MEASUREMENT OF VISCOELASTIC PROPERTIES OF DILUTE AQUEOUS POLYETHYLENE OXIDE SOLUTIONS USING ACOUSTIC METHODS

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ABSTRACT

The absorption coefficient and the velocity of longitudinal ultrasonic waves in aqueous polyethylene-oxide solutions at 0.025, 0.05, 0.1, 0.25 and 0.375% concentration by weight were measured at 10.1, 17.9 and 26.1 mc/sec at 23° C. using a pulse technique and were found to be the same as in water at these frequencies and temperature. A new method, involving the use of a pulsed, Y-cut, quartz crystal, for the measurement of shear resistance of low viscosity solutions was developed. This method was used to determine, in accordance with relaxation theory, the shear moduli of the polymer solutions at 7 mc/s at temperatures of 4° C., 23° C. and 43° C. These solutions displayed shear moduli at 4° C. of two orders of magnitude greater than those determined at 23° C. and 43° C. The large discrepancy in values measured at 4° C. compared with those measured at the other two temperatures is discussed.

$\underline{M} \sim 4 \times 10^6$

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

TABLE OF SYMBOLS AND ABBREVIATIONS

a	Absorption Coefficient (db/m)
C_p	Specific heat at constant pressure
f	Frequency, cycles per second
G_∞	Shear modulus at infinite frequency
K	Thermal conductivity
m_{eff}	Effective mass of oscillator
R_m	Mechanical resistance, gm/sec
R_s	Specific resistance, grams/cm^{2}sec
v	Particle velocity
x	Space coordinate
α	Absorption coefficient (nepers/meter)
γ	Ratio of specific heat at constant pressure to that at constant volume
η	Shear viscosity coefficient, poise
χ	Compressional viscosity
ρ	Density
ω	Circular frequency
τ_s	Relaxation time, seconds

1. Introduction

Among the commercially available synthetic compounds today are a number of water-soluble, long-chain hydrocarbons which have quite a wide range of applications due to their peculiar structural characteristics in solution. One compound, polyethylene oxide, whose dilute aqueous solutions were investigated as the subject for this thesis, is manufactured by Union Carbide Chemical Company under the trade name "Polyox", WSR301. It is widely used in adhesives, aerosol hair sprays, cosmetics, detergents and toothpaste (16). Polyox, as it will be referred to here, consists of a single, long-chain hydrocarbon molecule of approximately 50 microns length with one atom of oxygen per ethylene radical, and no side branches. The molecular weight of polyox is approximately 4,000,000, and it is soluble in water to concentrations of approximately 3% by weight.

This rather remarkable compound, in solution, displays distinctly non-Newtonian characteristics and, due to its quite long molecules, may find some application as a turbulence inhibitor. It was the purpose of this project to explore the visco-elastic characteristics of dilute polyox solutions using ultrasonic techniques.

Investigation of viscoelastic properties was confined to the low megacycle region of frequencies. The acoustic absorption coefficient was measured at 10, 18, and 26 megacycles per second using a X-cut quartz crystal transducer (a pulse-echo method) and the shear elastic properties were measured at 7 megacycles per second using a Y-cut quartz crystal in a reverberation method.

This paper is presented in the following order: The procedure used is described; first, for measurement of absorption of the longitudinal wave, and then for measurement of the loading effects on a shearing transducer. Next, the theories of behavior expected are presented, with suitable material and references to indicate sources of the theory. The results are then presented as a series of tables and graphs where deviations from theory are pointed out. As a conclusion, an analysis of the effectiveness of the methods used is presented and recommendations are made to improve the methods and to indicate the direction for further study of these solutions.

2. Procedure

A. Procedure (Absorption)

1. General

Assembly "A", shown in Figure 1, was designed and built to fit the base of a long glass column. The center electrode, which provides support for the crystal against the fluid in the column above it, was made sufficiently rough so that vibrational coupling between the crystal and the electrode is negligible. The aluminum coated, 1/4 mil thick "Mylar" film shown in the cross-section sketch of Figure 1 served as the ground electrode for the transducer and as a seal to protect the crystal from direct contact with the solution.

The crystal is bonded to the Mylar film in the following manner: The crystal, an X-cut, 2 mc/s fundamental frequency, 3/4 inch diameter quartz crystal is dusted off, a thin layer of Dow-Corning High Vacuum Grease is applied to one surface, and this surface is pressed firmly onto the center of the Mylar film which is stretched by a crocheting hoop. Air bubbles and excesses of grease between the crystal and Mylar are readily visible to the eye when the upper side of the Mylar is viewed in grazing incidence light. These irregularities can be removed by placing the crystal on a support with the Mylar side up and then gently smoothing the Mylar film outward from the center of the crystal with a flat-surfaced glass rod.

The hoop holding the Mylar and attached transducer is then placed over assembly "A", centering the crystal over the electrode carefully, and the Sealing Ring is then placed on top of the Mylar. By pressing the crocheting hoop down, the Mylar film is drawn tightly across the

face of the assembly. Holes are then punched in the film for the six screws and the Sealing Ring is secured in place, after which the excess film is cut off.

The Mylar film and the Sealing Ring is then sprayed with "Krylon" acrylic lacquer to seal and protect the aluminum coating from corrosion.

Assembly "A" is then inserted into the glass column. Clearances are such that the metal-to-glass fit is tight enough to keep the assembly in the tube with a full head of fluid in the tube. To affect a watertight seal, Cenco Tackiwax is pressed on the glass-metal joint on the outside of the tube.

The entire assembly is then clamped to a tripod-based stand at two points to insure rigidity. Coarse adjusting is done at this time to align the column with the stand. A small spirit level is used to set both stand and column approximately vertical.

The column is then filled with water from a reservoir consisting of a flask and hose connection to Assembly "A". A fluid column height of 10 centimeters is used. The reservoir is clamped to another stand at a suitable height to allow proper fluid height adjustment in the glass column. The shielded cable is connected to the BNC connector on the bottom of the electrode assembly and the circuit shown in Figure 2 is set up.

By pulsing the crystal at one of its odd harmonics using the pulsed oscillator, the crystal generates a longitudinal acoustic wave in the fluid above it. This wave travels up the column, is reflected from the surface without loss (but with 180° phase change), and returns to the crystal where it again is reflected. This travel is repeated

many times until the wave is damped out. Since the base on which the crystal is mounted is neither plane nor rigid, only the first echo is useful for making reliable absorption measurements. This, it is believed, eliminates considerations of diffraction and other interference and transmission effects that are generated by the non-ideal conditions described above.

"Tuning" the column consists of adjusting the stand so that the plane of the surface of the liquid in the column is exactly parallel to the plane of the surface of the crystal. This insures that the amplitude of the wave returning to the crystal is attenuated only by the travel in the fluid and not by any other effects. This condition is indicated on the cathode-ray oscilloscope by a maximum value of the first echo. A picture of such a CRO trace is shown in Figure 3.

Adjustment of the stand is accomplished by means of three threaded supports on the base. Tuning the column is a tedious and time consuming task as any vibration in the fluid column distorts the waves traveling in the fluid and, therefore, the pulse received by the crystal, and consequently shown on the CRO. Any adjustment of the stand, of course, creates a great deal of disturbance in the fluid column. The tuning procedure used is: An adjustment to tune is made, a wait for disturbances to die out, and then another adjustment is made.

2. Electronic Instrumentation

Figure 2 shows a schematic diagram of the equipment used. The time mark generator initiates each pulse of the pulsed oscillator and is set to initiate 100 pulses per second. The pulsed oscillator, when triggered by the time mark generator, applies about a three microsecond

long pulse of voltage at the frequency selected to the crystal.

The crystal oscillates mechanically in response to this voltage (and at this frequency) and generates a longitudinal acoustic wave train in the fluid and then is undisturbed until the acoustic wave echo returns. The crystal picks up this wave and generates the voltage pulse which is transmitted through the attenuator pad, the attenuator block, the preamplifier and amplifier. The amplified signal is presented on the trace on the cathode ray oscilloscope as shown in Figure 3.

The purpose of the attenuator pad is to eliminate any changes in pulsed oscillator driving voltage due to the loading effects caused by variation of attenuation inserted in the circuit by the attenuator block. The 93-ohm termination impedance is in the circuit for impedance matching considerations.

The time mark generator is also used to display its pulses on the face of the CRO for acoustic velocity determination in the solutions tested.

3. Data Collection

Data is collected from this setup in the following manner: The column is filled to the maximum height with the fluid to be studied. Care is taken to insure that the meniscus in the tube is of the same shape at this first reading as it is to be in all the others. Last minute checks are made on the tuning of the pulsed oscillator and adjustment of the pulse length. The criterion in these checks is that the first echo displayed on the CRO trace is of maximum amplitude.

An initial setting of the attenuator is made (usually 10 db) and the echo height is adjusted on the CRO face by means of the gain control on the amplifier. The height used is three centimeters so that there will be some scale remaining for pulse height-attenuation interpolation. (The CRO face is scribed for four centimeters.) The height of the fluid column is measured, by means of a cathetometer. The height of the column is then decreased about one centimeter by draining fluid to the reservoir. Since the path length of the sound travel in the fluid is decreased, the echo amplitude increases. More attenuation is added to the circuit in the attenuator block to reduce the echo to its former amplitude. The new, decreased height of the fluid column is measured with the cathetometer. This procedure is then repeated a number of times.

The data is plotted as shown in Figure 4 and the slope of the line calculated. This slope gives the plane wave attenuation coefficient per unit length in the fluid tested in decibels per centimeter. This sample plot is for a 0.1% polyox solution at 17.9 mc/sec. The slope is found to be 0.654 db/cm ± 0.012 db/cm. This may be compared with the absorption found for water by this same method of 0.676 db/cm ± 0.010 db/cm.

Sound velocity in these fluids is measured by counting the time marks on the CRO trace to the first echo for two different fluid column heights. The differences in the heights divided by the differences in the number of time marks yields the desired result of sound velocity in meters/second to an accuracy of about 0.5%.

