THE ABSORPTION OF ULTRASOUND IN AQUEOUS SOLUTIONS OF POLYETHYLENE GLYCOL

BY

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THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY

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I. INTRODUCTION

High-intensity, non-cavitating ultrasonic energy causes unique changes in biological systems (Barnard _et al_., 1955; Barnard _et al_., 1956; Fry, 1956). The effects on tissue structures appear to be produced at the level of organization of biological macromolecules, however, the physical mechanism(s) responsible have not yet been elucidated (Macloeb, 1966).

Both high- and low-intensity ultrasonic energy have been employed to study some of the possible mechanisms which could cause the observed biological changes. Hawley _et al_. (1963) suggest that intense, non-cavitating ultrasound causes relative motion (shearing) between a macromolecule and the suspending medium which produces degradation of the macromolecule and Dunn (1958) demonstrated that thermal processes may be considered unimportant as the primary mechanism.

Very low intensity ultrasound is employed to determine the amplitude absorption coefficients of biological macromolecules in aqueous solutions. Knowledge of the ultrasonic absorption coefficient as a function of frequency can aid in the identification of the particular mechanism(s) by which energy exchange processes can occur in solution at the molecular level from which possible degradation mechanisms may be inferred. The biological macromolecules which have been studied in this way are dextran (Hawley _et al_., 1965;

Kessler, 1966), polyglutamic acid (Burke et al., 1965), and hemoglobin (Carstensen et al., 1953, 1959; Edmonds, 1962).

Proteins are the logical biopolymer to observe for possible interaction mechanisms with ultrasound since they compose approximately 70% of the biological cell's dry weight and since some are readily available in highly purified forms. However, since biological polymers are structurally very complex, synthetic polymers in solution can sometimes serve as useful simpler models.

Polyethylene glycol (PEG) was chosen for this study because of its ease of availability in narrow distributions of molecular weight polymers produced by reacting ethylene oxide with ethylene glycol or water. Their structure may be written as

$$HO(C_2H_4O)_nC_2H_4OH$$

where the numeral n in the name of polyglycol designates the average molecular weight (Dow Chemical Co., 1962).

Hammes and Lewis (1966) have shown that aqueous solutions of polyethylene glycol of molecular weights 20,000 and 7500 and concentrations of about 5 and 9%, measured over the frequency range 10 to 185 MHz, appears to possess a single ultrasonic relaxation. In addition, they conclude that the relaxation process is attributable to a perturbation of the hydrogen-bonding equilibrium between polymer and solvent.

In the present study two molecular weights, 20,000 and

4500, are employed in aqueous solution at concentrations of $\sim$10 and $\sim$20%, at temperatures of 4.2 and 20.7°C and over the frequency range 1 to 80 MHz. It was shown that by extending the frequency range below 10 MHz, a distribution of relaxation times exist. This multiple relaxation should follow if a structural phenomenon is responsible for the relaxation process. In addition, it was observed that the absorption coefficient is linearly dependent on the concentration of the solution and is independent of molecular weight. Finally, it was determined that the absorption coefficient over the investigated frequency range is less than that predicted by Stokes.

II. DISCUSSION OF ACOUSTICAL ABSORPTION AND DISPERSION IN LIQUID MEDIA

A. Classical Effects

All fluids absorb acoustic energy by virtue of their possessing macroscopic properties of shear viscosity and heat conductivity. By considering viscosity, Stokes (1845) developed the first successful theory offering a mechanism by which the energy of the infinitesimal sound waves are absorbed. Kirchhoff (1868) considered heat conductivity to develop a theory which provides a second mechanism for explaining sound absorption of the infinitesimal sound waves in fluids. These two mechanisms of sound absorption are referred to as classical.

Whenever the layers of the fluid are in relative motion, laminar flow, the viscous forces opposing this relative motion must be overcome. This involves the transformation of the mechanical energy of the waves into heat. Thus viscosity is a manifestation of momentum transfer. When one portion of the fluid slides past another, the slower molecules will diffuse over to reduce the fluid momentum of the faster molecules. As a result, the region between the two layers is subjected to a shear stress $\mathfrak{D}$, proportional to the velocity gradient normal to the surface $\frac{\partial v}{\partial x}$, the proportionality constant being called the coefficient of viscosity

η,

$$D = -\eta \frac{\partial v}{\partial x} . \qquad (1)$$

For an adiabatic process, when the fluid is compressed during the propagation of an acoustic wave, the temperature is raised, while the temperature of the rarefaction is correspondingly lowered. Thus there is a tendency for heat to be conducted from the compression to the rarefaction. This passage of heat from a higher to lower temperature region implies an increase of entropy and, therefore, a dissipation of energy. As with any other diffusion process the rate of heat conduction (flux of heat) J, is proportional to the temperature gradient

$$J = -K \operatorname{grad} T \qquad (2)$$

where the proportionality constant K is called the thermal conductivity of the fluid.

The absorption of sound can be treated phenomenologically as resulting from the time lag of the change in density relative to the time varying acoustic pressure. When pressure and density are in phase, no energy is lost from the adiabatically propagating sound wave. However, when a phase difference exists, acoustic energy is degraded into some form of heat energy, the form depending on the macroscopic properties of the medium. The lag between pressure and density depends on the characteristic time, τ , or relaxation time, required for the process to proceed to within e^{-1} of its equilibrium value under an applied step-function in pressure (Figure 1).

For an acoustic wave propagating in a lossless, extended medium, the wave equation is

$$\frac{\partial^2 \xi}{\partial t^2} = c^2 \frac{\partial^2 \xi}{\partial x^2} \qquad (3)$$

where c is the velocity of propagation of the wave and ξ is the particle displacement from equilibrium position, along the x-axis (Kinsler and Frey, 1962). The term particle is understood to mean a volume element large enough to possess the macroscopic properties of a continuous fluid, yet small enough so that acoustic variables such as pressure, density, particle velocity, etc., may be considered as constants throughout the volume element.

In order to introduce dissipative terms into the general wave equation, the equation of state employed in deriving (3) must be modified from that of purely static considerations

$$p = -B \frac{\partial \xi}{\partial x} \qquad (4)$$

where p is the excess pressure at any point, B is the bulk modulus (the modulus which relates the change in

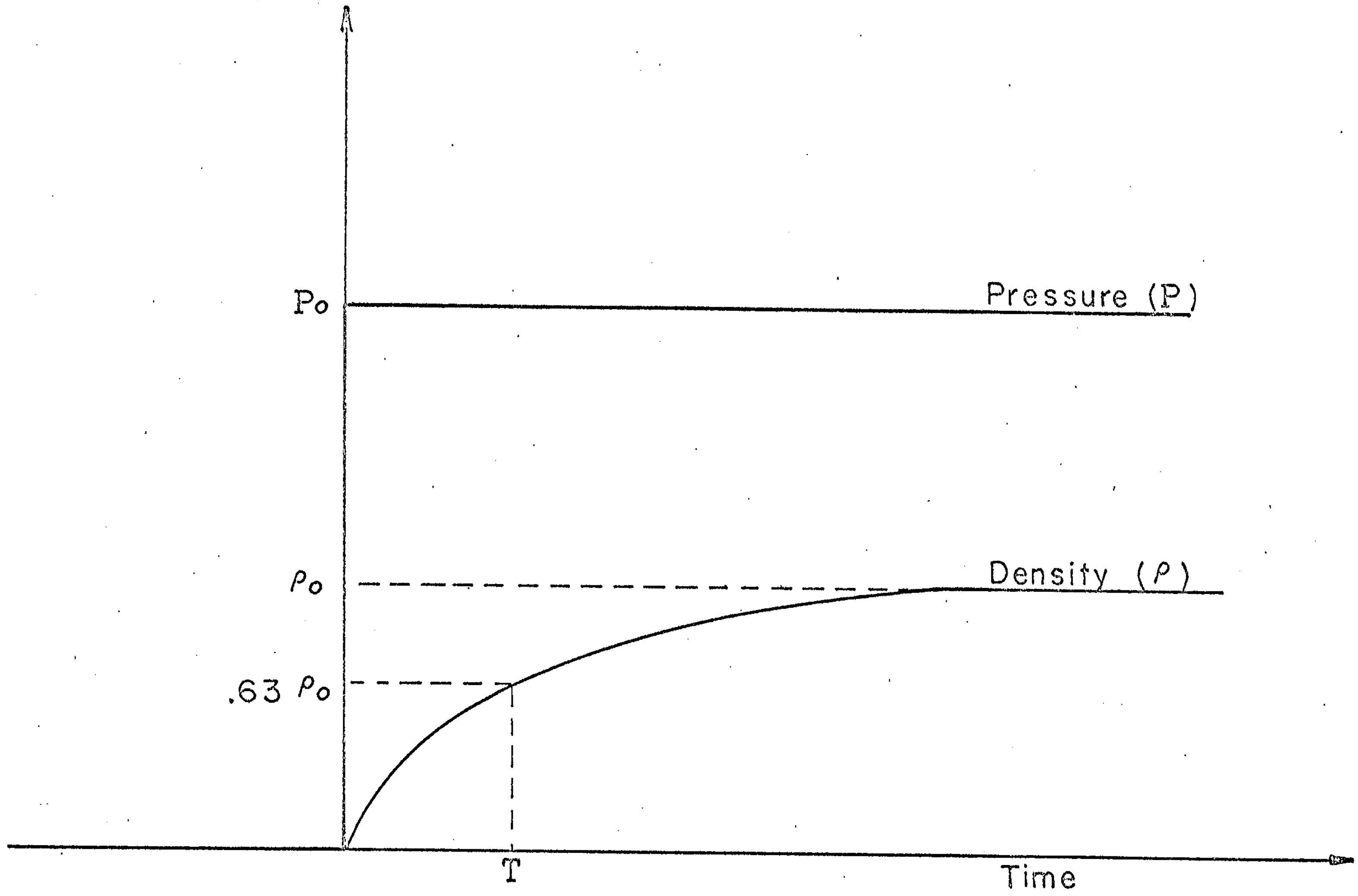

Figure 1 - REPRESENTATION OF RELAXATION TIME

hydrostatic pressure to a corresponding fractional change in volume) of the medium, and $\frac{\partial \xi}{\partial x}$ is the particle displacement gradient, so the instantaneous density lags behind the fluctuations in the acoustic excess pressure. Experience has shown that an equation of state after Stokes involving dynamical considerations

$$p = -B\frac{\partial \xi}{\partial x} - R\frac{\partial^2 \xi}{\partial x \partial t} \qquad (5)$$

is most useful for this purpose. Thus the analytic form of the wave equation for attenuated plane acoustic waves is given by

$$\frac{\partial^2 \xi}{\partial t^2} = c^2 \frac{\partial^2 \xi}{\partial x^2} + \frac{R}{\rho_0}\frac{\partial^3 \xi}{\partial x^2 \partial t} \qquad (6)$$

where the constant R contains the loss mechanism (Kinsler and Frey, 1962). Assuming a periodically propagating acoustic wave, the solution of (6) is given by the general form

$$g = Q e^{-\alpha x} e^{j\omega(t - x/c)} \qquad (7)$$

where g is any first order acoustic variable such as instantaneous density, acoustic pressure, particle velocity, etc., Q is the amplitude of the g variation at the origin of the coordinate system ($x=0$), ω is the angular frequency of the compressional wave, and α is the amplitude absorption coefficient of the medium per unit path length.

In liquids, with few exceptions, such as the liquid metals (Herzfeld and Litovitz, 1959), viscosity plays the significant role in the absorption of the propagated acoustic wave. Stokes was cognizant of the fact that liquids possessed both shear viscosity and bulk viscosity, η' , i.e., viscous reaction to a uniform compression from all directions (hydrostatic pressure), but with no direct method for measuring it, he assumed the effect of bulk viscosity to be zero. Therefore, the classical sound absorption due to shear viscosity is given by the Stokes' formula

$$\alpha_v = \frac{2\omega^2\eta}{3\rho_o c^3} . \qquad (8)$$

Stokes' formula also assumes that the product $\omega\tau$, τ being the relaxation time, is much less than unity ($\omega\tau \ll 1$) implying that the relaxation frequency is much greater than the operating frequency and that the fluids are not very viscous so that secondary effects due to viscosity are negligible.

