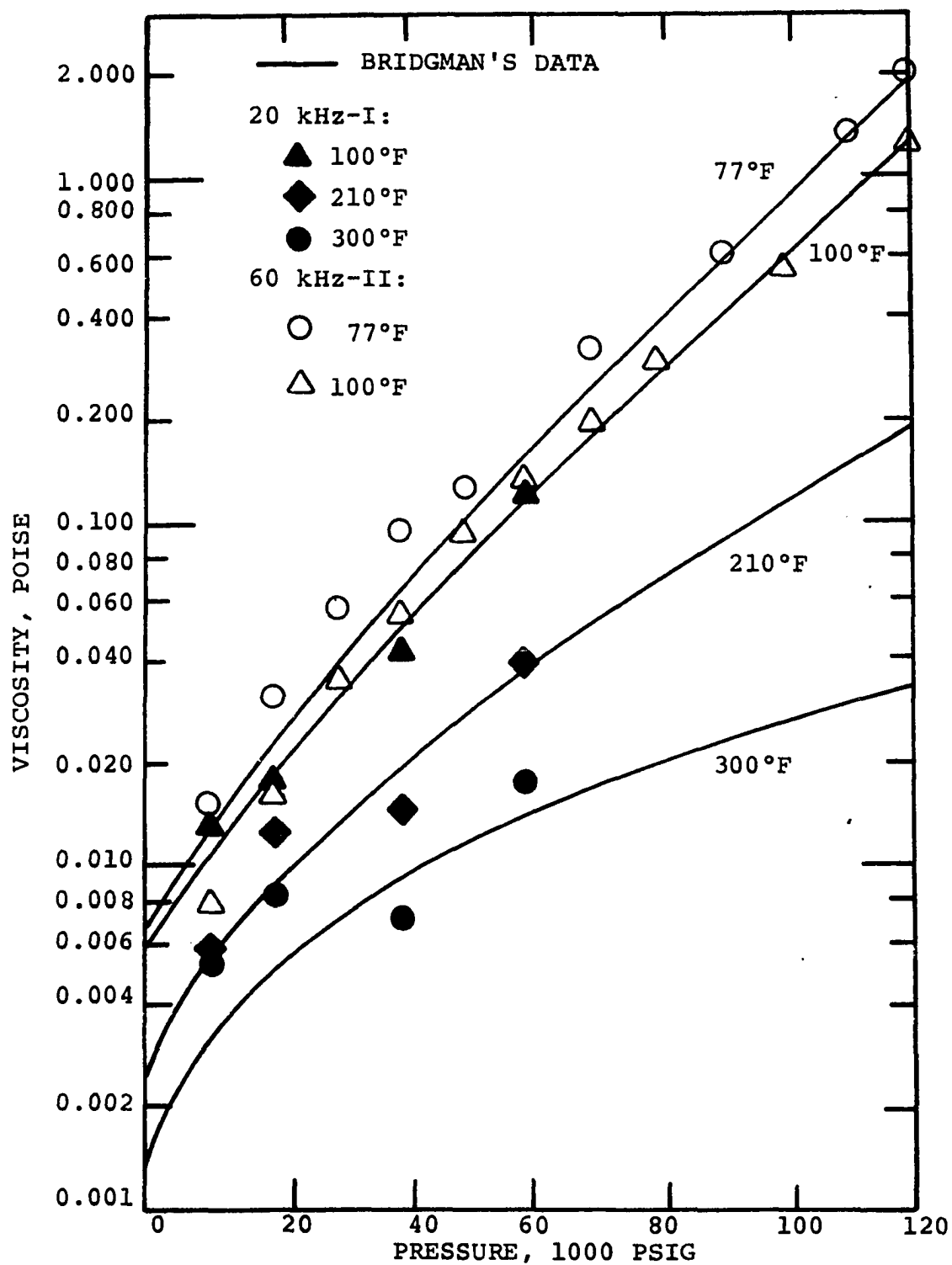


Figure 57. The Effects of Pressure and Temperature on the Viscosity of Methylcyclohexane.