B. Procedure (Resistive Loading of Shearing Transducer)

1. General

From the character of the solutions of the polymer it was felt that a method of shear loading measurement was required which would be accurate in the range of the coefficient of shear viscosity of water, i.e., 0.5 to 1.5 centipoise.

A search of the literature shows that there is only one method that has proven effective in practice in the desired frequency range (12). The method involves two matched quartz blocks with optically flat faces and two faces cut at precise angles. Procurement of such blocks was found to be too costly and time consuming for this project. The following method was, therefore, devised.

The most efficient way available to this researcher for generating a shearing wave at high frequencies was the use of a Y-cut quartz crystal. For frequencies in the megacycle range, the crystals are small enough and light enough to actually "float" on a droplet of water. If the drop of water and the floating crystal are placed on the electrode of asembly "A", as shown by Figure 5, with the "grounding plate" in place, this crystal can be pulsed with the pulsed oscillator and the decay of the excited oscillations can be observed on the CRO. The decay rate is determined, in part, by the viscous and elastic loading of the fluid in contact with the oscillating transducer.

By means of the circuit shown in Figure 6 the crystal is pulsed 100 times per second by the pulsed oscillator tuned to the fundamental frequency of the crystal or an odd harmonic of 7 mc/sec.

The crystal response to such pulsing differs slightly from that described earlier for the X-cut crystal. The Y-cut crystal behaves much like a damped harmonic oscillator when pulsed, the vibrations of the crystal dying out exponentially with time. Figure 7 shows pictures of the CRO trace for: (a) the crystal pulsed while lying on a dry electrode and, (b) the crystal pulsed while floating on a droplet of water. The differences between the two traces or rates of decay of vibration is due to the relative impedance loadings of the crystal by (a) the brass electrode and, (b) the water. Since the crystal is not coupled efficiently to the brass electrode, it merely vibrates freely on top of the electrode. For the case of the crystal floating on the water, the coupling between the water and the crystal causes the propagation of a shear wave into the water droplet and consequently increases the damping of the crystal.

Substitution of other fluids, such as analine, metacresol or glycerine in place of the water under the crystal showed a marked difference in reverberation decay rates of the pulsed crystal. The decay rates should be proportional to the shear viscosity and the shear modulus of the fluids.

In an effort to produce pure shearing waves in the fluids tested, it was decided to polish the crystals to a smooth finish. Investigation had shown that the crystals, as furnished, had been etched and that their surfaces were irregular in elevation. Pitting on the surfaces was estimated to be as much as 15 microns in depth. The overall crystal surface, prior to polishing, had the appearance of "frosted glass."

For polishing, three crystals of 1/2 inch diameter and 7 mc/s

basic frequency were cemented to a flat glass block with Duco cement. These crystals were, first, too small to hold individually and polish, and secondly, it was hoped that a flat polished surface on the crystal could be better achieved by using more than one crystal on a polishing wheel. Care was taken to cement the crystals with approximately the same layer of cement between the crystal and the glass block so that all three were at uniform elevation above the glass block. The three crystals were cemented at what were the apexes of a triangular figure to provide the best leveling possible for the glass block as it rested on the polishing wheel.

The crystals were then polished on a standard polishing wheel at low rpm with one micron sized diamond dust and with alcohol as a lubricant. This polishing procedure was not entirely successful since it was found that the crystals were being polished more around their edges than at the center. As a result, it was decided to stop polishing before the crystal surfaces were completely flat.

However, from inspection of the crystals under a 500 power microscope, it is estimated that the crystal face is 96% polished. The other 4% left is in the form of "pitting" in the surface. The appearance of the polished surface of the crystal, when viewed in grazing incidence light is that of clear glass with many minute "stiples" in it. It is estimated that these declivities are on the order of two microns in depth. The rounding over of the crystal at its edges due to the polishing occurred because the polishing wheel was equipped with a felt cover and this cover compressed under the crystals as the wheel rotated. More force was, therefore, exerted on the edges of the

crystals with the resultant greater polishing effect there.

One crystal was found to have lost 0.0059 gm mass (originally 0.0914 gm) and to have increased in frequency from approximately 7 mc/s to 7.10 mc/s due to the polishing operation.

2. Electronic Instrumentation

Figure 6 shows a schematic diagram of the equipment used in this series of measurements. The time mark generator initiates each pulse of the pulsed oscillator and is set to initiate 100 pulses per second. The pulsed oscillator is set to apply its longest pulse of voltage (about 20 microseconds) at 7 mc/sec to the floating crystal. Both the original pulse and the reverberation signal generated by the crystal go to the wide band amplifier to be amplified and then displayed on the CRO trace. The delayed pulsing of the pulsed oscillator is also used to trigger the exponential wave form generator. The signal from the waveform generator is also displayed on the CRO trace by means of a second channel input.

3. Data Collection

By matching the waveform generator trace with the crystal reverberation trace on the CRO, a decay rate of the crystal ringing (in db/sec) can be arrived at from readings of the waveform generator potentiometer setting. (The waveform generator had been previously calibrated.)

With the reading of the "decay rate" from the exponential waveform generator, computations may be made as described later to determine the effect on the crystal of shear modulus and shear viscosity of the solutions tested.

Data for the calibration curve shown in Figure 8 for the crystal were taken to determine the crystal response over a range of loadings and temperatures. By measuring the crystal ringing characteristics on distilled water at various temperatures and then plotting the reverberation decay rate versus the tabulated values of coefficient of shear viscosity of water the crystal response to load is shown. The temperature of the water sample is varied for temperatures below ambient by immersing assembly "A" in a dewar flask filled with ice water up to within .25 cm. of the upper face. As the water bath warms, measurements are taken on the sample of distilled water under the crystal. For temperatures above ambient, the assembly is set in a dewar flask and a hot air blower is used to heat the assembly to any temperature desired. The temperature of assembly "A" is measured by a thermocouple glued to the upper surface with Duco Cement and this is taken to be the temperature of the sample being tested.

Some difficulty was encountered in gathering this data as cleanliness of the crystal proved to be of utmost importance. Any inadvertent touching of the crystal with fingertips, for instance, apparently deposits enough oil on its surface so as to load the crystal and cause an excessively high decay rate when the crystal is pulsed. Another problem found is that condensation occurs on the upper face of the floating crystal as the water bath and assembly "A" are cooled with resultant excessive decay rates being observed again.

Some possible causes of variation in readings of crystal decay rate which were investigated and discarded as having no significant effect on the measurements are: 1) Amount of fluid in sample being

tested; 2) Leveling of electrode (and therefore, crystal) and; 3) Variation of output power of the pulsed oscillator (or proximity of crystal to the electrode).

The amount of solution under the crystal is not critical beyond a minimum amount, since the propagation distance of shear waves in water is approximately 10^{-5} cm at these frequencies (11). Therefore, a drop of approximately 0.5 cubic centimeters is more than sufficient, as this elevates the crystal about 0.3 cm. above the electrode.

The increase of output power of the pulsed oscillator or the decrease of distance between the crystal and the electrode affects only the amplitude of the signal from the crystal and not the decay rate of the vibration.

3. Theory

A. Theory (Absorption)

Several theories have been advanced to account for absorption of sound waves in water, the one most generally accepted being the theory of Hall (3). However, for purposes of this report, classical absorption, modified to include bulk viscosity, will serve to explain the phenomena observed. Considering only the classical viscosity and heat conduction as the source of dissipation, attenuation of the wave will be given by the formula (11):

$$\alpha(\text{nepers}/\text{cm}) = \frac{2\pi^2 f^2}{\rho v^3}\left[\frac{4}{3}\eta + \eta' + \frac{(\gamma-1)K}{C_p}\right]$$

A term involving η' accounts for losses due to bulk viscosity, the term involving η denotes losses due to shear viscosity and the term involving $(\gamma - 1)$ accounts for losses due to heat conductivity. This latter term is usually discarded since the effect is small in most liquids (11).

Using the first two terms and the experimentally determined absorptions for distilled water it is found that (6):

$$\frac{\alpha}{f^2} = \frac{\alpha_{\text{shear}}}{f^2} + \frac{\alpha_{\text{bulk}}}{f^2} = 24 \times 10^{-15}\ \text{sec}^2/\text{m}$$

where $$\frac{\alpha_{\text{shear}}}{f^2} = 8.1 \times 10^{-15}\ \text{sec}^2/\text{m}$$

or approximately one-third of total absorption.

The other two-thirds of the attenuation may be accounted for by the bulk viscosity. The data taken is discussed in the "Results" section of this report but it is to be noted here that absorption data taken on the polyox solutions shows that the absorption measured to be substantially that of distilled water.

B. Theory (Resistive Loading of Shearing Transducer)

When the transducer oscillates with a shearing motion when in contact with the solution, external sources of damping may be considered to be due to two factors: a resistance due to the shear viscosity of the fluid and to a radiation impedance due to the shearing modulus of the liquid. For fluids where $\omega t_s \ll 1$ both classical theory and relaxation theory agree that the mechanical resistance is given by (4):

$$R_s = \left(\frac{\omega\eta\rho}{2}\right)^{\frac{1}{2}}$$

This is true for water at the frequency of 7 mc/s used in this work since t_s is of the order of 10^{-10} sec (6). For the case of high viscosities or high frequencies, $\omega t_s \gg 1$, since t_s is proportional to η. Relaxation theory predicts that the resistance will reach a constant value, as $\omega\eta$ becomes large (4). The resistance is then given by:

$$R_s = \left(\rho G_\infty\right)^{\frac{1}{2}}$$

where G_∞ is the limiting shear modulus of the fluid.

Mason points out, in discussing his researches into solutions of polyisobuytlene in cyclohexane, that the viscous attenuation of sound waves at intermediate frequencies occurs in a slightly greater amount in polymer solutions than in the pure solvent (10). This is due to the fact that the motion of the solvent molecules causes only slight motion in the long chain molecules. This induced motion abstracts some energy from the sound wave. At very high frequencies, Mason found that the viscosity of the polymeric solution was essentially that of the pure solvent. He explains this as being due to the inability of the solvent molecules to cause the solute molecules to move at such high frequencies. Therefore, the solvent molecules move as through the solute were not present.