The loss of energy caused by heat conduction comes about because the fluctuations of pressure in the sound wave do not represent a condition of thermodynamic equilibrium. The theoretical equation for absorption associated with heat conduction, originally derived by Kirckhoff, is given by

$$\alpha_{hc} = \frac{K(\gamma-1)\,\omega^2}{2\rho_0\, c^3\, c_p} \tag{9}$$

where K , defined in (2), is the thermal conductivity of the fluid, c_p is the specific heat at constant pressure, and γ is the ratio of specific heat at constant pressure to specific heat at constant volume ($\gamma = c_p/c_v$).

With small absorption, it is a valid assumption to treat the mechanisms of absorption due to shear viscosity and to heat conductivity independently. Therefore, the classical absorption coefficient is given by the sum of the two

$$\alpha_{class} = \frac{\omega^2}{2\rho_0 c^3}\left[\frac{4\eta}{3} + \frac{K(\gamma-1)}{c_p}\right] . \tag{10}$$

The classical absorption coefficient divided by the square of the frequency for a given liquid at a stated temperature and pressure is a constant given by

$$\frac{\alpha_{class}}{f^2} = \frac{(2\pi)^2}{2\rho_0 c^3}\left[\frac{4\eta}{3} + \frac{K(\gamma-1)}{c_p}\right] . \tag{11}$$

B. Molecular Effects

With the exception of some very viscous liquids, monatomic liquids such as argon and mercury, and some diatomic liquids such as oxygen and nitrogen, the observed absorption is several times greater than that due to the classical mechanisms of shear viscosity and thermal conductivity (Vigoureux, 1951). Generally three molecular, or relaxational, effects can occur in the liquid to explain the observed absorption in excess of that due to the classical mechanisms. The three are thermal relaxation, structural relaxation and chemical relaxation.

Because the specific heat at constant pressure exceeds that at constant volume in all pure liquids, save water at 4°C, the propagation of a compressional wave will have a corresponding cyclical variation in temperature. Thermal relaxation requires this fluctuation in temperature as the acoustic wave is propagated. Here the excess absorption is associated with the energy exchange processes between the external degrees of freedom and internal vibrational and rotational degrees of freedom of the constituent molecules. Consequently, when the temperature is less than the equilibrium value, as in a rarefaction of a propagated acoustic wave, some energy is transferred from the internal to external degrees of freedom. Since this transfer of energy does not take place instantaneously, but rather at a finite rate, the changes in density will lag behind the applied pressure. Thus the variation in temperature is less than what it would be without this energy transfer, resulting in the conversion of acoustic energy into heat and hence attenuation of the propagated wave. Thermal relaxation is observed mainly in the non-associated non-polar liquids such as benzene.

During the compression phase of the propagated acoustic plane wave, the molecules of the liquid are brought closer together and also rearranged or repacked more closely. This structural rearrangement involves the redistribution of the mutual orientation or change in degree of association of the molecules of the liquid. Such configuration changes, which are influenced by both the shape of the molecule and mutual attraction, require the breaking of intermolecular bonds or the accumulation of enough kinetic energy to overcome the potential energy barriers restraining these bonds. This structural rearrangement causes a volume change due to the pressure, which suggests that the liquid has a volume (bulk) viscosity, and since the structural changes are time dependent, this leads to a relaxational phenomenon. The associated or hydrogen-bonded liquids like water and alcohols have, as their mechanism responsible for the observed excess absorption, structural relaxation.

Most liquids exhibit a volume (bulk) viscosity, the causes being due to both structural and thermal relaxation phenomena. However, distinction can be made between these two phenomena since for structural relaxation, the ratio of volume viscosity to shear viscosity, η'/η , lies between 0.5 and 10 and is sensibly temperature-independent, while for thermal relaxation the ratio is much greater than 20 with no obvious correlation between the temperature dependence

(Lamb, 1964).

Finally, a chemical relaxation phenomenon exists when the propagation of an acoustic wave will, in some way, perturb a chemical reaction from equilibrium. This perturbation will require energy to be transferred which results in the sound wave being attenuated.

Generally, thermal relaxation processes can be represented in terms of a single relaxation time, whereas structural mechanisms usually give rise to a distribution of relaxation times.

The relaxation processes (thermal, structural, and chemical) may occur simultaneously, the relative importance of each being determined by structure and composition of the fluid, or one may predominate over a certain frequency range while the others may constitute the important absorption mechanisms in different portions of the acoustic spectrum.

The total absorption per cycle squared (frequency-free absorption) for a single relaxation process is given by

$$\frac{\alpha}{f^2} = \frac{A}{1+\omega^2\tau^2} + B \qquad (12)$$

where B includes the classical effects (11) in addition to any other relaxation processes having characteristic frequencies much greater than τ^{-1} for the one in question.

C. Velocity Dispersion

The relaxational behavior of sound waves associated with viscous properties of the medium not only produces attenuation in amplitude but also dispersion in velocity of propagation. The phase velocity is given by

$$\gamma = c\left[\frac{2(1+\omega^2\tau^2)}{1+(1+\omega^2\tau^2)^{1/2}}\right]^{1/2} \qquad (13)$$

where τ is the relaxation time, ω is the angular frequency and c is the wave velocity (Kinsler and Frey, 1962). When structural relaxation is significant, notable velocity dispersion is observed over the relaxation region, whereas thermal relaxation rarely gives an appreciable dispersion (Lamb, 1964).

D. Representation of Data

In presenting the absorption data, it is customary to plot the frequency-free absorption, α/f^2, versus the log of frequency. In the case when the medium possesses only a single relaxation (12), the plot will have the shape of Figure 2 where the relaxation frequency ($f_r = \frac{1}{2\pi\tau}$) is the frequency when α/f^2 is equal to its point of inflection.

In addition, when plotting the measured excess absorption caused by molecular relaxation, that is

$$\frac{\alpha_{EXCESS}}{f^2} = \frac{\alpha}{f^2} - B = \frac{A}{1+\omega^2\tau^2} \qquad (14)$$

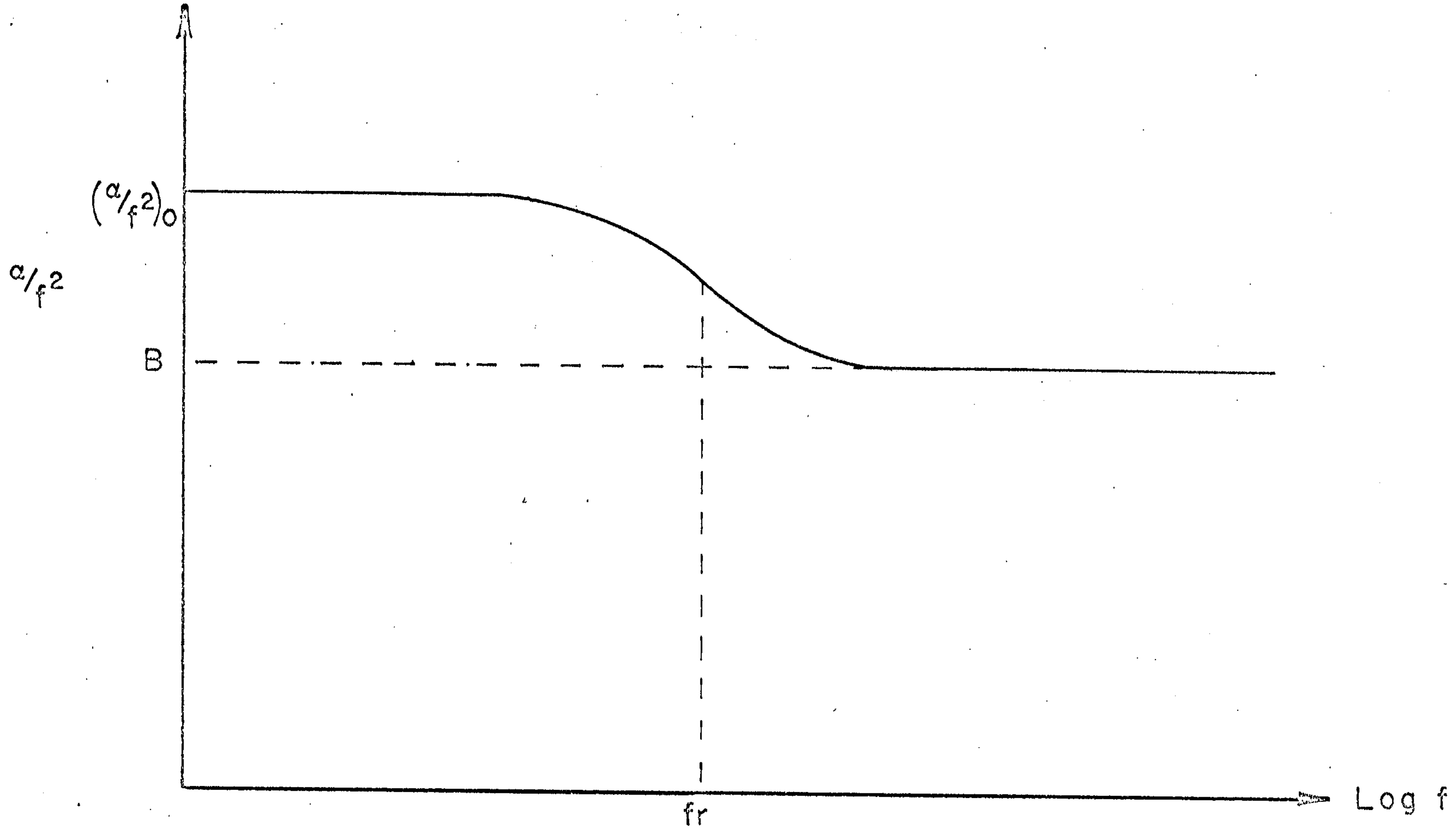

Figure 2 - FREQUENCY-FREE ABSORPTION VERSUS FREQUENCY FOR A SINGLE RELAXATION

there are two standard ways of presenting the information. First a plot of the ratio $\frac{\alpha_{EXCESS}}{f}$ versus the log of frequency, and second the product $\alpha_{EXCESS}\lambda$, i.e., the absorption in nepers per wavelength, against the log of frequency. In both cases the curve for a single relaxation peaks at the relaxation frequency ($\omega_r = 2\pi f_r = \frac{1}{\tau}$). This is represented in Figure 3. It should be noted that the plots of α_{EXCESS}/f and $\alpha_{EXCESS}\lambda$ will be the same for the case when no velocity dispersion exists.

By using the formulas of relaxation theory for a single relaxation process Mikhailov (1953) showed that

$$\frac{\omega^2}{2c^3\alpha} = \frac{\tau}{(C_\infty^2 - C_o^2)}\,\omega^2 + \frac{1}{(C_\infty^2 - C_o^2)\tau} \qquad (15)$$

where C_∞ and C_o are the velocities of sound at very high and very low frequencies, respectively, and τ is the relaxation time of the process. Therefore, a plot of $\frac{\omega^2}{2c^3\alpha}$ versus ω^2 would yield a straight line for which the slope and intercept yield relations from which the velocity dispersion and relaxation time can be computed.