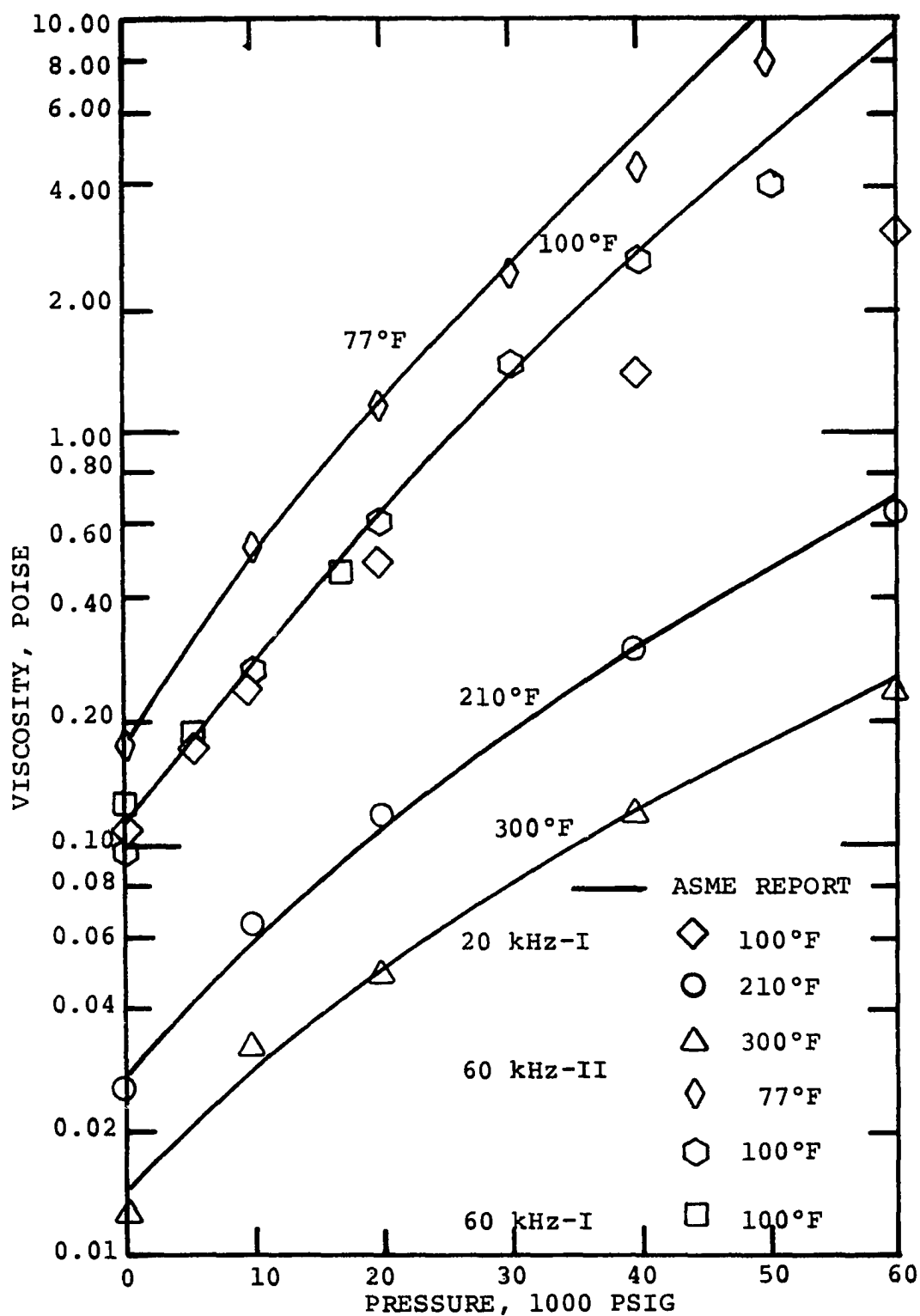


Figure 58. The Effects of Pressure and Temperature on the Viscosity of Di-(2-Ethylhexyl) Sebacate.