Mason's phenomenological explanation is considered to describe the situation in the polyox solutions at 7 mc/s. Since the longitudinal absorption data collected shows that there is no apparent increase in $\eta + \lambda$ shear and bulk viscosity in these solutions, the excess damping of the Y-cut quartz crystals by the polyox solutions over that of water is assumed to be due to a shear radiation resistance of the hydrated polyox molecules in the water solution.

Since the resistance offered to the vibrating crystals by the polyox solutions was found to be greater than that offered by the distilled water, a series resistance effect is assumed to best describe the solutions tested. The equation describing this behavior, in terms of specific resistance is:

$$R_{TOTAL} = R_{CRYSTAL} + R_{WATER} + R_{POLYOX}$$

where R_{TOTAL} and $(R_{CRYSTAL} + R_{WATER})$ were measured. By means of

this equation and use of the relaxation theory equation to describe the effects of the hydrated polyox molecules, a value for the shear modulus of the polyox molecules may be determined.

For the method used for determination of shear moduli, a conversion from observed decay rate of the signal to mechanical resistance of the subject solution was derived. Basically, assumptions must be made concerning the vibrational behavior of the Y-cut quartz crystal afloat on the droplet of solution. If the crystal is regarded as a damped harmonic oscillator which is set into motion by the pulsing from the pulsed oscillator, the decay rate of the crystal vibrations after pulsing is a function of the crystal mass and the impedance presented to the crystal by itself and the solution upon which it floats. The resistance may be computed from the relation, $R_m = 2\alpha m_{eff}$ which is derived by considering that the differential equation of motion,

$$m\ddot{x} + R_m\dot{x} + kx = 0$$

to have the solutions, $x = Fe^{\Gamma t}$

where
$$\Gamma = -\alpha \pm j\beta$$
$$= -\frac{R_m}{2m_{eff}} \pm \sqrt{\left(\frac{R_m}{2m_{eff}}\right)^2 - \frac{k}{m_{eff}}}$$

where $\frac{k}{m_{eff}} > \left(\frac{R_m}{2m_{eff}}\right)^2$ is assumed.

By considering the crystal to be vibrating in a one dimensional normal mode with particle velocity:

$$\bar{v} = v_0 \cos k_n x$$

and kinetic energy: $KE = \frac{1}{2} m v^2 = \frac{\rho s}{2} \int_0^L \bar{v}^2 \cos^2 k_n x \, dx$;

the boundary conditions $\bar{v} = v_0$, $x = 0, L$

apply and $k_n = n\pi / L$. Solving for the effective mass, it

is found that $m_{eff} = \frac{\rho s L}{2} = \frac{m_{actual}}{2}$ for all normal mode frequencies.

4. Results

A. Absorption Measurements

Table No. 1 displays the results of the measurements of absorption in distilled water and polyox solutions of 0.025%, 0.05%, 0.1%, 0.25%, and 0.375% (by weight) at the frequencies of 10.1, 17.9 and 26.1 mc/s. The theoretical values of absorption in distilled water are listed also, for comparison purposes, and were determined from the square law dependence formula, $\alpha/f^2 = 24 \times 10^{-15}\ \mathrm{sec}^2/\mathrm{meter}$ as described previously. Table No. 2 contains the values measured for the velocity of ultrasonic pulses in water and the polyox solutions.

It is apparent that the absorption coefficient and the velocity for longitudinal waves in the solutions studied is equal to that in pure water at the same temperature and frequency, to within experimental uncertainty.

B. Shearing Transducer Measurements

Figures 9 and 10 display the results of measurements taken on the polymer solutions with the shearing crystal.

Following the argument presented in section 3B, the damping resistance due to the shear modulus of the solution is determined by multiplying by appropriate constants, the difference between the decay rate of the reverberation in the transducer when in contact with the solution and when in contact with water (at the same temperature). This difference is thus assumed to be entirely due to propagation of elastic shear waves into the fluid by the transducer. Figures 9 and 10 are plots of shear moduli versus temperature and solution concentration respectively.

C. Experimental Uncertainties

1. Absorption Measurements

The general uncertainties in the measurement of the absorption of longitudinal waves have been discussed. To be more specific, the following estimation of uncertainties is included. Each height measured in the fluid column was measured with a cathetometer to ± 0.01 cm. Attenuation required to be added to the circuit as acoustic path length was decreased was limited by the equipment to ±1db. However, with interpolation on the CRO face this uncertainty is reduced to ± 0.2 db. The net uncertainty in each reading is, therefore, no greater than 2% since at least 10 db of initial attenuation was placed in the circuit. Figure 5, referred to previously, is a typical plot of the data taken in absorption measurements and the uncertainty in slope, or absorption per unit length, is also typical at ± 0.012 db/cm.

Velocity measurements were taken as differences in column heights (± 0.02 cm) divided by differences in time. The time differences were taken by counting one microsecond time marks, from initial pulse to first return of first echo for each height and then subtracting. Again, interpolation was performed between individual time marks to ± 0.1 microsecond. Therefore, time was measured to ± 0.2 microseconds. For an overall path difference of 10 cm and time difference of approximately 66 us, the uncertainty in velocity is ± 0.5%.

2. Shearing Transducer Measurements

Since temperatures were determined with a chromel-alumel thermocouple to ± 0.05 C., no correction was made for temperature uncertainties.

Determination of the decay rate of the crystal ringing characteristic is a function of calibration of the exponential waveform generator and fitting of the exponential trace to the ringing signal. Calibration of the waveform generator was carried out to an estimated uncertainty of ± 0.3 db/ms. The fitting of the wave form to the ringing trace is estimated to be good to ± 1.5 db/ms. The large uncertainty is due to the lack of uniformity in the decay rate trace with different solutions and temperatures and the requirement of fitting the curves in exactly the same manner each time a measurement is taken. Therefore, the difference in decay rates of polyox solution and water has an uncertainty of ± 3 db/ms or, the shear modulus has an estimated uncertainty of ± 550 dynes/cm^2. This uncertainty is quite large for the values of moduli of the low concentration solutions (0.025, 0.05 and 0.10%) at the temperatures of 23°C and 43°C. However, it is quite good for the 0.5% by weight polyox solution since the range of moduli measured for it are on the order of 10^4 to 10^5 dynes/cm^2.

5. Discussion of Results

A. Absorption

Since both the velocity of sound and the absorption characteristics of the polyox solutions are the same as those of water, the assumption made in describing the theory of behavior of these solutions, that the shear viscosity of the polyox solutions is substantially the same as that of water, seems to be correct.

This result appears at first glance, surprising. First, in physical appearance, these solutions are distinctly more viscous than water. For example, the ordinary shear viscosity coefficient for a 0.1% solution at 20° C. is 20 centipoise (18). It might be expected, then, that the attenuation of a longitudinal acoustic wave will be somewhat greater in the polymer solutions than in water.

The explanation of this apparently anomalous behavior is that a part of the shear viscous effects have "relaxed" at the high frequencies. In fact, it has been found that the value of α/f^2 for some concentrated polymer solutions varies inversely with the frequency (2). However, the solution components were not identified in the reference cited and it is assumed that they did not include a polar solvent such as water.

The errors between the theoretical and measured values of absorption in water shown in Table No. 1 are typical of the accuracy of the equipment at the frequencies used. The large error at 10 mc/s occurred, in part, because of the longer column length needed to avoid diffraction effects requiring, therefore, finer tuning of the column which was, apparently, not possible. Further, there are small, inherent errors in the method of measurement, which are mag-

nified at the lower frequencies due to the smaller absorption in water at these frequencies. These inherent errors lie in the requirement of interpolating between two values of attenuation (introduced into the circuit at the attenuator block) with the amplitude of the first echo displayed on the CRO face. In this interpolation, rounding off to ± 0.1 db is used. In addition, the attenuation pad is not completely effective in isolating the variable attenuator from the pulser so that there is some slight variation in pulse amplitude introduced by the increasing level of electrical attenuation is the circuit as the acoustic path length is decreased.

The most fruitful ways to improve the system accuracy of this method of absorption measurement are, first, to eliminate the vibration present in the long fluid column by some method of vibration isolation of the tripod-based stand; and, secondly, to use an attenuator block with more and smaller graduations of attenuation for more accurate attenuation determination.

B. Shearing Transducer Measurements

The reverberation decay rate of the crystal mounted on a water sample subtracted from the decay rate of the crystal on the polyox solution sample should eliminate the effect of loading on the crystal due to the water. Since the resulting difference is only multiplied by the appropriate constants and then squared to yield the value of the shear modulus, no extraneous effects are introduced into the data by processing.

The method of measurement has also ruled out aberrations in the measuring devices from effect on the data. For instance, the crystal

transducer used experiences at least one change in mode with temperature and/or loading. This is demonstrated by Figure 8, a plot of crystal reverberation decay rates measured as a function of viscosity of fluid (water in this case). The comment that temperature effect is shown by this plot is made on the basis that the crystal and the water sample were heated/cooled to take some data points where water has a low/high coefficient of shear viscosity. An additional value of this curve is that it shows exactly the behavior of the crystal in contact with the solvent of the test (aqueous) solutions. It is noted that one other fluid, analine, was used in collecting data for this curve. It was used to find the reverberation decay rate for a fluid with a coefficient of shear viscosity of 4.4 centipoise.