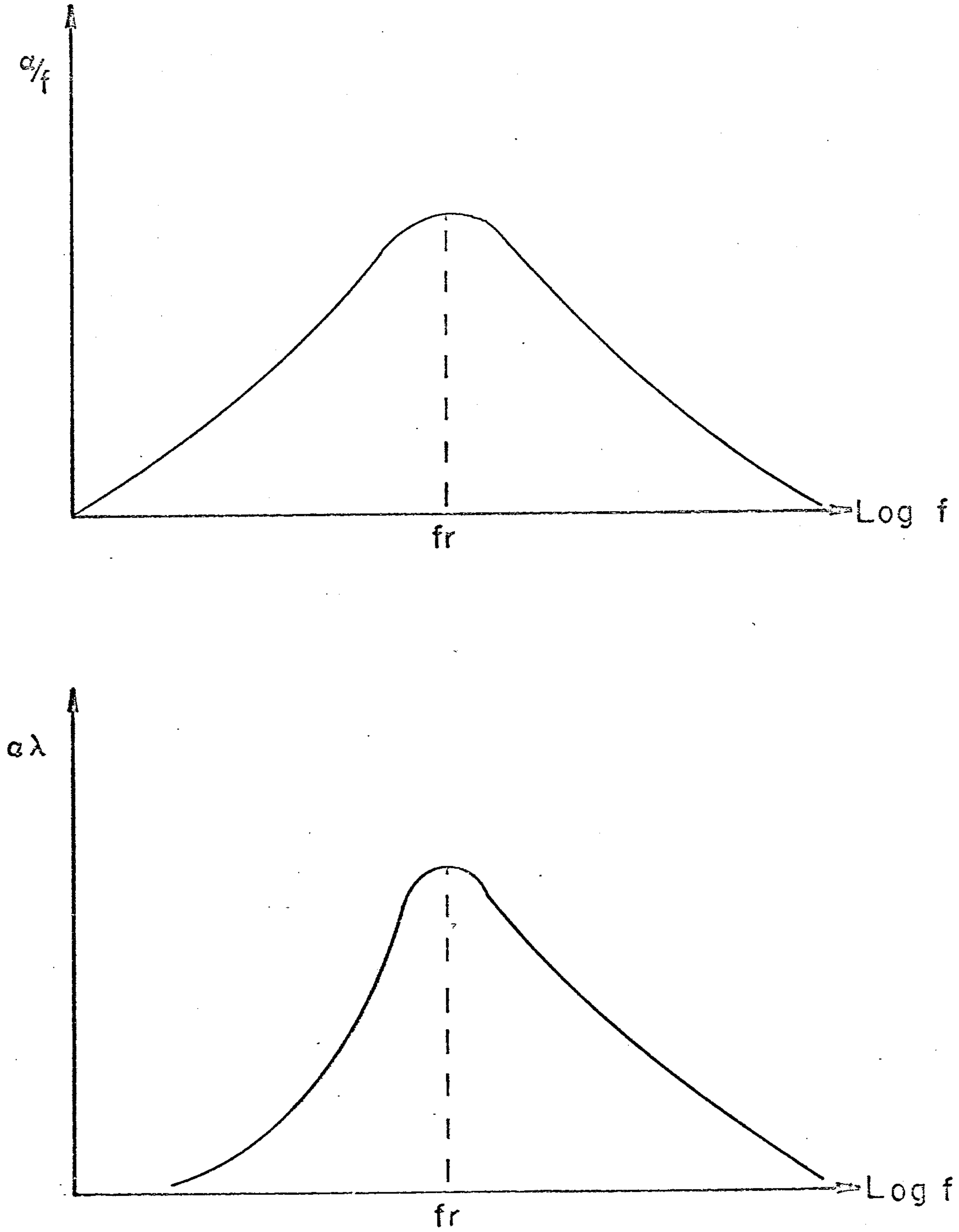

Figure 3 - ADDITIONAL METHODS OF GRAPHICALLY REPRESENTING A SINGLE RELAXATION

III. MEASUREMENT TECHNIQUES AND INSTRUMENTATION

A. Techniques

Pulse techniques developed as a means of investigating the absorption and velocity of ultrasound in liquids appeared as an offshoot of radar technology developed during World War II. Pellam and Galt (1946) and Pinkerton (1949) were among the first to use this method to investigate liquids. The two main advantages of the pulse technique over continuous wave methods are the elimination of standing waves and the minimization of local heating effects (Herzfeld and Litovitz, 1959).

The pulse technique works as follows. A radio frequency (rf) signal of the desired frequency, modulated by a square wave, is impressed across an X-cut quartz crystal (or cast ceramic piezoelectric transducer such as barium titanate) which operates at odd multiples of the fundamental thickness mode. The square wave is of such duration as to allow at least fifteen cycles of the rf signal to be transmitted. The acoustic wave is received by a second transducer, which has the same fundamental mode thickness as the transmitting crystal, and the received signal is processed by the appropriate electronics. After all transients have decayed, the process is repeated. This allows for a pulse repitition rate of around 200 pps.

Since a single experimental arrangement is generally limited to less than two decades of frequency, two experimental set-ups were utilized in the present study. Figures 4 and 5 show block diagrams of the absorption measuring system for the low frequency (500 KHz to 15MHz) and high frequency (8MHz to 80 MHz without delay rods), respectively. With slight modifications, as indicated in Figures 4 and 5, the system can also measure the velocity of sound in the liquids.

In the low frequency system, two chambers are utilized, as shown in Figure 6. One chamber contains the unknown liquid and the other contains a reference liquid such as water, whose velocity and absorption are known, separated by an acoustically transparent window such as polyethylene or Saran Wrap (Dow Chemical trade name). The two transducers are mounted on a movable assembly, which moves along the axis of the chambers, with the transmitting transducer in one of the liquids and the receiving transducer in the other. The mechanical separation of the crystals is fixed.

As the transducer assembly is moved, automatically by a synchronous motor, the length of the path of the wave in the unknown liquid compared with that in the known is continously changing. For example, when the transducer assembly is in position 1, Figure 6, the acoustic plane wave is attenuated almost entirely due to the known liquid. As the transducer asembly moves continuously to the right toward position 2, less and less of the known liquid is responsible