APPENDIX C

TABULATION OF f_o , Δf_o , AND $\Delta f_o/f_o$

TABLE XI

DATA ON f_o , Δf_o , AND $\Delta f_o/f_o$

Crystal	Temp °F	Pressure 1000 psig	f_o Hz	Δf_o Hz	$\Delta f_o/f_o \times 10^5$
20 kHz-I	100	Atm	19997.6	0.0	0.00
		10.0	19997.9	0.3	1.50
		20.0	20000.9	3.3	16.50
		40.0	20005.2	7.6	38.00
		60.0	20013.4	15.8	79.00
	210	Atm	20000.4	0.0	0.00
		10.0	20001.0	0.6	3.00
		20.0	20002.0	1.6	8.00
		40.0	20006.5	6.1	30.50
		60.0	20013.1	12.7	63.50
	300	Atm	20000.9	0.0	0.00
		10.0	20001.3	0.4	1.90
		20.0	20002.2	1.3	6.50
		40.0	20005.5	4.6	23.00
		60.0	20010.4	9.5	47.50
60 kHz-II	77	Atm	59077.2	0.0	0.00
		10.0	59083.3	6.1	10.30
		20.0	59085.8	8.6	14.60
		30.0	59092.1	14.9	24.90
		40.0	59102.2	25.0	42.30
		50.0	59109.2	32.0	54.20
		70.0	59132.8	55.6	94.10
		90.0	59106.0	82.8	140.00
		110.0	59187.7	110.0	185.00
		120.0	59204.9	127.0	214.00
	100	Atm	59081.2	0.0	0.00
		10.0	59086.9	5.7	9.56
		20.0	59093.2	12.0	20.30
		30.0	59100.2	19.0	32.20
		40.0	59108.1	26.9	45.50
		50.0	59113.3	32.1	54.30
		60.0	59126.4	45.2	76.50
		70.0	59136.1	55.9	94.60
		80.0	59154.6	73.4	124.00
		90.0	59165.7	84.5	143.00
		100.0	59179.2	98.0	166.00
		110.0	59192.9	112.0	189.00
		120.0	59206.9	126.0	213.00

APPENDIX D

TABULATION OF DENSITY DATA ON TEST FLUIDS

TABLE XII

CALCULATED DENSITIES AND PISTON DISPLACEMENTS

Fluid	Temp °F	Pressure (1000 psig)	Displacement in	Density g/cm ³
Humble	100*	Atm	----	0.873
		10.0	6.500	0.905
		20.1	10.937	0.932
		39.8	17.812	0.970
	210*	Atm	----	0.836
		10.0	7.312	0.872
		19.9	12.750	0.902
		40.4	20.375	0.945
	300*	Atm	----	0.803
		10.0	9.000	0.846
		19.9	14.812	0.882
		39.5	22.812	0.925
	480	Atm	----	0.739
		10.0	15.750	0.817
		19.9	23.625	0.858
		39.7	33.500	0.895
Humble FN-3158 + 10 vol% 0839	100	Atm	----	0.873
		9.80	7.127	0.905
		19.9	12.375	0.932
		38.2	19.500	0.970
	210	Atm	----	0.836
		10.1	8.125	0.871
		20.0	13.937	0.902
		40.0	22.312	0.945
	300	Atm	----	0.803
		9.9	9.875	0.846
		20.1	16.625	0.882
		40.0	25.250	0.925

*Measurements at these temperatures were made using an oversize (0.660 inches Dia.) intensifier high-pressure piston.

TABLE XII--Continued

Fluid	Temp °F	Pressure (1000 psig)	Displacement in	Density g/cm ³
Humble FN-3158 + 10 vol% 0839	482	Atm	----	0.739
		10.0	17.375	0.817
		20.1	26.375	0.858
Mobil XRM-109	100	Atm	----	0.839
		10.0	7.250	0.871
		20.0	12.500	0.899
		36.3	18.825	0.937
	210	Atm	----	0.806
		10.0	8.125	0.842
		20.0	14.187	0.872
	300	Atm	----	0.778
		9.9	9.750	0.821
		19.8	16.438	0.855
	100	Atm	----	1.88
		10.0	10.000	1.96
		19.9	16.375	2.04
		25.3	19.250	2.06
	210	Atm	----	1.76
		10.2	12.750	1.88
		19.7	19.875	1.97
		28.0	24.125	2.02
	300	Atm	----	1.67
		10.1	16.625	1.82
		19.9	24.750	1.92
		23.8	27.250	1.95
		26.4	28.500	1.96
Krytox	437	Atm	----	1.50
		10.0	22.375	1.73
		19.9	32.000	1.87
		21.9	33.500	1.89