Figure 11 is included to demonstrate the nature of distortion in measurements that are present in the use of the shearing transducer. This plot of the variation in coefficient of shear viscosity of water with temperature has an entirely different shape than that of Figure 8, the crystal calibration curve. It may be assumed, then, that the reverberation decay rate of the crystal transducer is not only a function of loading, but that other factors enter into consideration. This is further evidenced by the following: if water is considered to have no elasticity at 7 mc/sec, the assumption that the pulsed shearing crystal vibrates as a damped harmonic oscillator enables us to calculate the coefficient of shear viscosity of water as measured by the crystal. Such a calculation yields a value for decay rate of 82 db/msec of $\eta = 0.6$ centipoise for the temperature of 23° C. The actual value (from viscosimeter data) is 0.94

centipoise. A possible reason for this is that there is some uncertainty as to the exact mode of vibration of the crystal (the shear vibrations may be coupled to flexural vibration modes). Another is the possibility of imperfect generation of plane shear waves into the water sample, due to the previously mentioned surface roughness and the rounded edges of the crystal.

As pointed out before, however, these effects should have been removed by the nature of the measurements and computations. The values determined for the shear moduli then, should be the true values for the hydrated polyox molecules.

Mason has published results of measurements of the characteristics of the polymer polyisobutylene and the characteristics of solutions of polyisobutylene in cyclohexane (11). These solutions may be assumed generally to approximate, in macroscopic behavior, the characteristics of the polyox solutions studied here since the molecular weight of polyisobutylene is approximately 3,900,000 and the density of cyclohexane is about 0.8 gm/ml.

The characteristics of the variation of shear elasticity of the polyisobutylene solution as a function of temperature as found by Mason are approximately an order of magnitude less than those found for polyox solutions. However, the shear moduli of the polyox solutions at 4° C. are three orders of magnitude greater than those of the polyisobutylene solution.

This discrepancy at the temperature of 4° C. for the solvent cannot be explained by the uncertainty in the data. While the uncertainty in measurements made with the shearing crystal is quite

large ($\pm$ 550 dynes/cm^2), the value of the shear moduli of the polyox solutions measured at 4° C. is large enough that the percentage uncertainty is quite small.

As far as it can be determined from the work of Mason and others the shear elasticity does not increase so radically with lowered temperatures. In examining the theory used in this paper to describe behavior of these solutions there is one assumption that may prove faulty and explain the wide variation in moduli with temperature. That is, based on the absorption measurements at 23° C., it is assumed that the shear viscosity of the polymer solutions is the same as that of water, since the absorptions were virtually the same. At the temperature of 4° C., this may not be true, and the effect measured may be due to a changed shear viscosity.

The fact that there is a large change in slope of the shear elasticity curve when plotted against reciprocal absolute temperature would mean that these solutions do not conform to Eyring's theory (1). Mason has noted that the solutions of polyisobutylene in benzene do not conform either. This theory, based on a molecular model and motions of the molecules in whole or in part with respect to potential wells, yields a viscosity proportional to $\exp(-\Delta E/RT)$ where ΔE is the activation energy for shear motion. That these solutions exhibit non-Arrhenius behavior should not be surprising since the solute molecules are so large and long compared to the solvent molecules. Motion on the part of these molecules in solution as, has been pointed out in reference (7) requires that a "cooperative effect" must play a role in response to shearing forces. The cooperation exists between polymer molecular segments.

The shear modulus of these solutions, as determined by the method outlined in section 3B, does not conform to either measurements made of other, generally similar solutions, (Mason's work), or to theory advanced to explain a more uniform behavior. However, with the data collected, no more information on the behavior of these solutions can be deduced. To draw some concrete conclusions for polyox solutions, more data are required.

The data which would be of immediate value are the longitudinal wave absorption coefficients at 4° C. in these solutions. This information would show immediately if the assumption that these solutions have the same shear viscosity as water is correct at all temperatures.

In addition, the possibility of propagation of a non-uniform shearing wave into the samples under the shearing transducer requires exploration. The "semi-polished" crystal transducer used to collect the data in this project was found to be somewhat more uniform in response to pulsing under loading than an unpolished transducer. From this, it may be expected that a transducer with an optically flat and polished face might give even better results in measurements.

6. Conclusions and Recommendations

It is concluded from the data gathered that the sound absorption coefficient and the acoustic wave velocity in dilute polyethylene oxide solutions at room temperature is the same as that found in water under similar conditions. Since there is additional damping of the shearing transducer on the polymer solutions over that of water, it must be explained by the presence of a shear modulus. It is concluded that relaxation of shear viscosity in these solutions occurs at frequencies lower than 7 mc/sec.

Further, the simplified relaxation theory of behavior of these solutions, as described in this paper, is insufficient to describe the effects existent in the solutions at low temperatures, since the solutions demonstrate non-Arrhenius behavior.

Last, it is concluded that better precision in determination of shear moduli must be achieved before more concrete results will be obtained.

With respect to the use of a shearing crystal as described herein it is recommended that a Y-cut or BT-cut crystal with at least one optically flat and polished face be substituted for the partially polished crystal used in this project. It is also recommended that absorption of these solutions be measured at low temperatures at the frequencies previously used to clarify the behavior of these solutions at those temperatures. Lastly, to determine more information on the relaxation of the shear viscosity, it appears that the frequency range should be extended into the low kilocycle per second range.

7. BIBLIOGRAPHY

1. Eyring, H. Viscosity, Plasticity and Diffusion as Examples of Absolute Reaction Rates. J. Chem. Phys. v. 4, April, 1936: 283-291.

2. Gotlib, Yu. Ya. and K. M. Salikhov. Theory of Ultrasonic Absorption in Concentrated Polymeric Solutions. Soviet Physics-Acoustics, v. 9, Mar., 1963: 246-251.

3. Hall, L. The Origin of Ultrasonic Absorption in Water. Phys. Rev., v. 73, April, 1948: 775-781.

4. Herzfeld, K. F. and T. A. Litovitz. Absorption and Dispersion of Ultrasonic Waves. Academic Press, 1959.

5. Hueter, T. F. and R. H. Bolt. Sonics; Techniques for the Use of Sound and Ultrasound in Engineering and Science. J. Wiley & Sons, Inc., 1955.

6. Kinsler, L. E. and A. R. Frey. Fundamentals of Acoustics, 2nd Ed. J. Wiley & Sons, Inc., 1962.

7. Litovitz, T. A. and G. E. McDuffie, Jr. Comparison of Dielectric and Mechanical Relaxation in Associated Liquids. J. Chem. Phys. v. 39, August, 1963: 729-734.

8. Markham, J. J., R. T. Beyer and R. B. Lindsay. Absorption of Sound in Fluids. Rev. of Modern Physics, v. 23, October, 1951: 353-411.

9. Mason, W. P. Electromechanical Transducers and Wave Filters. D. Van Nostrand Co. 1948.

10. Mason, W. P. Measurement of the Viscosity and Shear Elasticity of Liquids by Means of a Torsionally Vibrating Crystal. Trans. ASME, v. 51, May, 1947: 359-370.

11. Mason, W. P. Piezoelectric Crystals and Their Application to Ultrasonics. D. Van Nostrand Co., 1950.

12. Mason, W. P., W. O. Baker, H. J. McSkimin and J. H. Heiss. Measurement of Shear Elasticity and Viscosity of Liquids at Ultrasonic Frequencies. Phys. Rev., v. 75, March 1949: 936-946.

13. Mason, W. P., W. O. Baker, H. J. McSkimin and J. H. Heiss. Mechanical Properties of Long Chain Molecule Liquids at Ultrasonic Frequencies. Phys. Rev., v. 73, May, 1948: 1074-1091.

14. Mason, W. P. and H. J. McSkimin. Mechanical Properties of Polymers at Ultrasonic Frequencies. Bell System Tech Journal, v. 32, January 1952: 122-171.

15. Oceanic Research Group, U. S. Naval Ordnance Test Station, Pasadena, California. Note on Torpedo Drag Reduction With a Non-Newtonian Turbulent Boundary Layer, by A. G. Fabula, July, 1961. Tech Note P 508-18.

16. O'Neil, H. T. Reflection and Refraction of Plane Shear Waves in Viscoelastic Media, Phys. Rev., v. 75, March, 1949: 928-935.

17. Rouse, P. E. A Theory of the Linear Viscoelastic Properties of Dilute Solutions of Coiling Polymers. J. Chem. Phys., v. 21, July, 1953: 1272-1280.

18. Union Carbide Chemicals Company, Division of Union Carbide Corporation. "UCAR" Polyox Water Soluble Resins. October, 1962. Advance Technical Information Bulletin F-40246-B.

19. Wilkinson, W. L. Non-Newtonian Fluids; Fluid Mechanics, Mixing and Heat Transfer. Pergamon Press, 1960.

20. Zimm, B. H. Dynamics of Polymer Molecules in Dilute Solution: Viscoelasticity, Flow Birefringence and Dielectric Loss. J. Chem. Phys., v. 24, February, 1956: 269-278.