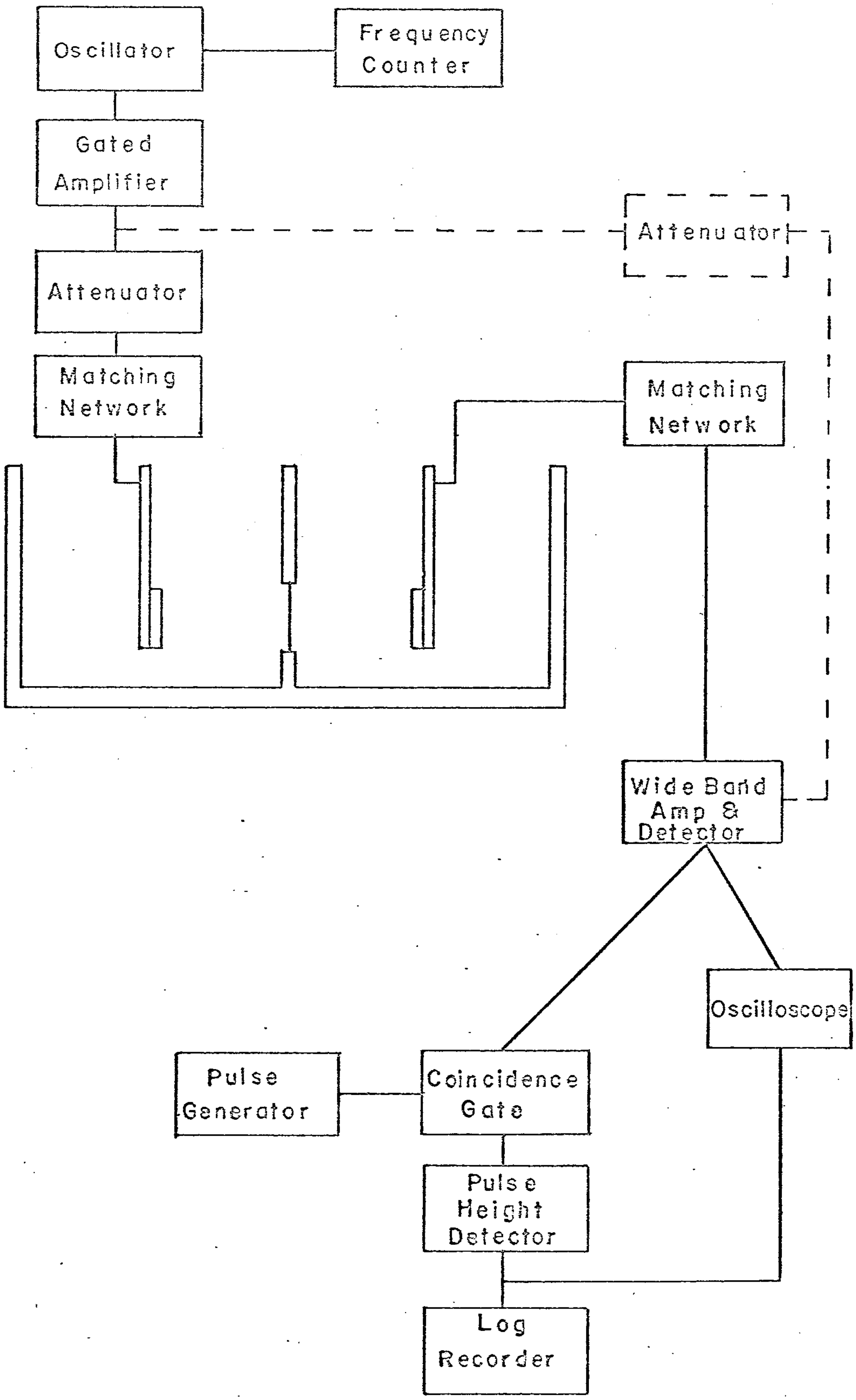

Figure 4 - LOW FREQUENCY BLOCK DIAGRAM FOR ABSORPTION AND VELOCITY (---) MEASUREMENTS

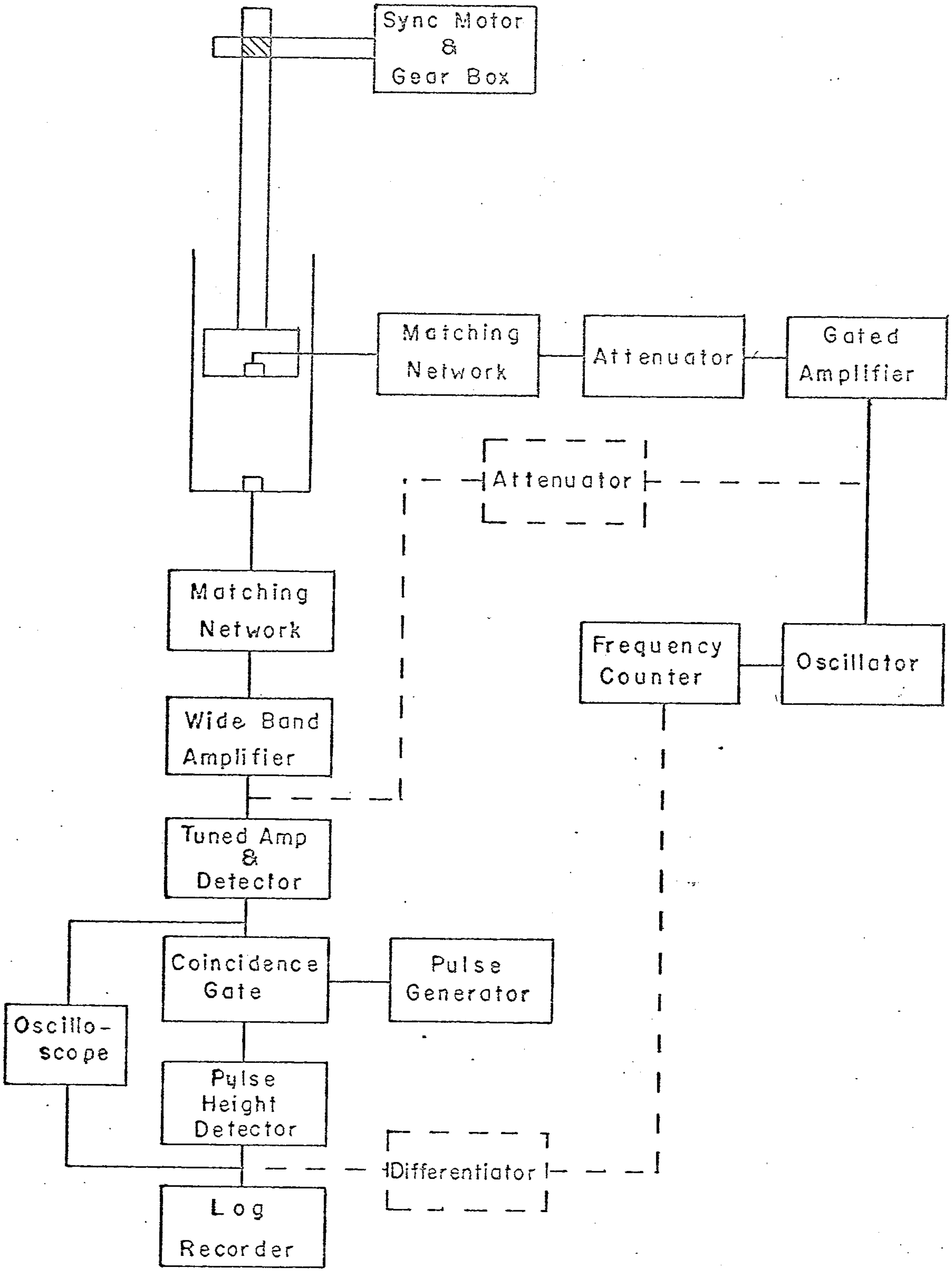

Figure 5 - HIGH FREQUENCY BLOCK DIAGRAM FOR ABSORPTION AND VELOCITY (---) MEASUREMENTS

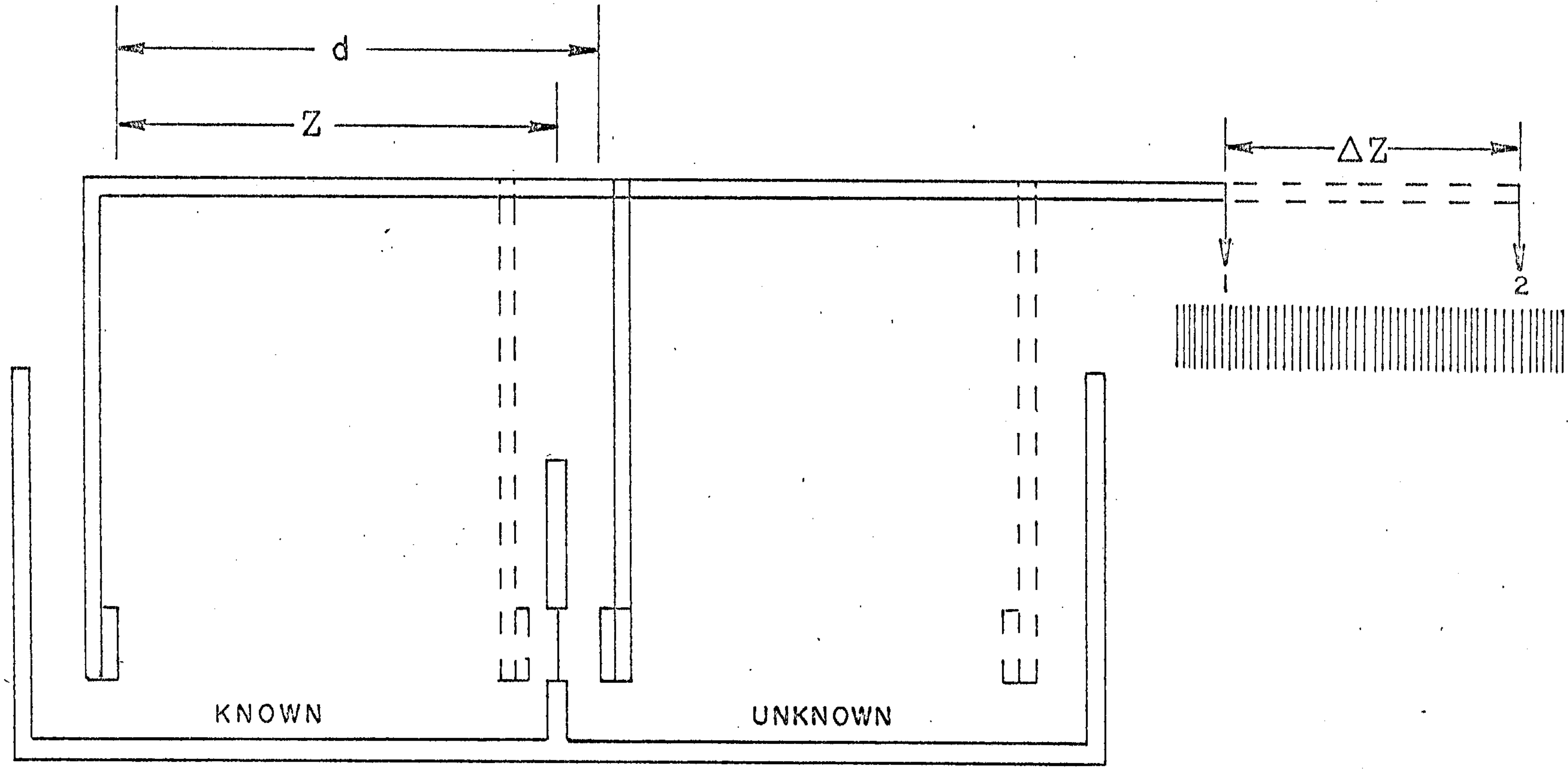

Figure 6 - LOW FREQUENCY CHAMBER

for the absorption of the acoustic signal which the unknown liquid becomes the predominant source of absorption.

Because the two liquids possess different acoustic impedances (the product of the density times the speed of sound in the liquid), the propagated acoustic wave will have some of its energy reflected at the plastic film window where a discontinuity of the acoustic impedance exists. However, since this reflection is a constant, its effect, although not negligible, is not necessary to consider since this system measures only the differences in absorption of the two media. In addition, the signal from the reflection, having been reflected from the transmitting crystal, appears at the receiving crystal later in time than the original signal and can be gated out, if necessary.

In the high frequency system, the acoustic plane wave signal is propagated through only the unknown liquid. The mechanical path length is varied by a synchronous motor causing the upper transducer to move with reference to the fixed, receiving transducer. As the upper transmitting transducer moves away from the lower one, the total attenuation of the signal increases, thus decreasing the amplitude of the received signal in an exponential manner.

The received signal is processed in the same manner for each system. The low level signal received by the transducer is amplified and detected and the video signal is fed into a pulse height detector whose output is then fed into a logarithmic chart recorder operated by a synchronous motor. The slope of the recorded straight line is proportional, by appropriate conversion factors, to the absorption coefficient. The coincidence gate is used only when the absorption is so small that the second, or third, etc., pulse must be recorded in order to increase the path length over which the signal traverses to achieve sufficient absorption for an accurate determination.

The fundamental principles of measurement of the velocity of sound in the unknown liquid are essentially the same with both systems. When the output of the generator (reference signal) is added algebraically to the received signal, the resultant signal will either peak or null, depending upon the phase of the signals. A null will occur only when both signals are of equal amplitude and out of phase by 180°. However, if both signals are not the same amplitude, the resultant signal will change amplitude as the two signals change their phase orientation, but there will be on null.

Carstensen (1954) has described a technique for the direct measurement of the absolute difference between the velocity of sound in the two liquids. The experimental set-up is that of the low frequency system. Water is choosen as the reference since it can be assumed dispersionless and the speed of sound in water is known with sufficient accuracy (Greenspan and Tschiegg, 1959). The phase of the received signal depends upon the number of acoustic wavelengths which separate the source and receiver. Using the notations in Figure 6

$$n = \frac{z}{\lambda_w} + \frac{d - z}{\lambda_x} \tag{16}$$

where λ_w and λ_x are the wavelengths of sound in water and in the unknown liquid, respectively. If the transducer assembly is moved a distance Δz until the received signal undergoes m number of 360° phase shifts, the acoustic path length is altered to (L. W. Kessler, 1968)

$$n \pm m = \frac{z + \Delta z}{\lambda_w} + \frac{d - z - \Delta z}{\lambda_x} \tag{17}$$

since the number of wavelengths can either increase or decrease. Subtracting (16) from (17)

$$\pm m = \frac{\Delta z}{\lambda_w} - \frac{\Delta z}{\lambda_x} \tag{18}$$

or

$$\pm m = \left(\frac{1}{c_w} - \frac{1}{c_x} \right) f \Delta z \tag{19}$$

where c_w and c_x are the speeds of sound in water and in the unknown liquid. Solving for the speed of sound in the unknown yields

$$C_x = \frac{C_w}{1 \mp \frac{C_w m}{f \Delta z}} \qquad (20)$$

By observing the null pattern on the oscilloscope, the transducer assembly can be moved an integral number of nulls, m , each successive null being 360° out of phase. In addition, using a micrometer with a travelling microscope, the distance Δz can be measured very accurately. However, a separate experiment must be performed to determine whether or not the speed of sound in the unknown liquid is greater than that in water.

For the high frequency system, when the output of the rf generator is algebracially added to the received signal, the output of the pulse height detector has the waveshape of a rectified sinusoidal. This signal is then differentiated and fed into the time interval counter.

With the speed of the piston accurately known, the speed of sound in the unknown liquid can be determined by recording the time required for the piston to move one wavelength at a known frequency,

$$C = r f t \qquad (21)$$

where r is the piston speed, f is the frequency of the propagated sound wave, and t is the time for the piston to travel one wavelength.

Hawley (1966), in designing the high frequency system, utilized the following criteria so that the resulting diffraction at low frequencies would be of the free field form. The measurements must be made in the Fresnel region so that the entire sound beam is intercepted by the receiving crystal and secondly, the radius of the cylindrical container is at least twice that of the source transducer to eliminate wave guide effects. Thus, for water and other low absorbing materials, Hawley (1966) reported that the low frequency limit is about 500 KHz. However, to eliminate numerous diffraction corrections in this study, the low frequency limit for this study will be 8.8 MHz.

Without ultrasonic delay rods, the high frequency limit for the high frequency system is about 80 MHz. The utilization of delay rods will extend this frequency limit to around 200 MHz, at which point parallelism between the two crystals become the limiting factor.

The low frequency limit of the low frequency system is designed for 300 KHz although meaningful absorption measurements at this frequency have not yet been obtained due to the low absorption coefficient of PEG for the concentrations considered. The lowest frequency at which PEG has been examined is 1.5 MHz. This low limit is in part due to the closeness of the intrinsic absorptions of water and polyethylene glycol solutions at the lower frequencies.

The high frequency limit has not been investigated in the low frequency system. Frequencies as high as 19 MHz have been achieved in this system using crystals with a fundamental mode thickness of 1 MHz.

B. Instrumentation

Two continuous wave, sinusoidal oscillators (rf generators) are employed to cover the extended frequency range, the Hewlett Packard Test Oscillator model 650A with a frequency range from 10 Hz to 10 MHz and the Measurements Standard Signal Generator, Boonton, N. J., model 80-R with a frequency range from 5 MHz to 475 MHz. The oscillator's output is fed into the Arenberg Ultrasonic Laboratory, Inc., Jamaica Plain, Mass. Below 70 MHz, it is operated in the gated amplifier mode in which the cw signal from the rf generator is gated to the desired duration and pulse repetition rate. Also, both direct and delayed triggering outputs are available; the delayed source triggers both the Tektronix type 453, dc to 50 MHz oscilloscope and the General Radio Unit Pulse Generator type 1217-C with type 1203-B Unit Regulated Power Supply.

The output from the rf generator is continuously monitored by the Systron Donner Frequency Counter, model 1037. This counter is capable of direct frequency measurements up to 50 MHz and period measurements with resolution of 0.1μ seconds. The plug-in model 1291, a heterodyne converter, extends the frequency range to 500 MHz. In addition, the plug-in model 1926A, a time interval counter, is employed in measuring the velocity of sound for the high frequency system.

The 93 Ω attenuators, manufactured by Arenberg Ultrasonic Laboratory, Inc., are employed where indicated in Figures 4 and 5.

The L matching networks (Everitt and Anner, 1956), designed to match the crystal impedance to the system impedance, are utilized to increase the efficiency of the power transfer to and from the crystal. These lossless impedance-transformers were built in this lab for this specific purpose.

The received signal, after passing through the matching network, is amplified by the Hewlett Packard model 460A wide band amplifier with a 20 db gain for the high frequency system. The amplified signal is then fed into the Matec tuned amplifier and detector model PR201, acquired from Matec, Inc., Providence, R. I. The Arenberg wide band amplifier and video detector, model WA-600-D is employed to amplify the received signal for the low frequency system.

The coincidence gate, described in Millman and Taub (1965), receives the video signal only when gating of pulses is necessary. Otherwise, the video signal is fed into the pulse height detector, similar to the peak sensing amplifier in the G. E. Transitor Manual (1964). The dc output from the pulse height detector is recorded as the logarithm as a function of time, on the Sergent Recorder model SRL. The chart paper is driven by a three-speed synchronous motor at 10 inches per minute (ipm), the other speeds available being 1 and 5 ipm.