TABLE XII--Continued

Fluid	Temp °F	Pressure (1000 psig)	Displacement in	Density g/cm ³
3 wt% S-109 Polystyrene in Toluene	77	Atm	----	0.865**
		9.96	----	0.903**
		19.9	6.74	0.941
		29.9	12.00	0.972
		49.9	20.1	1.02
		69.9	26.5	1.054
		90.0	31.9	1.085
		110.0	36.6	1.111
		120.0	38.7	1.123
	100	Atm	----	0.850**
		9.96	----	0.894**
		20.0	6.81	0.932
		30.0	12.1	0.963
		40.0	16.5	0.988
		50.0	20.3	1.010
		59.9	23.7	1.029
		69.9	26.9	1.047
		79.9	29.7	1.063
		100.0	34.6	1.093
		117.6	38.8	1.115

**Densities of toluene at these conditions.

APPENDIX E

TABULATION OF VISCOSITY DATA ON TEST FLUIDS

TABLE XIII

DATA FOR VISCOSITY CALCULATIONS AND CALCULATED VISCOSITIES

Fluid	Temp °F	Pressure 1000 psig	R_E k Ω	R_M g/cm ² -sec	f Hz	X_M g/cm ² -sec	η' poise	η'' dynes-sec/cm ²
<u>60 kHz-I Crystal</u>								
Humble FN-3158	100	Atm	649	347	62083.8	335	0.682	----
		4.92	967	525	62034.0	491	1.49	----
		9.94	1376	760	61943.6	773	3.34	----
		10.1	1333	736	61972.0	684	2.86	----
		18.1	2298	1313	61793.6	1242	9.08	----
Humble FN-3158 + 10 vol% 0839	100	Atm	741	396	62054.6	426	0.992	----
		5.3	1161	631	61999.9	597	2.17	----
		10.2	1641	07	61915.1	862	4.44	----
		18.4	2827	1615	61748.4	1383	12.4	----
Mobil XRM-109	100	Atm	1489	796	61947.1	762	3.72	----
		2.24	1718	924	61917.8	854	4.78	----
		5.0	1736	943	61894.3	927	5.26	----
		9.64	2622	1419	61775.6	1298	11.1	1.22
DuPont Krytox 143-AB	100	Atm	1291	690	61963.3	712	1.35	----
		2.42	1721	925	61840.4	1092	2.74	----
		5.38	2324	1263	61714.7	1485	5.03	----
		9.80	3257	1799	61435.6	2358	11.2	----

TABLE XIII--Continued

Fluid	Temp °F	Pressure 1000 psig	R _E kΩ	R _M g/cm ² -sec	f Hz	X _M g/cm ² -sec	η' poise	η'' dynes-sec/cm ²
60 kHz-II Crystal								
3 wt% S-109 Polystyrene in Toluene	77-b*	Atm	166.0	68.8	59064.1	49.2	0.0211	0.00721
		9.96	177.0	76.5	59063.6	67.2	0.0307	0.00397
		19.94	192.0	87.4	69065.5	80.4	0.0407	0.00339
		29.90	213.0	102.0	59069.4	90.4	0.0519	0.00613
		49.90	269.0	141.0	59081.4	108.0	0.0824	0.02270
		69.90	346.0	196.0	59095.6	132.0	0.1360	0.05480
		89.90	444.0	265.0	59108.3	177.0	1.2410	0.09990
		110.00	562.0	350.0	59115.6	257.0	0.4510	0.14200
		120.00	628.0	398.0	59116.1	313.4	0.6210	0.14900
	100-a*	Atm	168.0	69.7	58068.1	49.2	0.0218	0.00773
		9.96	178.0	77.5	59070.6	56.6	0.0265	0.00843
		20.00	192.0	87.5	59074.1	64.2	0.0321	0.01030
		30.00	210.0	100.0	59078.6	72.3	0.0412	0.01360
		40.00	231.0	115.0	59083.8	81.6	0.0523	0.01830
		50.00	255.0	133.0	59089.7	92.4	0.0670	0.02470
		59.90	284.0	153.0	59096.2	105.0	0.8640	0.03290
		69.90	315.0	175.0	59103.0	120.0	0.1120	0.04310
		79.90	350.0	201.0	59110.0	139.0	0.1460	0.05510
		100.00	431.0	259.0	59124.4	186.0	0.2460	0.08350
		120.00	525.0	327.0	59138.2	250.0	0.4110	0.11200
	100-b*	Atm	152.0	60.8	59069.5	44.3	0.0171	0.00548
		9.96	164.0	69.2	59069.4	60.9	0.0254	0.00324
		20.00	179.0	79.7	59071.3	74.0	0.0344	0.00251