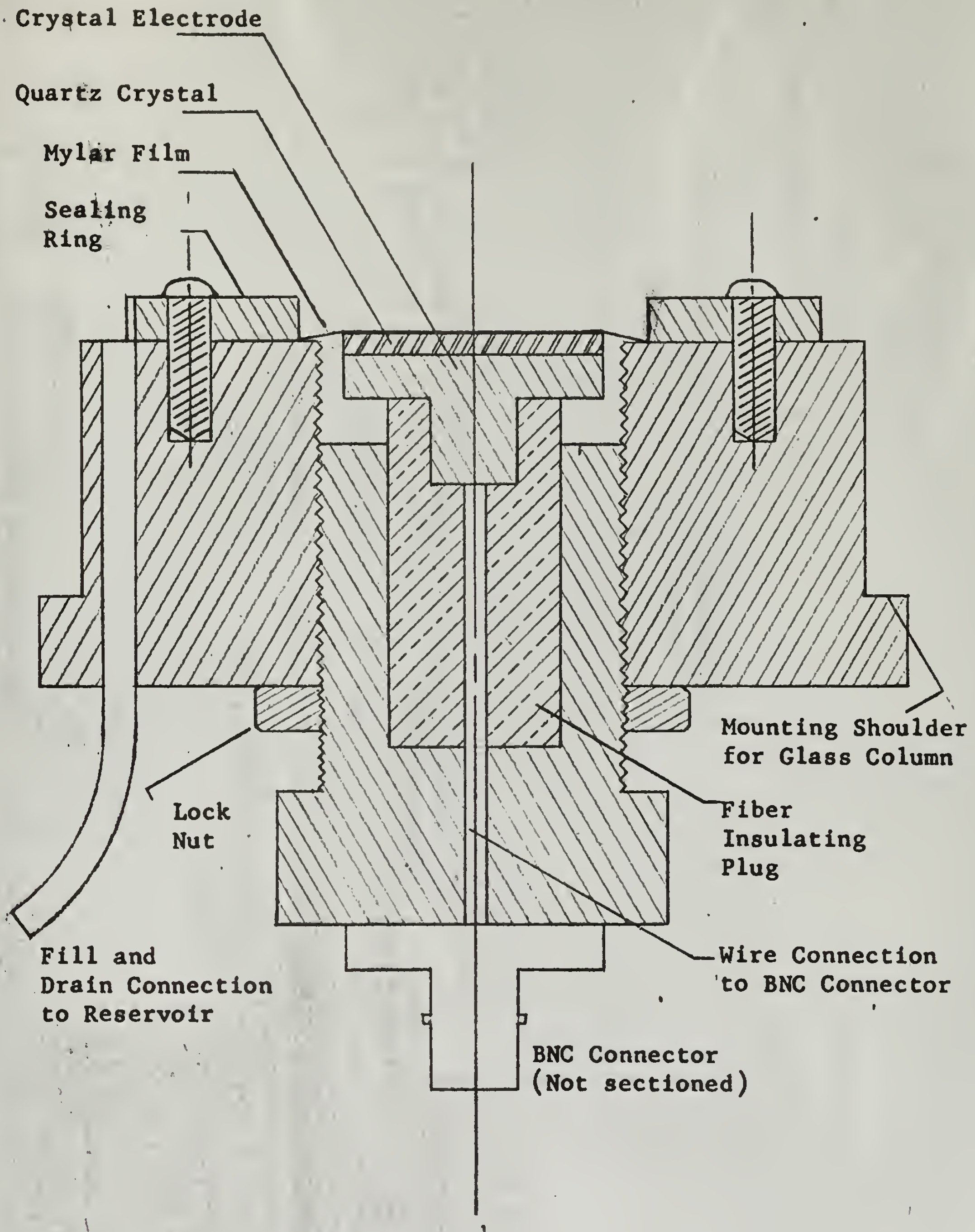


Figure 1
Assembly "A"
Transducer Mounting Assembly as used for Absorption Measurements
Scale 1" = 1/2" actual

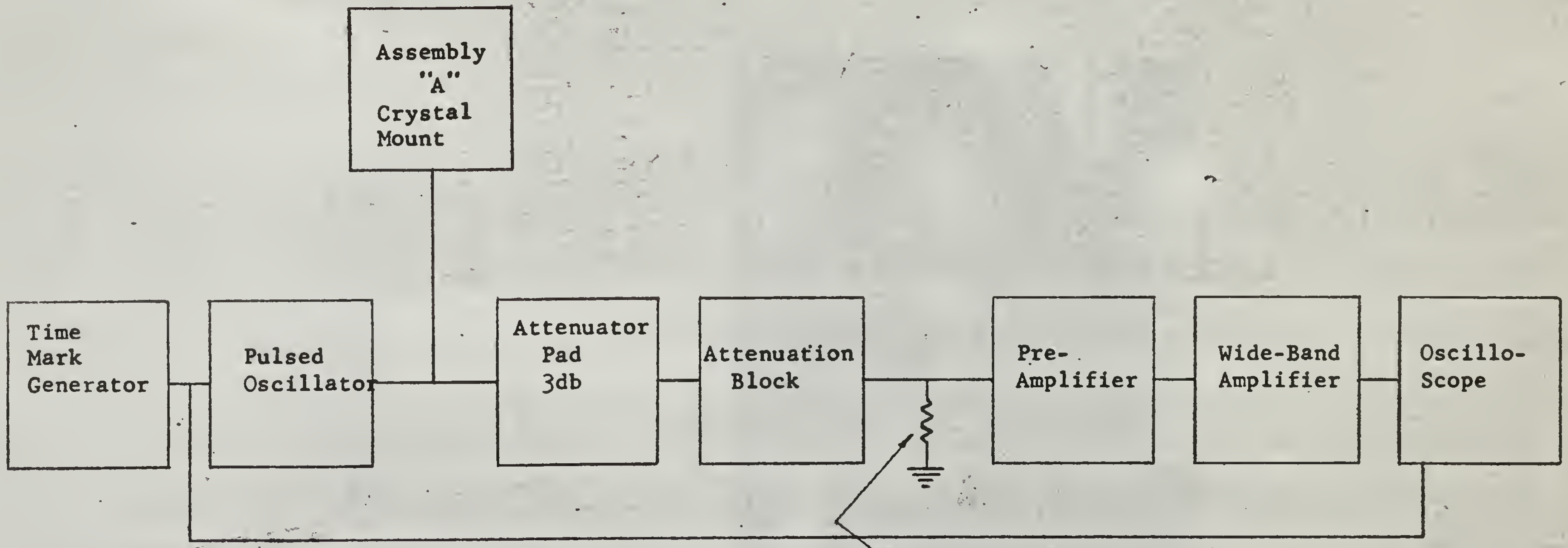
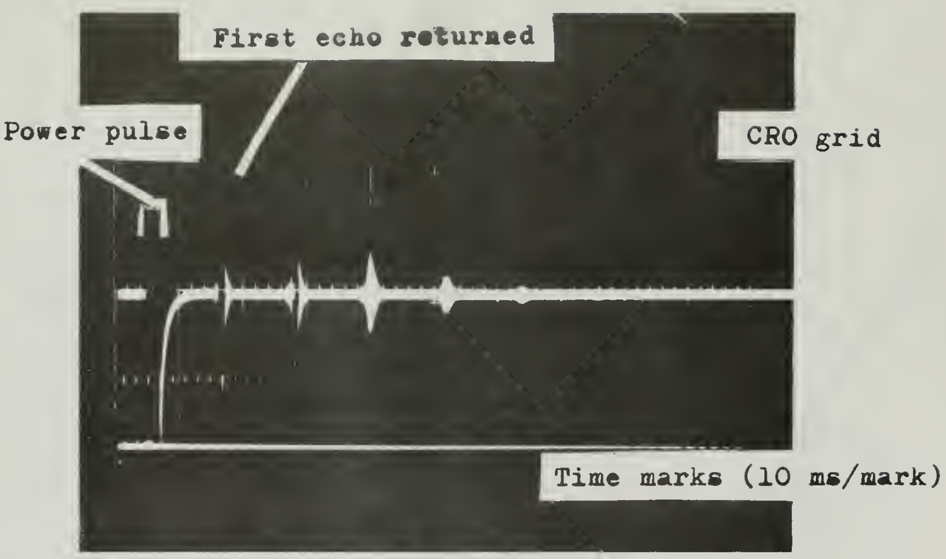


Figure 2
Circuit Schematic
Absorption Measuring
Circuit



f = 17.9 mc/sec

FIGURE 3:

TYPICAL OSCILLOSCOPE TRACE
ABSORPTION MEASUREMENT

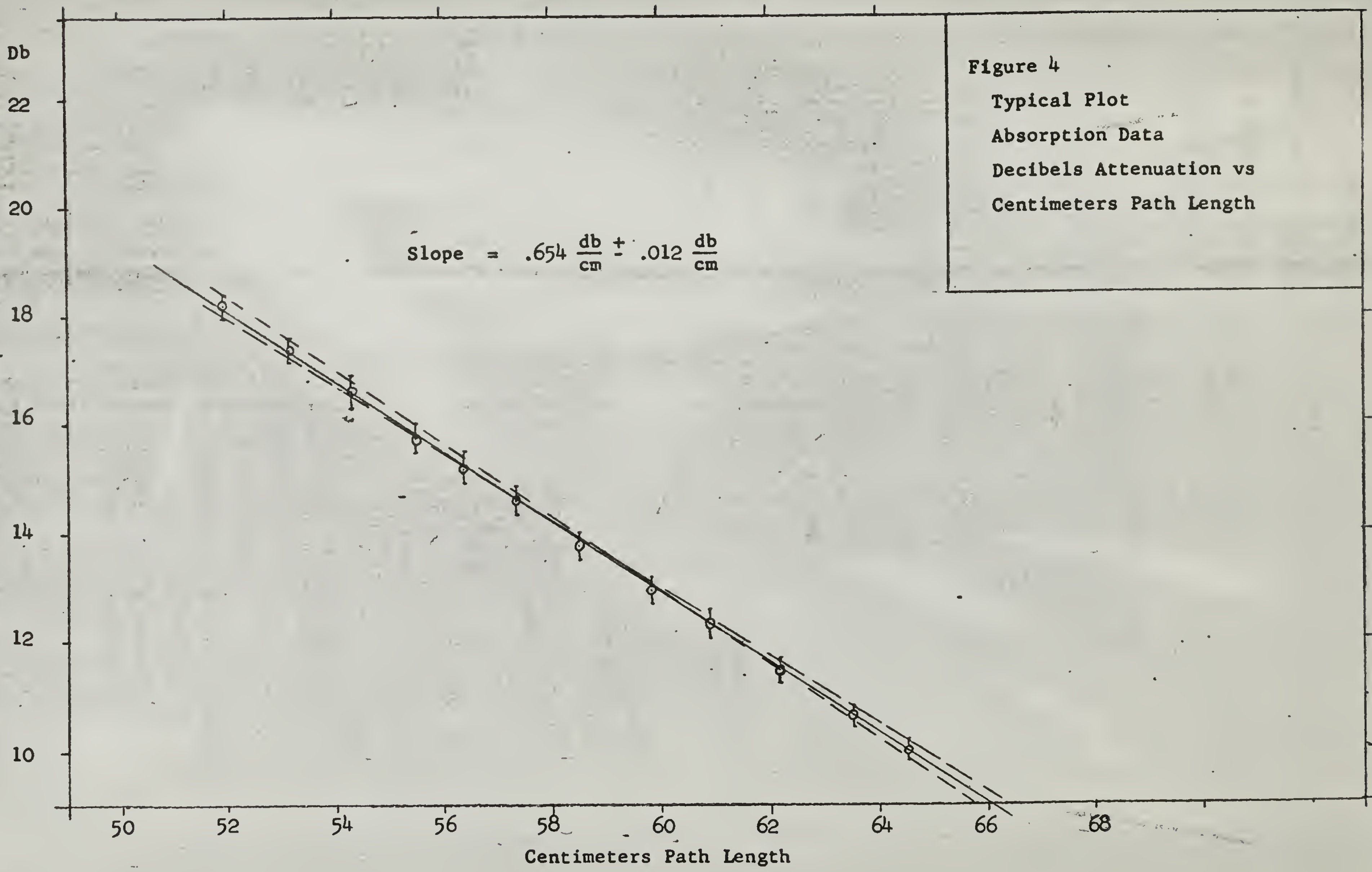


Figure 4
Typical Plot
Absorption Data
Decibels Attenuation vs
Centimeters Path Length