IV. DISCUSSION OF ERRORS

A. Diffraction Corrections

For the discussion of absorption and velocity dispersion, the propagated sound wave is assumed to be a plane wave, that is, acoustic parameters such as pressure, particle displacement, density changes, etc., have common phases and amplitudes at all points on a given plane perpendicular to the direction of wave propagation. This assumption is not completely true since a circular piston, which is employed in this study, is constrained to a finite surface area and the amplitude of vibrations near the edge of the crystal is somewhat less than at the center. However, this edge effect may be neglected when the radius, a, of the circular crystal is very much greater than the wavelength, λ, of the propagated sound wave, i.e., $ka \gg 1$ where k is the wave number given by $2\pi/\lambda$. This approximation is only valid close to the crystal, and off the central axis (Pinkerton, 1949).

All the measurements in this study are made in the Fresnel region. For the high frequency system, the termination of the Fresnel region, at 8.8 MHz, occurs 90 cm from the transmitting crystal, whereas at 26 MHz, this distance is 3.6 meters, with a crystal diameter of 2.54 cm and velocity of sound of 1500 m/s. Since the receiving crystal is always within 10 cm of the transmitting crystal, the received signal is obviously within the Fresnel zone.

Mechanically, the crystal separation in the low frequency system is about 18 cm, although the acoustic path length varies due to the differences in sound speed in the two media. With a crystal diameter of 7.62 cm, the extent of the Fresnel region occurs at 97 cm and 2.6 meters for frequencies of 1 MHz and 4 MHz, respectively. It is assumed here that the speed of sound is approximately 1500 m/s in the two media, which is a good approximation in this study.

Because the receiving crystal is not always very close to the transmitting crystal, and the absorption of ultrasound is low in the PEG solutions considered in this study, the effects of diffraction must be considered. With a higher absorption coefficient, the effects due to diffraction become less important, although they still occur.

The method of correcting for diffraction of Del Grosso (1964) is applied to the absorption data. The diffraction effect for the velocity data, which will be demonstrated, is negligible. Considered here is the effect of free-field diffraction, that is, the signal is assumed to be propagated into a semi-infinite, half-space. This means that no reflections occur at boundaries, or that these reflections may be time-separated. Del Grosso obtained the 2nd-order approximation to Bass' approximation (1958) for the real and imaginary components of the average rms pressure $\langle p \rangle_{REL}$ relative to a plane wave, viz.,

$$\mathrm{Re}\,\langle p\rangle_{REL} = 1 - \left[J_0 \cos X + J_1 \sin X\right]\left[1 - \frac{1}{2}\left(\frac{X}{ka}\right)^2 - \frac{1}{8}\left(\frac{X}{ka}\right)^4\right] - J_1 \frac{\sin X}{X}\left[\left(\frac{X}{ka}\right)^2 + \frac{1}{4}\left(\frac{X}{ka}\right)^4\right] \tag{22a}$$

and

$$\mathrm{Im}\,\langle p\rangle_{REL} = \left[J_0 \sin X - J_1 \cos X\right]\left[1 - \frac{1}{2}\left(\frac{X}{ka}\right)^2 - \frac{1}{8}\left(\frac{X}{ka}\right)^4\right] - \frac{J_1 \cos X}{X}\left[\left(\frac{X}{ka}\right)^2 + \frac{1}{4}\left(\frac{X}{ka}\right)^4\right] \tag{22b}$$

where the J's are Bessel Functions of the first kind of the order indicated and of arguement M given by

$$M = \frac{ka^2}{Z} - \frac{ka^4}{Z^3} \tag{23}$$

and

$$X = \frac{k}{2}\left[\left(Z^2 + 4a^2\right)^{1/2} - Z\right] \tag{24}$$

and Z is the cylindrical coordinates along the path of propagation.

Values of the average rms pressure relative to a plane wave,

$$\langle p \rangle_{REL} = \sqrt{(\mathrm{Re}\,\langle p \rangle_{REL})^2 + (\mathrm{Im}\,\langle p \rangle_{REL})^2} \qquad (25a)$$

and phase difference relative to the plane wave phase

$$\langle \theta \rangle_{REL} = \tan^{-1} \frac{\mathrm{Im}\,\langle p \rangle_{REL}}{\mathrm{Re}\,\langle p \rangle_{REL}} \qquad (25b)$$

are tabulated in Del Grosso (1964) for certain values of ka ($= \frac{2\pi a}{\lambda}$) from 4π to 100π . For values of $ka > 100\pi$, the 100π table is used. A sample calculation will now be given. The receiving piston moves from $z_2 = 7.1$ cm to $z_1 = 1.4$ cm with respect to the transmitting crystal while recording the absorption at 14 MHz in a solution with the speed of sound $c = 1600$ m/s. It must now be determined how much of the recorded absorption is due to diffraction. Since the crystal diameter is 2.54 cm, $ka = 275\pi$, thus the $ka = 100\pi$ table will be used to determine the relative pressures at positions 1 and 2. The distances are first normalized to that of the Fresnel region which is unity. For $a^2/\lambda = 140$ cm, the normalized distances are $z_1 \lambda / a^2 = 0.01$ and $z_2 \lambda / a^2 \simeq 0.05$. Reading from the $ka = 100\pi$ table, the average rms pressures relative to the plane wave are $\langle$ $\langle p \rangle_{REL\,1} = 9724$ and $\langle p \rangle_{REL\,2} = 9510$. The ratio of $\langle p \rangle_{REL\,1}$ to $\langle p \rangle_{REL\,2}$, or the relative change in pressure from z_1 to z_2 , is 1.023. Expressing this change in nepers yields a

0.0227 neper difference in pressure over the traversed path. Dividing by the distance the transmitting crystal traveled, 5.7 cm, gives the contribution of absorption due only to diffraction of the sound beam, $\alpha_d = 0.00398$ nepers/cm. Depending upon whether or not the recorded value of the absorption coefficient is an appreciable magnitude to will determine if this contribution should be subtracted off.

A relatively large path length is traversed in the high frequency system so that the anomalies in the $\langle \rho \rangle_{REL}$ versus $z\lambda/a^2$ curve, Figure 7, can generally be neglected and thus errors in the recorded absorption indicate an excessive loss. However, for the low frequency system, although the traveled path length is much less, differential anomalies in absorption may be either negative or positive and thus cause either an additional loss or an apparent gain (Del Grosso, 1964). Therefore, acoustical path length between the transducers must be known accurately to eliminate this source of error. As indicated from Figure 7, the larger ka is, the smoother the $\langle \rho \rangle_{REL}$ curve is, and hence this source of error is decreased.

The inherent advantage of the low frequency system over that of the high frequency system is the magnitude of diffraction. The path length essentially is unchanged in the low frequency system whereas there is a considerable change in path length for the high frequency system. Nevertheless,

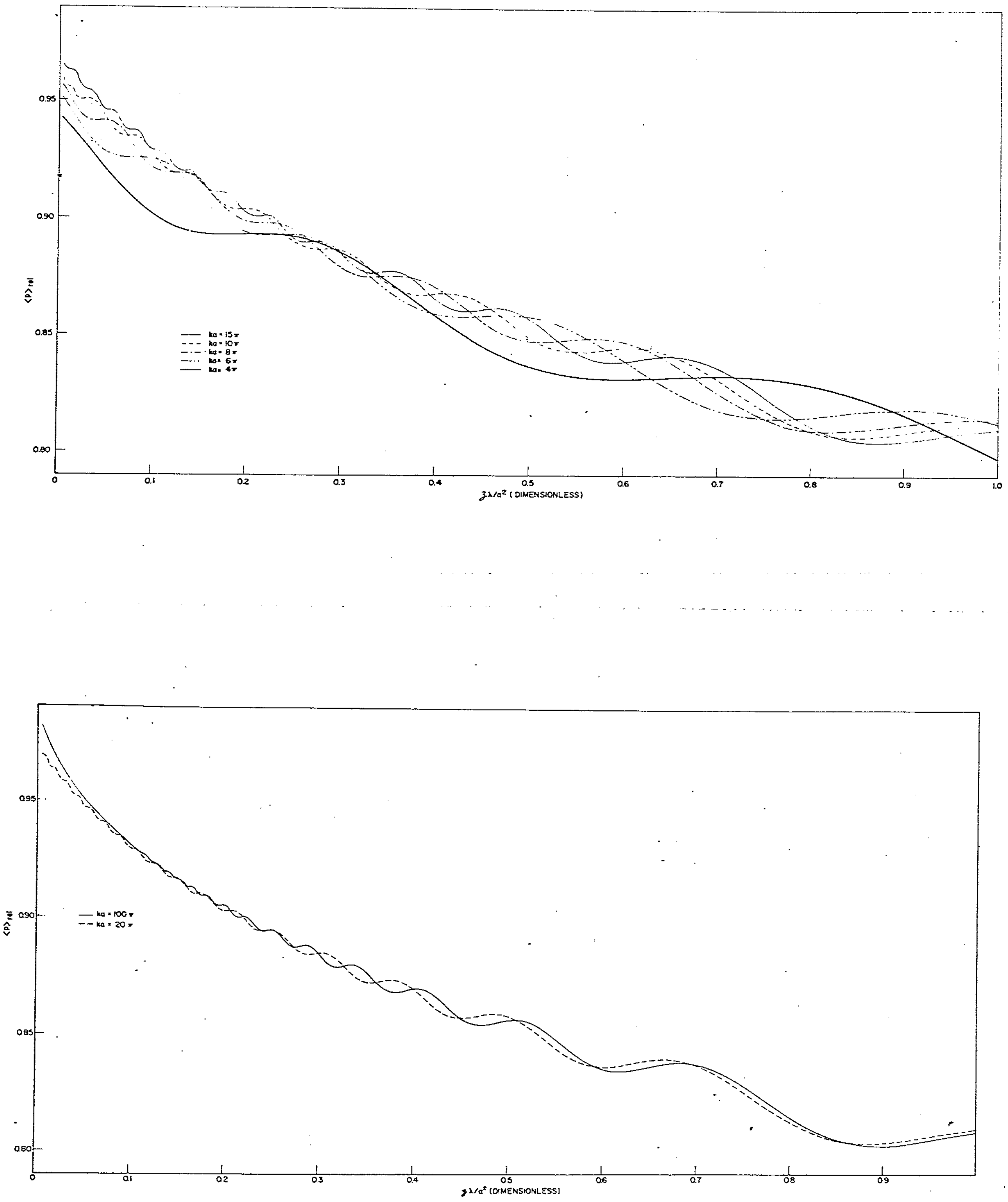

Figure 7 - AVERAGE RELATIVE PRESSERE (DEL GROSSO, 1964)

when the absorption coefficient of the unknown liquid is comparable with that of the reference liquid, diffraction corrections must be considered for the low frequency system.

The diffraction corrections for the velocity of sound in the solution can be considered negligible, as is demonstrated by the following example. In the high frequency system at a frequency of 8.795 MHz and for a piston speed of 0.015875 cm/s, the recorded velocity of sound is 1614 m/s. The initial position of the piston z_1 is 2.84 cm and the final position z_2 is 1.0 cm, approximately. The value of ka is calculated to be 172π so the $ka = 100\pi$ table for $\langle \Phi \rangle_{REL}$ is used. The normalized distances from the transmitting crystal in the Fresnel region are $z_1 \lambda / a^2 = 0.01136$ and $z_2 \lambda / a^2 = 0.03209$ which corresponds to relative phases of $\langle \Phi \rangle_{REL\,1} = 0.02443$ radians and $\langle \Phi \rangle_{REL\,2} = 0.04125$ radians, or a relative phase difference of 0.01682 radians. For this distance interval, 1.84 cm, the plane wave phase is 628 radians. This would yield an error of (0.01682/628)100% = 0.00268% or 0.04 m/s in 1600 m/s, which is insignificant when compared with the accuracy of the reading.

B. Doppler Effect

The error introduced by the Doppler effect is negligible for the velocity measurements in the high frequency system. When the source, transmitting crystal, is moving at a velocity V_s with respect to the fixed, receiving crystal, the doppler frequency f_d , the frequency the receiving crystal detects, is given by

$$f_d = f_0 \left[1 \pm \frac{v_s}{c} \right] \qquad (26)$$

where f_0 is the transmitting frequency and c is the speed of sound in the liquid. Assuming an approximate speed of sound c = 1600 m/s, with the piston moving towards the receiver at v_s = 0.000185 m/s, the ratio of the received to transmitted frequency is given by

$$1 + \frac{0.000370}{1600} = 1.0000001156$$

and is seen to be negligible.