*-a and -b were designated for different data runs.

TABLE XIII--Continued

Fluid	Temp °F	Pressure 1000 psig	R _E kΩ	R _M g/cm ² -sec	f Hz	X _M g/cm ² -sec	η' poise	η'' dynes-sec/cm ²
<u>60 kHz-II Crystal</u>								
3 wt% S-109	100-b*	29.9	197.0	92.3	59075.1	84.7	0.0445	0.00378
Polystyrene		49.9	242.0	124.1	59086.7	103.0	0.0701	0.01310
in Toluene		69.9	299.0	165.0	59101.8	125.0	0.1090	0.03110
		90.0	368.2	215.0	59117.9	158.0	0.1760	0.05540
		110.0	449.0	274.0	59132.6	211.0	0.2930	0.07720
		120.0	494.0	306.0	59138.7	248.0	0.3820	0.08100
<u>20 kHz-I Crystal</u>								
Humble	100	Atm	791.0	162.0	19949.0	165.0	0.4890	----
FN-3158		10.0	1336.0	302.0	19897.9	340.0	1.8200**	----
	210	Atm	290.0	59.5	19985.2	51.7	0.0586	----
		10.2	433.0	98.0	19970.8	103.0	0.1840	----
		20.1	568.0	147.0	19951.0	173.0	0.4510**	----
		39.9	977.0	261.0	19923.1	283.0	1.2500	----
	300	Atm	187.0	38.3	19988.7	41.4	0.0315	----
		10.2	258.0	58.4	19984.0	58.7	0.0645	----
		20.1	354.0	91.7	19977.9	82.4	0.1370	----
		40.5	548.0	146.0	19957.4	163.0	0.4120**	----
Humble	100	Atm	1107.0	227.0	19938.6	200.0	0.8320	0.10400
FN-3158 +								
10 vol%	210	Atm	333.0	78.5	19977.3	78.5	0.1180	----
0839		10.1	486.0	110.0	19970.1	105.0	0.2110	0.01010
		20.1	714.0	185.0	19939.8	211.0	0.6910**	----

**These values calculated from $\eta' = 2R_M^2/\omega\rho$ instead of $2R_M X/M\omega\rho$ for reasons explained in text, page 98.

TABLE XIII--Continued

Fluid	Temp °F	Pressure 1000 psig	R_E k Ω	R_M g/cm ² -sec	f Hz	X_M g/cm ² -sec	η' poise	η'' dyne-sec/cm ²
Humble FN-3158 + 10 vol% 0839	300	Atm	198.0	40.6	19987.2	46.5	0.0374	----
		10.1	297.0	67.2	19981.0	68.9	0.0872	----
		20.0	386.0	100.0	19972.2	102.0	0.1840	----
		40.5	638.0	170.0	19942.7	213.0	0.6270**	----
	100	Atm	1894.0	388.0	19863.2	456.0	3.3900**	----
		10.2	3234.0	732.0	19806.2	651.0	8.8000	1.04
	210	Atm	505.0	104.0	19967.2	113.0	0.2310	----
		9186	767.0	174.0	19939.7	208.0	0.6850**	----
		20.00	1058.0	274.0	19892.0	373.0	1.8800**	----
	300	Atm	281.0	57.6	19984.0	57.3	0.0676	----
		9.96	439.0	99.4	19974.0	92.6	0.1790**	----
		19.90	510.0	132.0	19952.8	168.0	0.4130**	----
		26.90	564.0	151.0	19948.8	192.0	0.5270**	----
		40.10	941.0	289.0	19916.3	319.0	1.6400**	----

**These values calculated from $\eta' = 2R_M^2/\omega\rho$ instead of $2R_M X_M/\omega\rho$ for reasons explained in text, page 98.