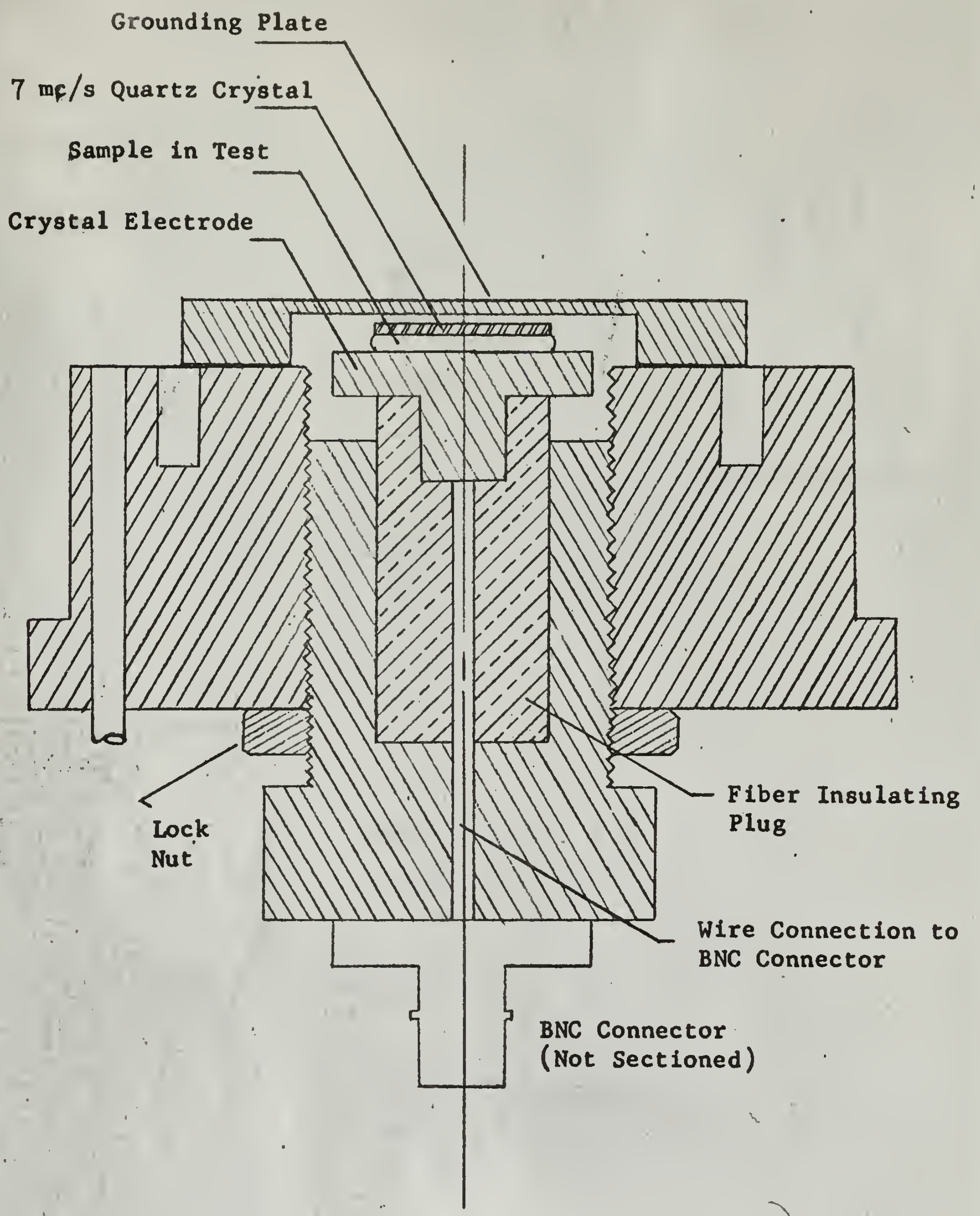


Figure 5

Assembly "A"

Transducer Mounting Assembly

As used for Shearing

Resistance Measurements

Scale 1" = 1/2" Actual

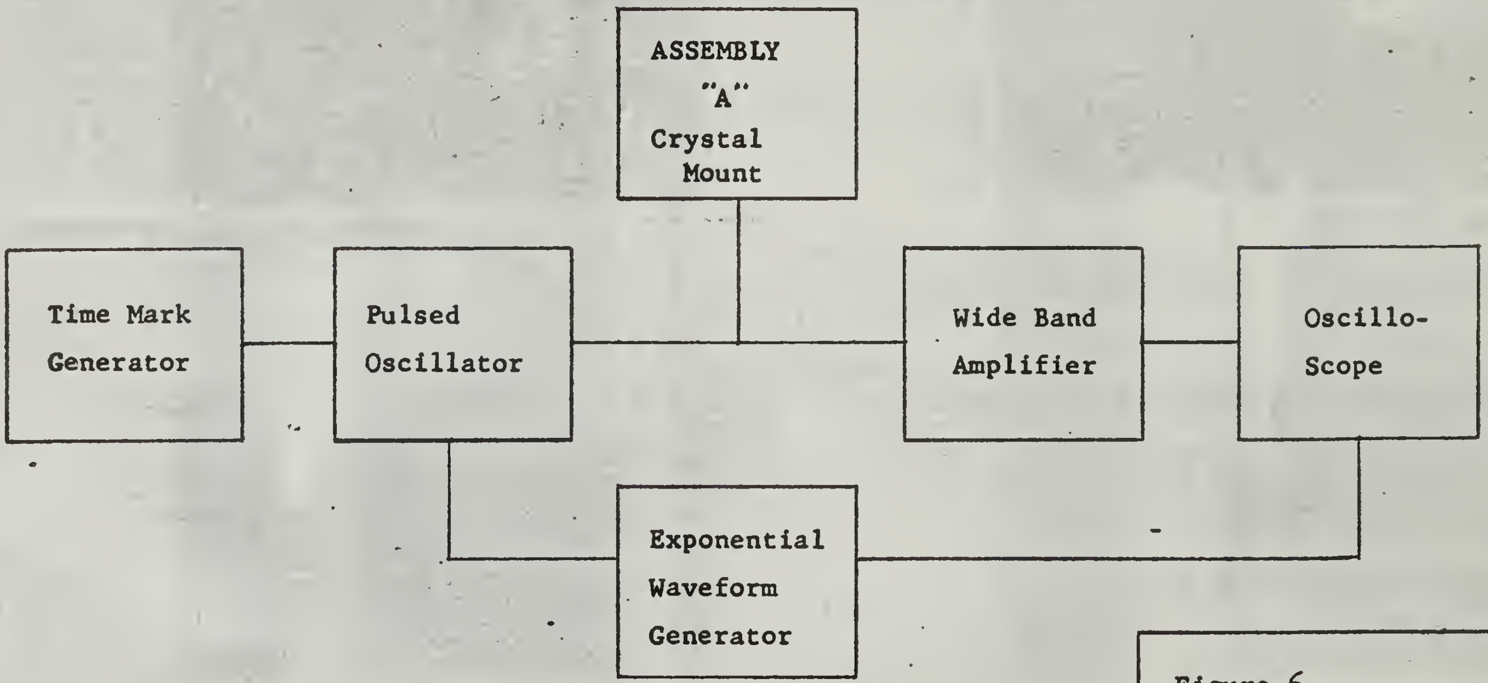
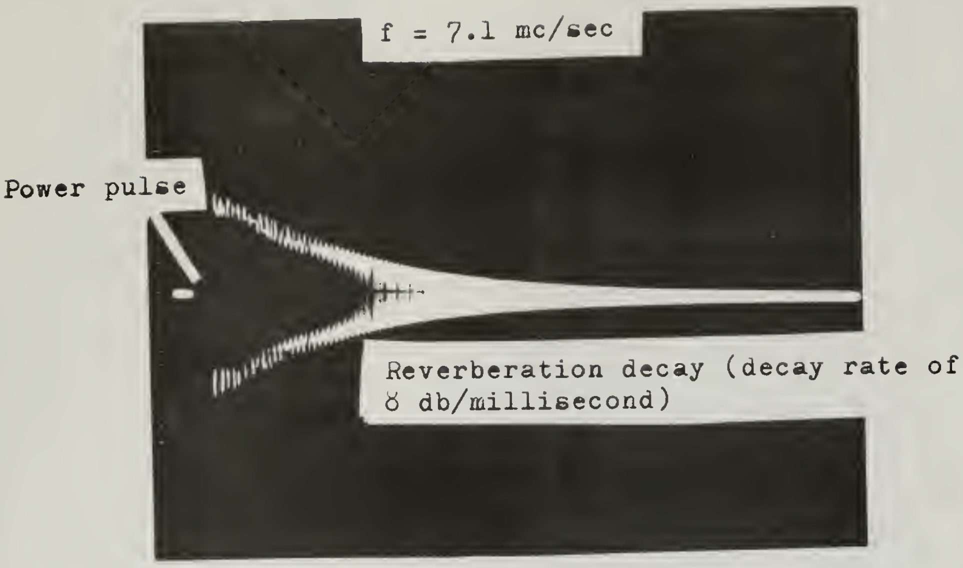
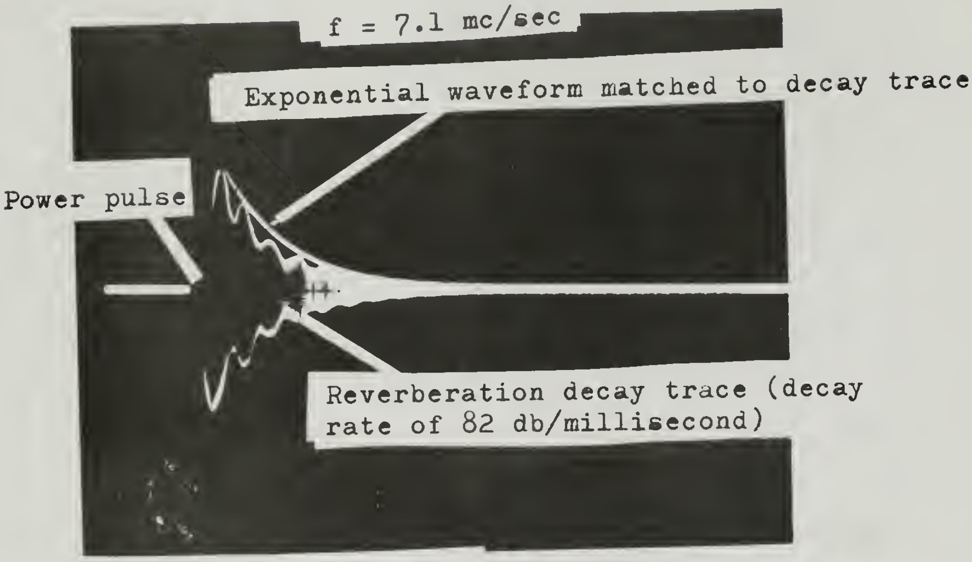