C. Measurement Errors

The ultrasonic absorption coefficient is obtained from the slope of the log of the relative amplitude recorded logarithmically. Since the motors in both systems, along with the recorder motor, are synchronous with the line frequency, conversion factors relating the distance the piston, or the transducer assembly, is displaced versus chart paper displacement can be calculated. Thus by the appropriate proportionality constant, the absorption coefficient is easily obtainable for a particular slope. Accuracies in reading the slope from the chart paper are of the order of 0.05 db for 30 inches of chart paper, full scale being 20 db, so, for example, the accuracy of 0.5% is expected for a relative change of 10 db over at least 30 inches whereas only 5% accuracy is expected for a 1 db change in attenuation. By selecting the proper gear ratios, a change in relative amplitude in excess of 7 db is usually maintained, save for the low frequencies ($<$ 3 MHz) where changes of only 1 db are obtainable.

When ultrasonic energy in the form of pulsed oscillations is propagated, the frequency content within the pulse is not the pure rf signal received from the oscillator but has an infinite number of harmonics. However, Pellam and Galt (1946) have shown that the fractional error of the absorption, $\Delta\alpha/\alpha$, is roughly one part in 250 provided the pulses of rf employed in the measurements contain about 15 oscillations. Therefore, errors due to pulsed oscillations in this study are negligible.

Finally, considering system errors and diffraction correction errors, absorption coefficients obtained at frequencies greater than 3 MHz are obtained with an accuracy of ± 1.5% whereas data for lower frequencies have somewhat greater errors. This error is primarily associated with the low absorption coefficient at these lower frequencies.

V. PREPARATION OF LIQUID

Polyethylene glycol is highly soluble in water at the concentrations and temperatures used in this study. Four liters of each of the concentrations and molecular weights to be investigated were prepared using singly distilled water obtained from the laboratory still. Two approximate concentrations (10 and 20%) of the E-20,000 of Lot E23 were prepared along with one concentration (20%) of the E-4000 of Lot E77, with average molecular weights of 20,000 and 4500, respectively. The solutions were then passed through membrane filters of 0.5 micron pore size to remove foreign particles and stored in sealed bottles at 5°C until utilized in the experiment.

A sample was extracted during each experiment to determine the concentration of the PEG solution accurately. A known amount of the liquid sample was evaporated and the dry weight was then measured to determine the concentration to an accuracy of at least 0.05%.

VI. DISCUSSION OF RESULTS AND CONCLUSIONS

The ultrasonic absorption coefficients of aqueous solutions of polyethylene glycol were measured for two molecular weights, 20,000 and 4500, at two concentrations of approximately 10% and 20% and at two temperatures, 4.2°C and 20.7°C. The frequency range of investigation extended from 1.5 MHz to 80 MHz.

Values of total absorption of the PEG solutions versus concentration, presented in Figure 8, indicate that the absorption coefficient is linearly dependent on concentration to at least 20%. Therefore, the absorption divided by the concentration yields a convenient means of comparing results.

The value of absorption predicted by classical theory (8) for polyethylene glycol is much greater than the experimentally measured values for molecular weight 20,000. But for molecular weight 4500, the classical and experimental values of absorption are the same order of magnitude, as is shown in Table 1. This indicates that the viscosity has relaxed out for the higher molecular weight PEG but not necessarily so for the lower, 4500, molecular weight.

If structural relaxation exists in solutions of polyethylene glycol, then a distribution of relaxation frequencies will be present. Therefore, a major point of interest in PEG was to investigate whether or not it did, in fact,

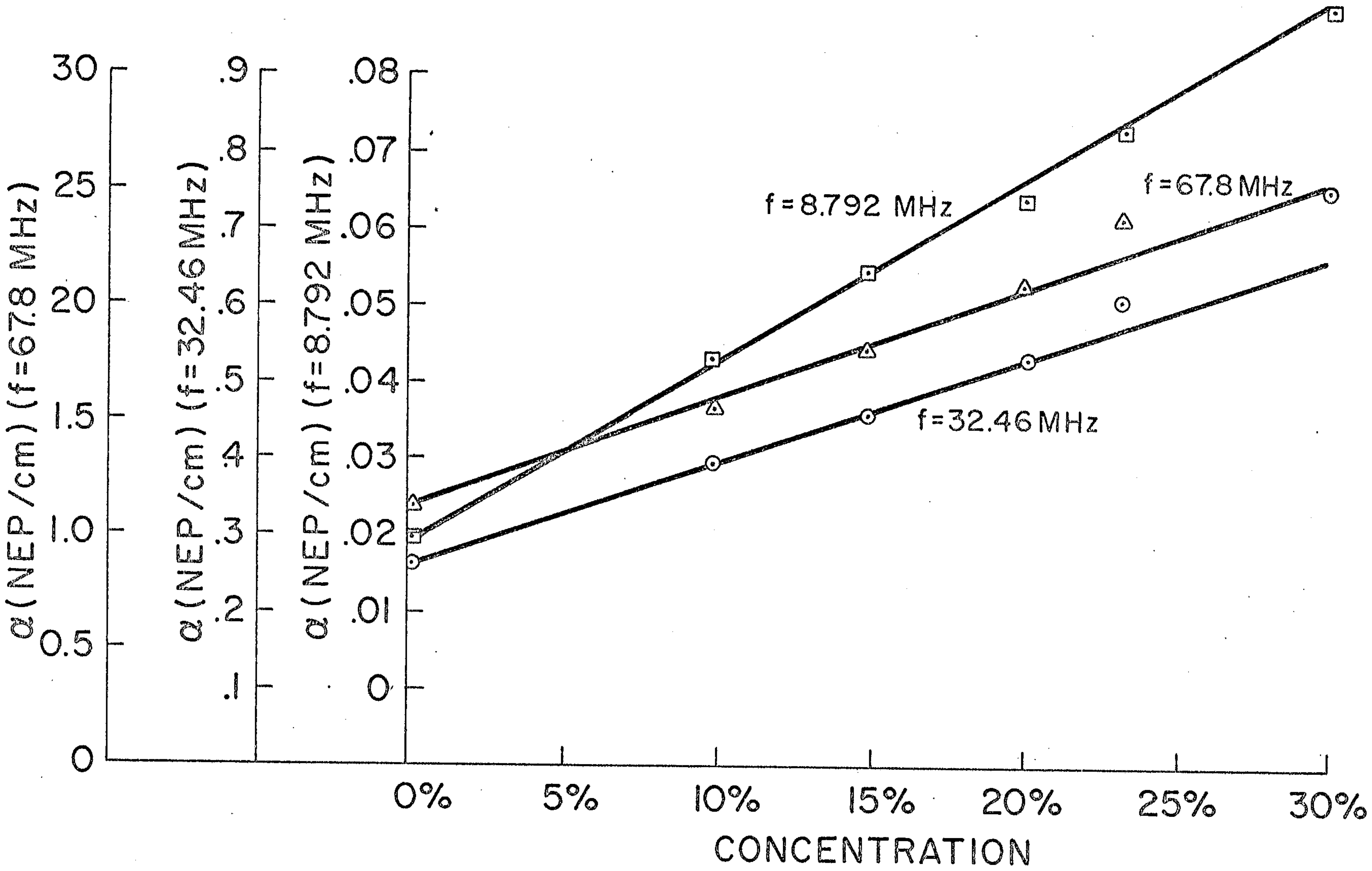

Figure 8 - ABSORPTION VERSUS CONCENTRATION
(TEMPERATURE = 20.7°C)

TABLE 1

COMPARISON BETWEEN CLASSICAL AND EXPERIMENTAL VALUES FOR FREQUENCY-FREE ABSORPTION COEFFICIENTS PER UNIT CONCENTRATION.

Molecular Weight 20,000

Concentration 20%

	Frequency-free absorption coefficients per unit concentration (sec^2-cc/cm-gm)	
Temperature	Classical*	Experimental
4°C	3154×10^{-17}	450×10^{-17} (4 MHz)
20°C	1750×10^{-17}	400×10^{-17} (1.5 MHz)

Molecular weight 4500

Concentration 20%

	Frequency-free absorption coefficients per unit concentration (sec^2-cc/cm-gm)	
Temperature	Classical*	Experimental#
4°C	699×10^{-17}	300×10^{-17} (14 MHz)
20°C	320×10^{-17}	200×10^{-17} (14 MHz)

*Values of viscosity obtained from Dow Chemical Co. (1962).

#Molecular weight 4500 measured only in high frequency system.

possess a single relaxation as Hammes and Lewis (1966) and Lewis (1965) reported.

The absorption data are shown in Figures 9 and 10 where the contribution due to water has been subtracted off ($\frac{\alpha}{f^2} = \frac{\alpha_{TOTAL}}{f^2} - \frac{\alpha_{H_2O}}{f^2}$) at the temperature of concern, and the difference is divided by the concentration (gm/cc) of the polyethylene glycol solution. From these plots of frequency-free absorption coefficients per unit concentration, the best fit single relaxation equation was obtained as follows. A least squares fit process was applied to the following equation to obtain the best fit single relaxation equation (Andreae <u>et al</u>., 1965),

$$\frac{\alpha}{f^2 \, conc} = \frac{A}{1 + \left(f/f_r\right)^2} + B \qquad (27)$$

Since Hammes and Lewis did not investigate PEG solutions in the frequency range below 10 MHz, two best fit curves were calculated, one for all the data and the other for the data greater than 10 MHz. In addition, the absorption data obtained by Lewis (1965) for PEG solutions were treated as above and the best fit single relaxation equation was obtained. The parameters of (27) are tabulated in Table 2.

For the data from this investigation, if a single relaxation did exist, both best fit equations would yield approximately the same relaxation frequency f_r along with comparable values to the parameters A and B. The values

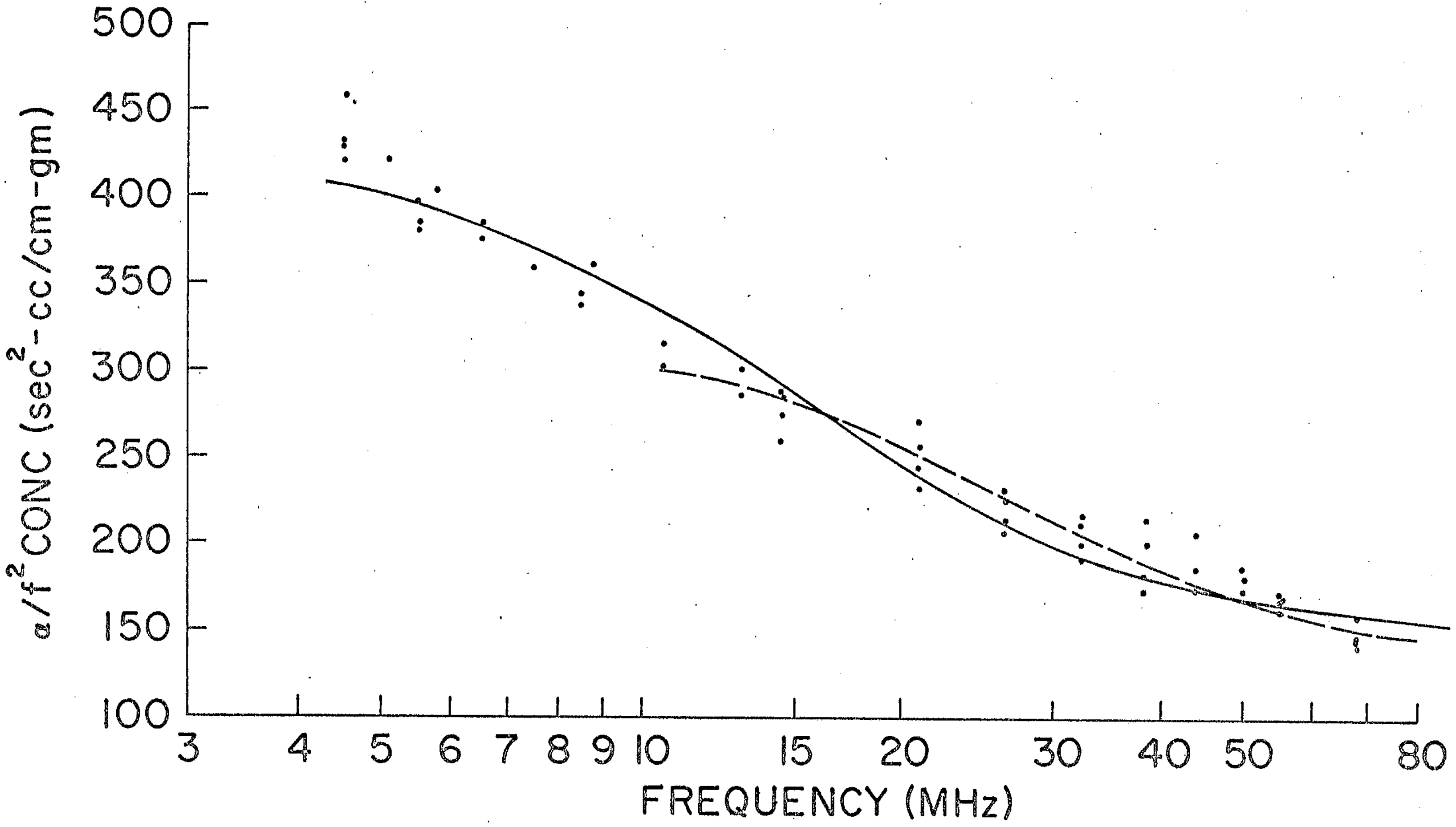

Figure 9 - FREQUENCY-FREE ABSORPTION PER UNIT CONCENTRATION VERSUS FREQUENCY AT 4.2°C. LINES ARE BEST FIT SINGLE RELAXATION FOR ALL DATA (——) AND DATA GREATER THAN 10 MHz (---).