APPENDIX F

TABULATION OF REDUCED VISCOELASTIC PROPERTIES ON POLYMER SOLUTION

TABLE XIV
TABULATION ON REDUCED PROPERTIES FOR THE SOLUTION OF
3 WT. % S-109 POLYSTYRENE IN TOLUENE

$\omega_r 10^{-5}$ rad/sec	ω_R	η'_r poise	$(\eta'_r - \eta_s)/$ $(\eta - \eta_s)$	$G'_r \times 10^{-3}$ dyne/cm ²	$G'_r \times$ M/cRT	$G''_r \times 10^{-3}$ dyne/cm ²	$(G''_r - \omega \eta_s)$ $\times$ M/cRT
<u>77-b*</u>							
3.711	1.874	0.211000	0.9227	2.677	0.8028	7.830	1.729
5.627	2.841	0.019390	0.8212	1.411	0.4231	10.910	2.333
8.124	4.103	0.172600	0.6949	1.170	0.3509	14.020	2.851
11.250	5.679	0.155100	0.5909	2.062	0.6183	17.440	3.356
21.230	10.720	0.125500	0.4151	7.334	2.1990	26.640	4.450
38.890	19.640	0.010940	0.3197	17.160	5.1450	42.560	6.278
72.020	36.370	0.010240	0.2777	30.540	9.1580	73.720	10.100
140.200	70.780	0.009652	0.2430	42.600	12.7800	135.300	17.200
199.600	107.900	0.009259	0.2196	44.350	13.3000	184.800	22.140
<u>100-a*</u>							
3.048	1.539	0.025860	1.2050	2.800	0.8396	7.882	1.855
4.583	2.314	0.019870	0.8499	2.903	0.8706	9.107	1.967
6.592	3.329	0.016560	0.6531	3.444	1.0330	10.915	2.174
8.888	4.488	0.015080	0.5638	4.408	1.3220	13.380	2.530
12.140	6.131	0.013700	0.4835	5.817	1.7440	16.640	2.965
16.380	8.271	0.012800	0.4299	7.723	2.3160	20.960	3.555
22.050	11.130	0.012080	0.3869	10.140	3.0490	26.620	4.307
29.500	14.900	0.011510	0.3530	13.050	3.9150	33.940	5.269
39.860	20.130	0.010920	0.3181	16.480	4.9420	43.510	6.403
71.500	36.110	0.010050	0.2667	24.420	7.3220	71.870	9.630
129.300	65.280	0.009139	0.2125	32.180	9.6490	118.100	13.870

*-a and -b were designated for different data runs.

TABLE XIV--Continued

$\omega_r \times 10^{-5}$ rad/sec	ω_R	η'_r poise	$(\eta'_r - \eta_s) /$ $(\eta - \eta_s)$	$G'_r \times 10^{-3}$ dyne/cm ²	$G'_r \times$ M/CRT	$G''_r \times 10^{-3}$ dyne/cm ²	$(G''_r - \omega \eta_s)$ $\times$ M/CRT
100-b*							
3.048	1.539	0.02028	0.8743	1.9850	0.5952	6.183	1.346
4.583	2.314	0.01909	0.8034	1.1150	0.3345	8.748	1.860
6.591	3.329	0.01738	0.7021	0.8374	0.2511	11.460	2.337
8.887	4.488	0.01627	0.6359	1.2300	0.3688	14.460	2.854
16.380	8.271	0.01339	0.4648	4.0860	1.2250	21.930	3.844
29.500	14.900	0.01121	0.3357	9.4260	2.8270	33.070	4.999
54.290	27.420	0.009576	0.2385	16.3900	4.9160	51.990	6.538
94.980	47.970	0.008960	0.2019	22.4000	6.7160	85.100	9.683
129.300	65.280	0.008487	0.1738	23.8000	6.9800	109.700	11.350

*-a and -b were designated for different data runs.