Figure 6
Circuit Schematic
Shearing Resistance
Measuring Circuit



a) Crystal on Dry Electrode



b) Crystal on Water Droplet

FIGURE 7:

OSCILLOSCOPE TRACES; SHEARING RESISTANCE MEASUREMENTS

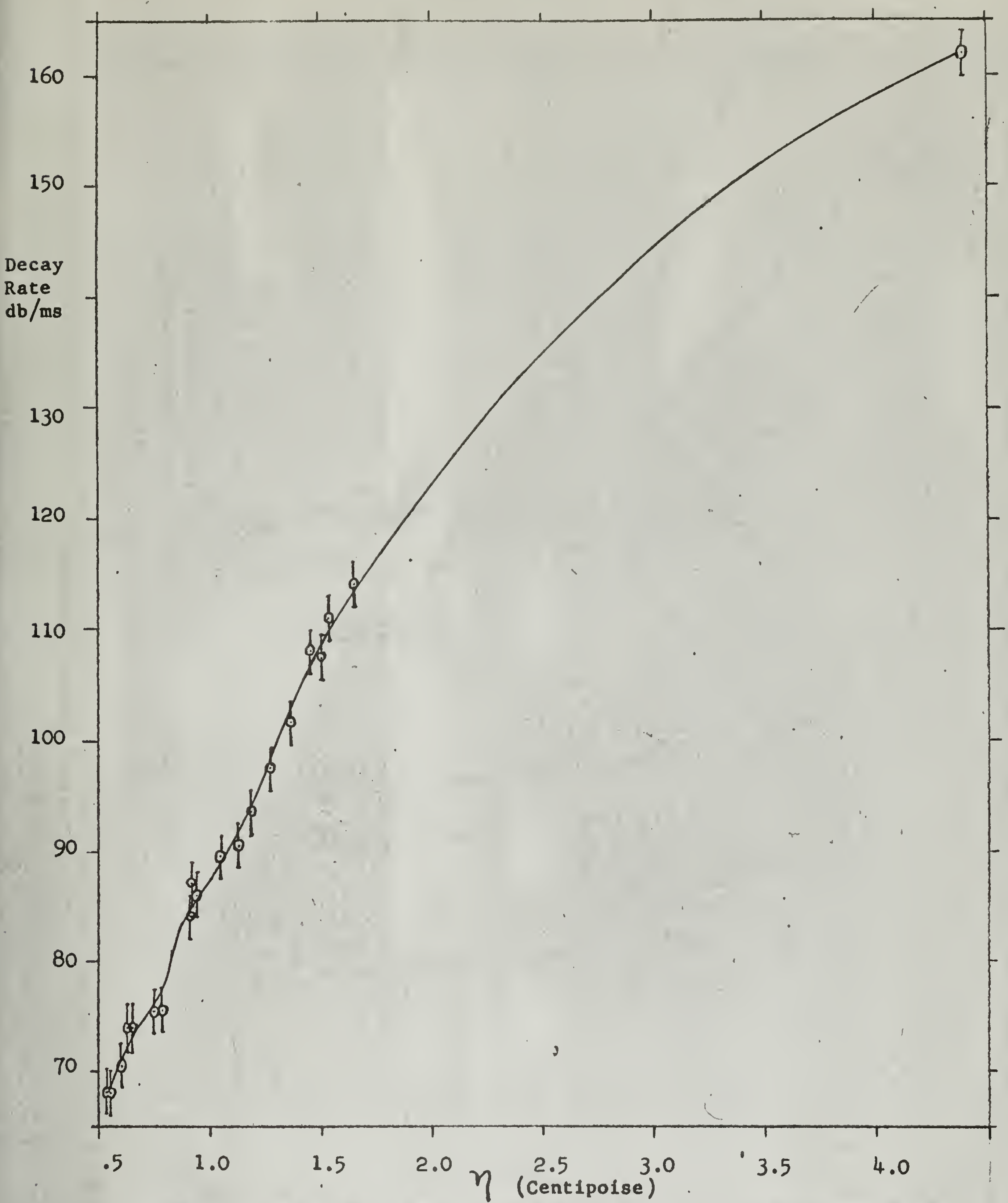


Figure 8. Crystal Calibration Curve for 7 mc/s Y-Cut Quartz Crystal Reverberation Decay Rate (db/ms) vs Coefficient of Shear Viscosity of Solution under Crystal

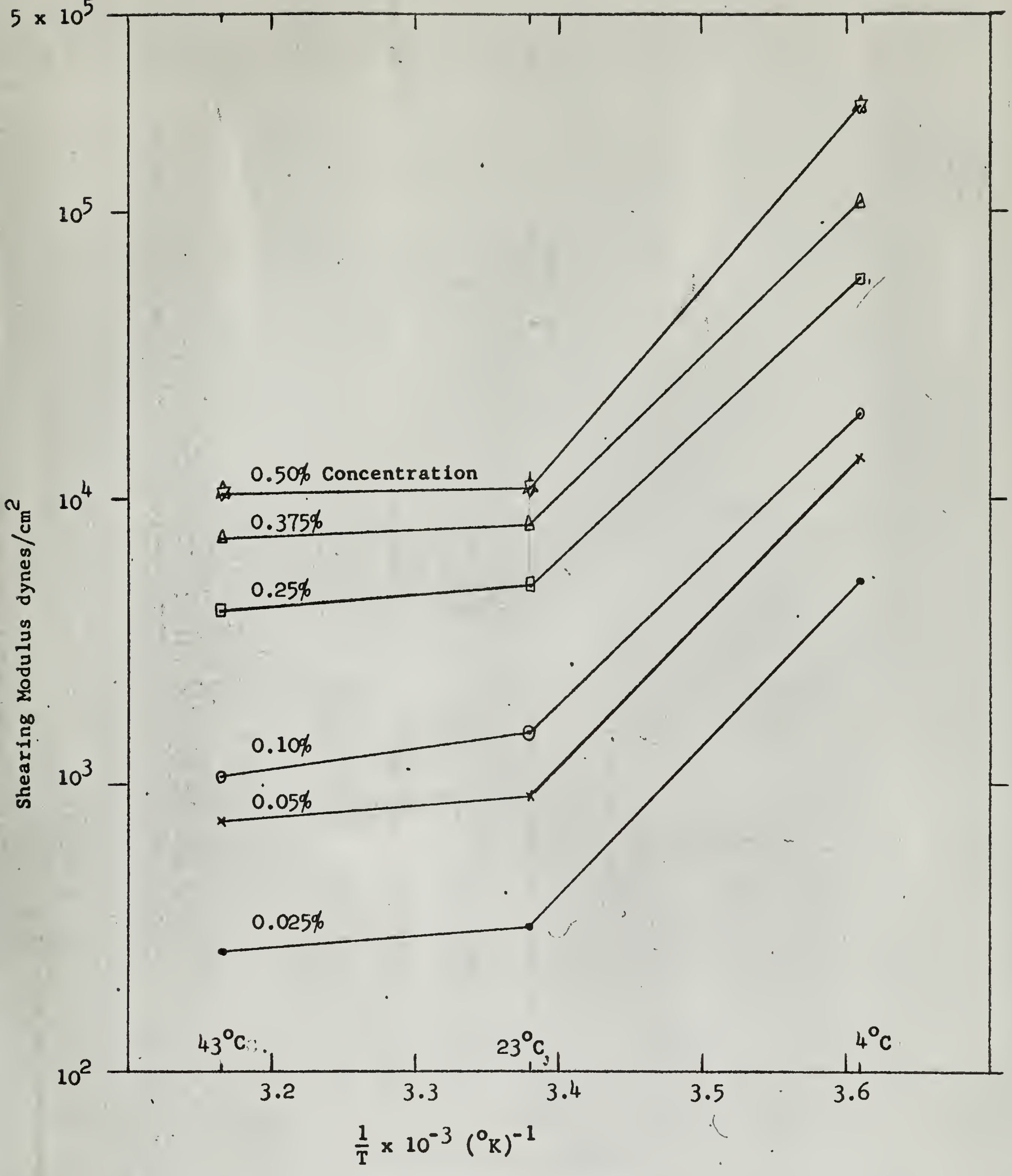


Figure 9. Plot of Shearing Moduli versus Reciprocal Absolute Temperature for Several Concentrations of Dilute Polyox Solutions