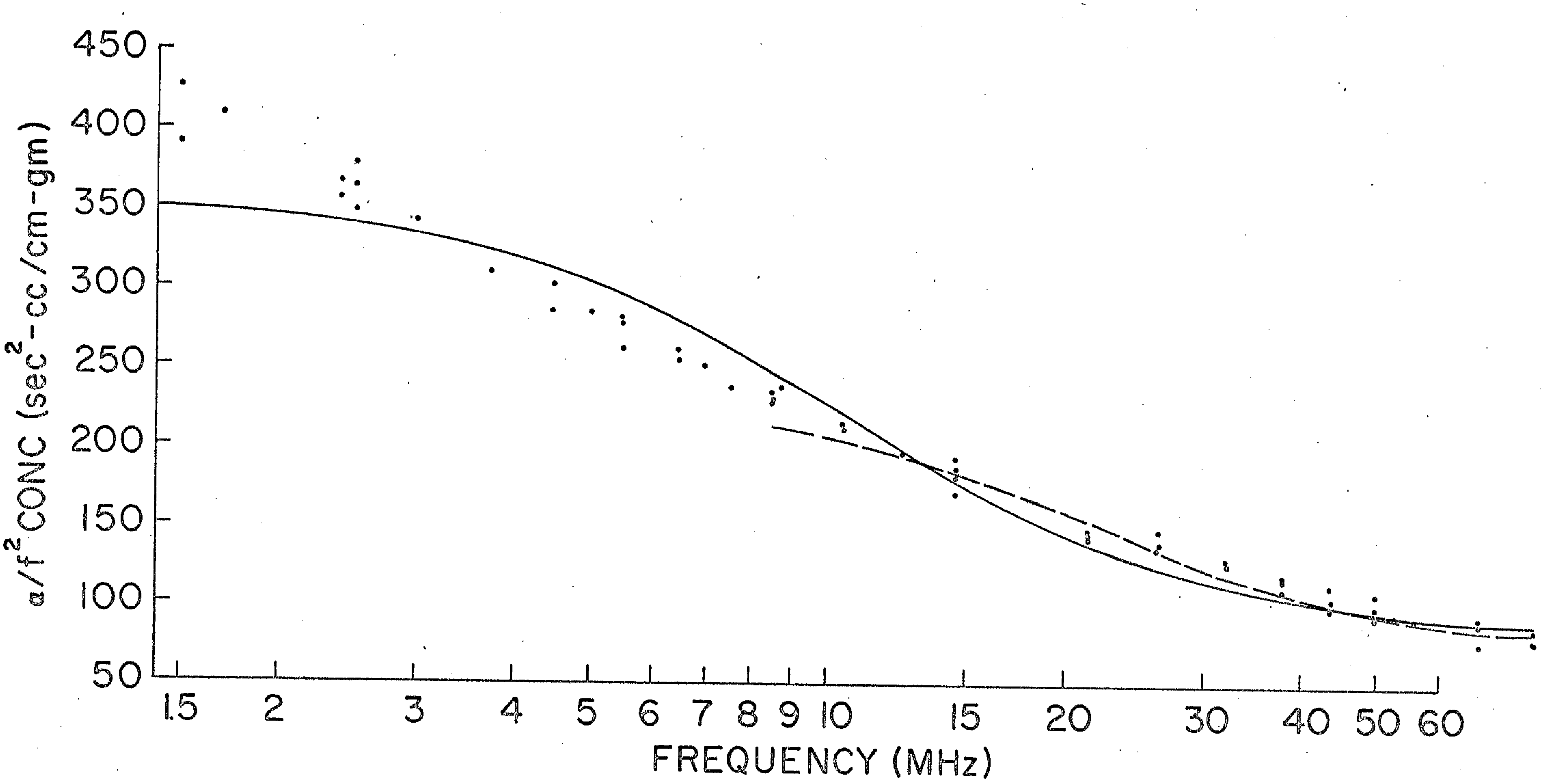

Figure 10 - FREQUENCY-FREE ABSORPTION PER UNIT CONCENTRATION VERSUS FREQUENCY AT 20.7°C. LINES ARE BEST FIT SINGLE RELAXATION FOR ALL DATA (——) AND DATA GREATER THAN 10MHz (---).

TABLE 2

PARAMETERS TO BEST FIT SINGLE RELAXATION EQUATION

Temperature (°C)	Data Considered	A	B	f_r (MHz)
		(10^{-17} sec^2-cc/cm-gm)		
4.2	All	282	150	14.2
4.2	10 MHz	198	131	25.2
20.7	All	265	90	10.4
20.7	10 MHz	161	82	19.1
10.0	H & L	195	116	18.9
25.0	H & L	144	52	21.1

H & L - Lewis (1965) and Hammes and Lewis (1966) of Table 2 indicate this is not the case. However, the relaxation frequencies for the data truncated at 10 MHz compares well with the relaxation frequencies obtained from the data of Hammes and Lewis (1966) and Lewis (1965).

It should be observed from Figures 9 and 10 that the data below 14 MHz continues to rise and does not level off so that the distribution is broad relative to the frequency range of investigation. Also, the plotted best fit single relaxation curves for all the data deviate from the actual data points. The shape of these curves for the experimental data suggest a multiple relaxation phenomenon exists.

The Mikhailov plots, Figures 11 and 12, would yield straight lines, as predicted by (15), if a single relaxation process existed. Since $\omega^2/2\alpha c^3$ is not linearly dependent on ω^2, the relaxing process cannot be due to a single relaxation.

Plots of the speed of sound in aqueous solution of PEG versus temperature are presented in Figure 13. The speed of sound in distilled water is given as a reference. In Figure 14, the speed of sound in water has been subtracted off the speed of sound in solutions of PEG at the appropriate temperature. This difference is then divided by the appropriate concentration of the PEG solution. All of the treated data points fall approximately on the same line, save for ethylene glycol (molecular weight of 62.05). This indicates that the excess speed of sound in the PEG solutions is linearly depen-