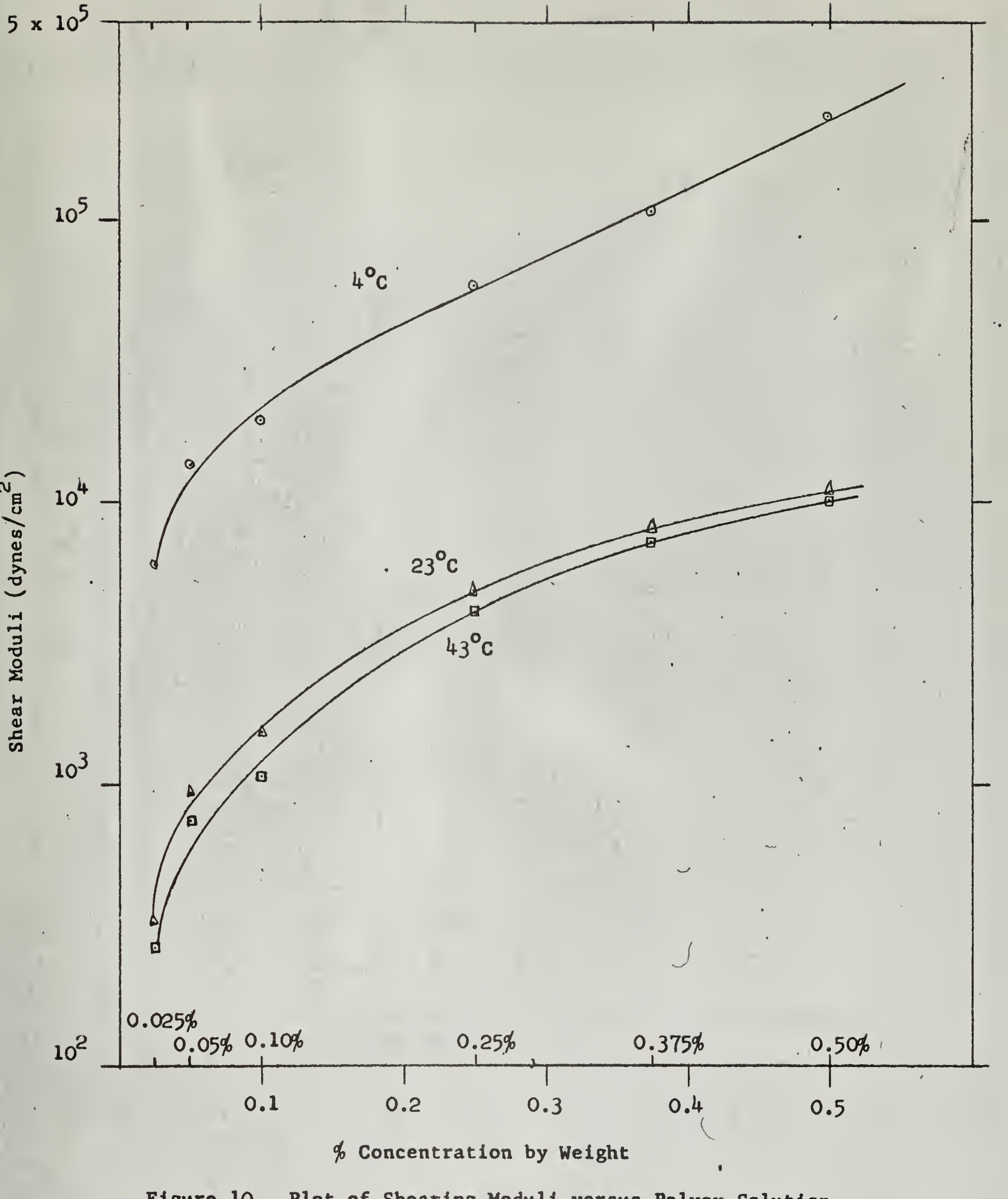


Figure 10. Plot of Shearing Moduli versus Polyox Solution Concentration for Three Temperatures

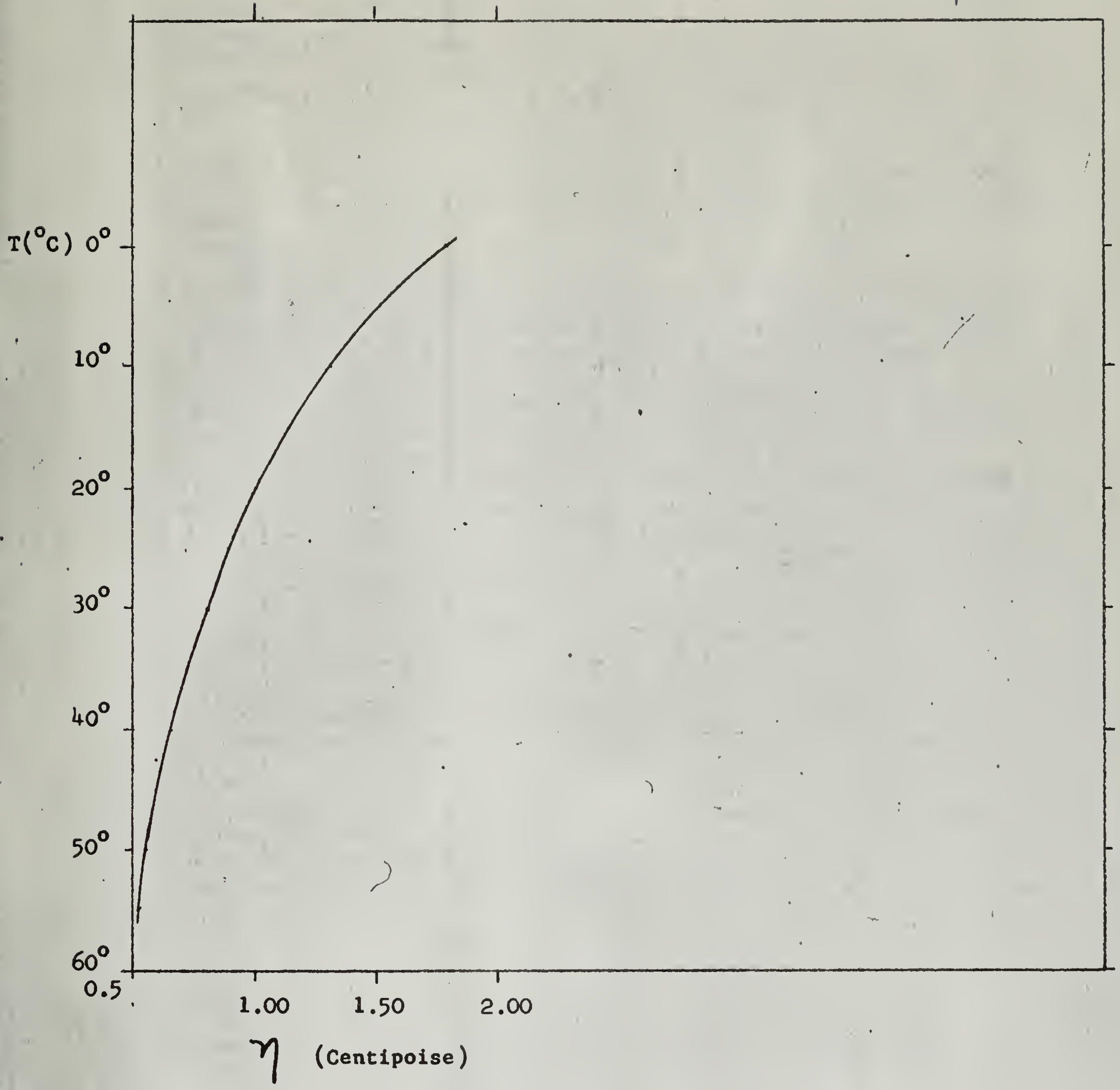


Figure 11. Plot of Temperature Coefficient of Shearing Viscosity for Distilled Water*

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*Bingham and Jackson, Bull. Bur. Stds. 14, 75 (1918)

frequency Solution Concentration (By Weight)	10.1 mc/s	17.9 mc/s	26.1 mc/s	Density gm/cc
H_2O (Theoretical)	0.212 db/ms	0.668 db/ms	1.41 db/ms	--
H_2O (Measured)	0.229	0.676 db/ms	1.43 db/ms	0.998
Error: Measured vs. Theoretical	8%	1.2%	1.4%	--
0.025% Polyox	0.223 db/ms	0.676 db/ms	1.38 db/ms	0.998
0.05% "	0.220 "	0.636 "	1.40 "	0.998
0.10% "	0.220 "	0.654 "	1.38 "	0.998
0.25% "	0.228 "	0.664 "	1.38 "	1.000
0.375%	0.228 "	0.667	1.41 "	1.002
Typical Uncertainty	±0.012	±0.012	±0.020	
Path length where first note diffration effects in data	40 cm	30 cm	24 cm	

TABLE #1

Measured Absorptions for Longitudinal Acoustic Waves in Polyox Solutions

frequency Solutions Concentration	10.1 mc/s	17.9 mc/s	26.1 mc/s
H_2O (Theo)	1481 m/s	1481 m/s	1481 m/s
H_2O (Measured)	1486 m/s	1479 m/s	1495 m/s
Polyox Solution			
0.025% P	1487 "	1497 "	1485 "
0.05% P	1495 "	1495 "	1486 "
0.10% P	1493 "	1493 "	1491 "
0.25% P	1495 "	1480 "	1500
0.375	1479 "	1480 "	1482
Typical Uncertainty	0.5%	0.5%	0.5%

TABLE #2

Measured Velocities for Longitudinal Acoustic Waves in Polyox Solutions