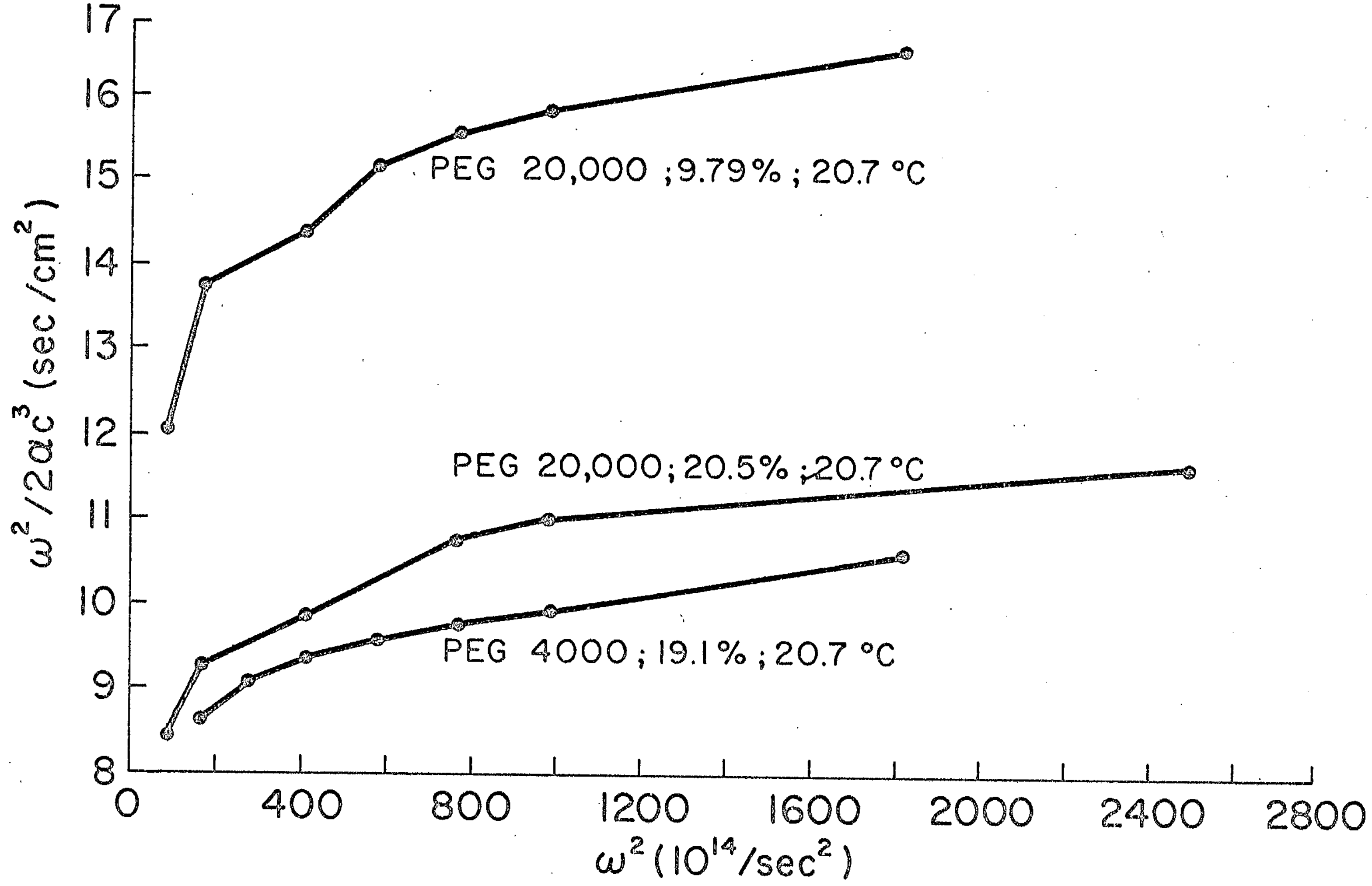

Figure 11 - MIKHAILOV PLOT FOR HIGH FREQUENCY DATA

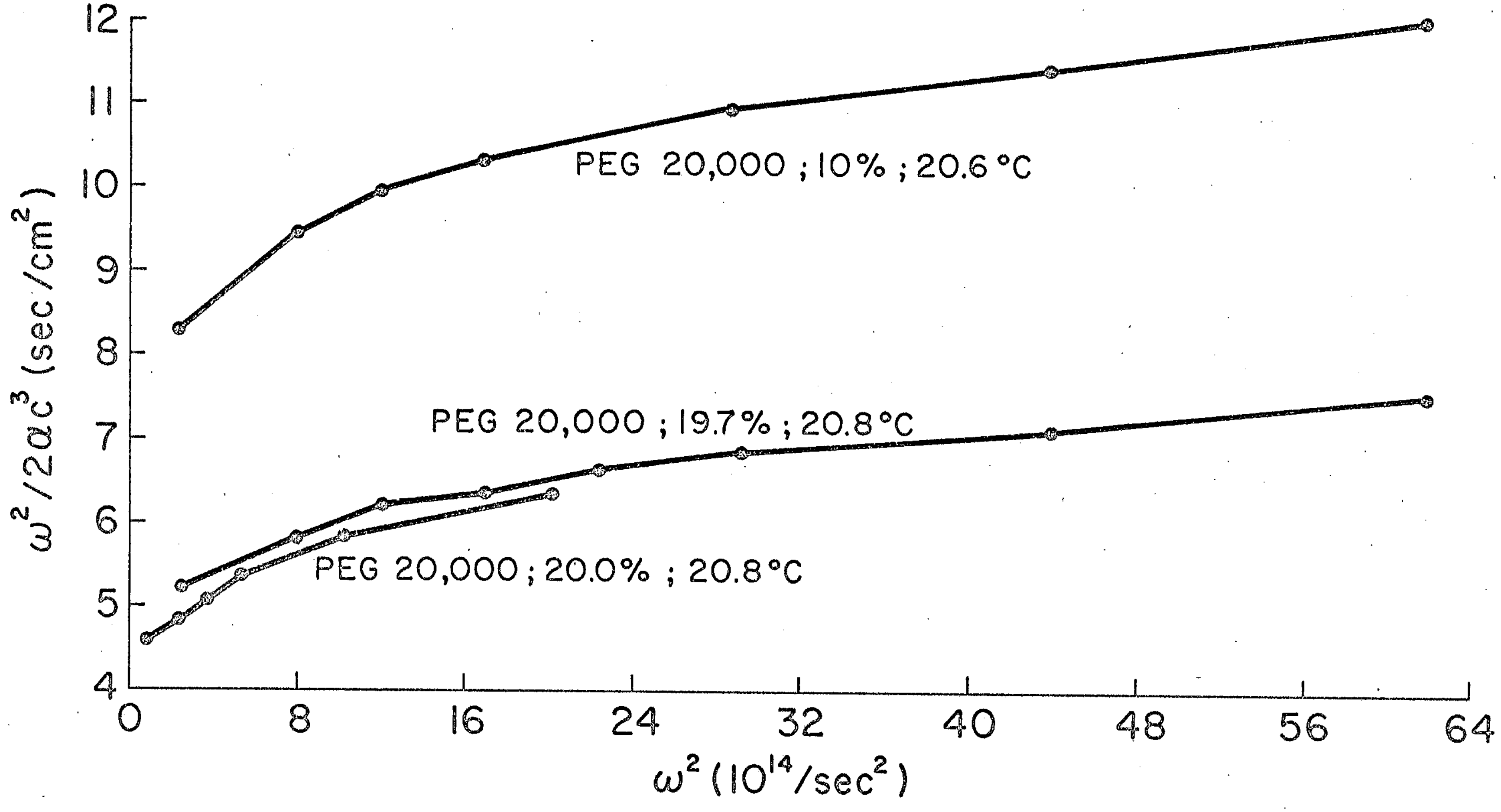

Figure 12 - MIKHAILOV PLOT FOR LOW FREQUENCY DATA

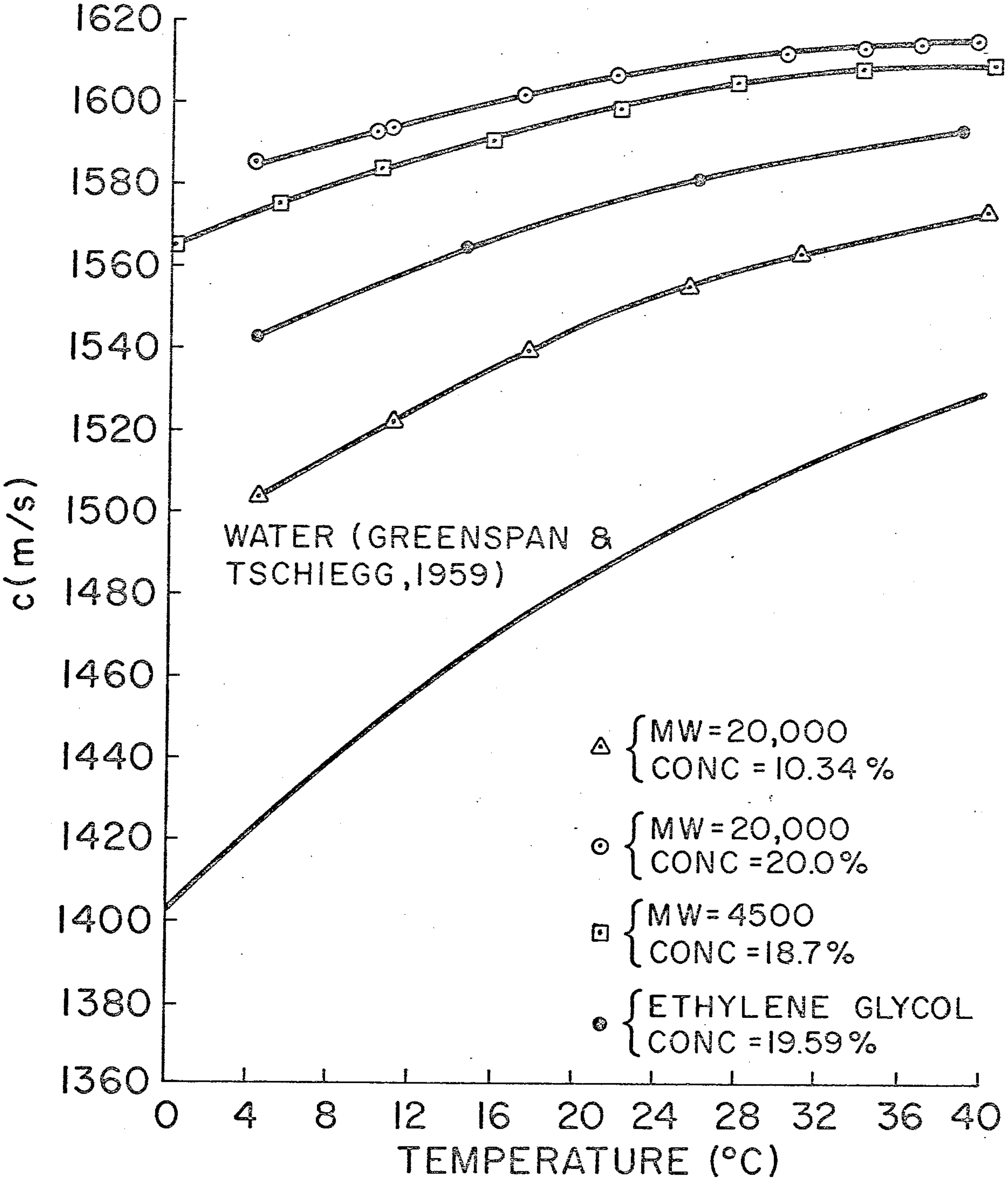

Figure 13 - SPEED OF SOUND VERSUS TEMPERATURE (FREQUENCY = 8.8MHz).

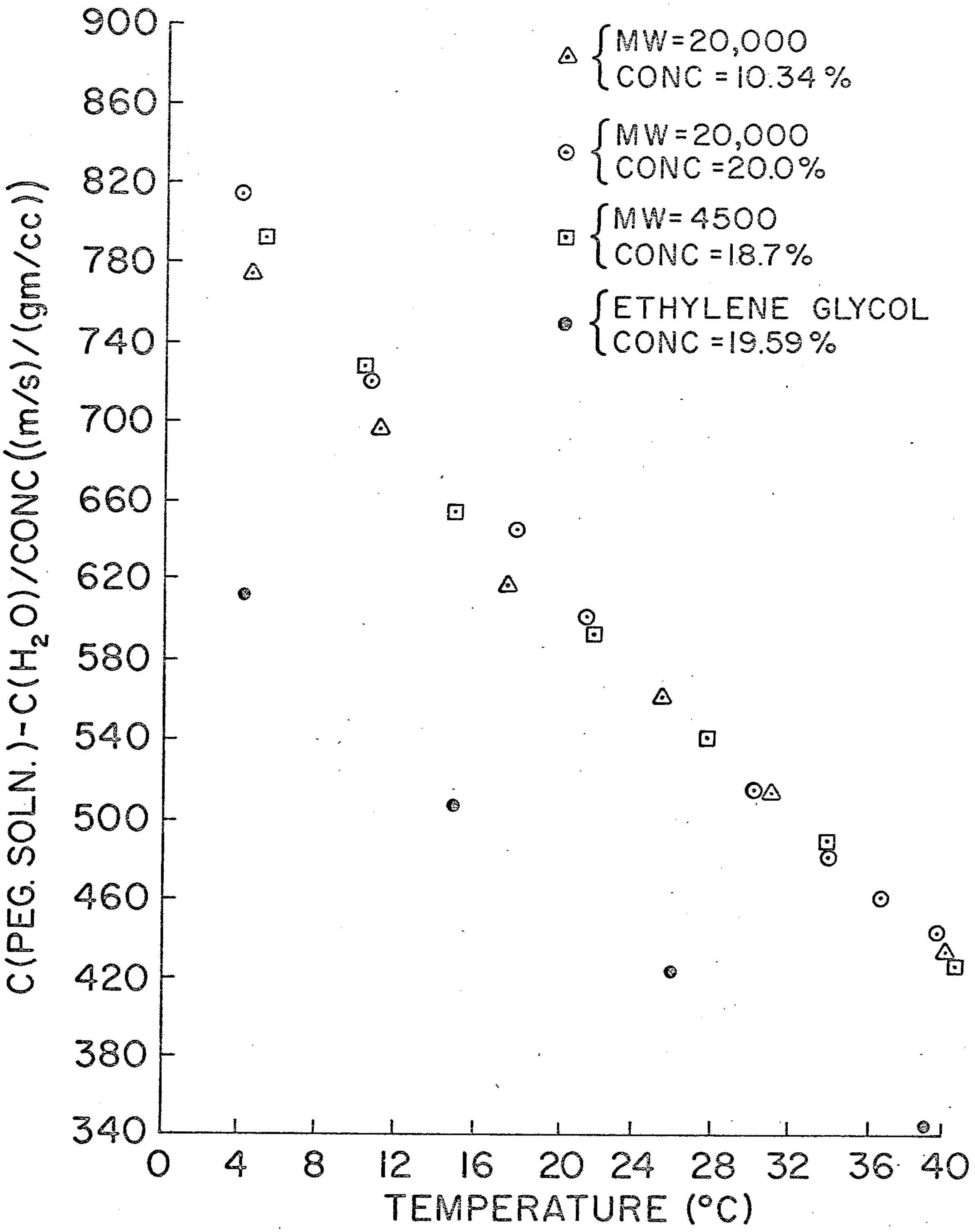

Figure 14 - EXCESS SPEED OF SOUND PER UNIT CONCENTRATION VERSUS TEMPERATURE (FREQUENCY = 8.8MHz).

dent on the solution concentration and independent of molecular weight.

In summary this study of polyethylene glycol indicates that the absorption coefficient can be characterized by multiple relaxation frequencies, as compared to the results presented by Hammes and Lewis (1966) and Lewis (1965), who reported a single relaxation phenomenon. Also, for concentrations of PEG solutions less than 20%, the absorption coefficient is linearly dependent on concentration. In addition, the frequency-free absorption coefficient per unit concentration is independent of the molecular weight of polyethylene glycol solutions between 4500 and 20,000. Finally, the excess speed of sound in solutions of PEG is independent of molecular weights 4500 and 20,000 and linearly dependent on concentration.

The mechanism(s) by which the ultrasonic absorption in aqueous solutions of macromolecules such as polyethylene glycol has been attributed to cooperative phenomena between solvent and solute (Lewis, 1965; Hammes and Lewis, 1966). However, attempts to elucidate the mechanism(s) of excess absorption on the basis of particle scattering, viscous and thermal mechanism, rotational isomerism and relative motion between solvent and solute have been inadequate (Hawley, 1966). It is obvious that experimental work must continue if these mechanism(s) are to be established.

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