

# Ultrasonic Absorption in Aqueous Solutions of Polyethylene Glycol<sup>1a</sup>

by L. W. Kessler,<sup>1b</sup> W. D. O'Brien, Jr., and F. Dunn

*Bioacoustics Research Laboratory, University of Illinois, Urbana, Illinois 61801 (Received February 16, 1970)*

Ultrasonic absorption spectra have been determined for aqueous solutions of polyethylene glycol, a linear molecule which assumes a random coil configuration, as a function of molecular weight (62–20,000) and frequency (1.5–163 MHz). The broad frequency range employed in this investigation revealed the presence of multiple relaxation processes. Similarities between the absorption dependence upon frequency and molecular weight of polyethylene glycol and dextran, another macromolecule which assumes a similar spatial configuration in solution, are pointed out. It is concluded that the observed ultrasonic absorption cannot be fully accounted for by shear viscoelasticity and that the presence of a bulk viscosity must be taken into account.

## Introduction

The ultrasonic velocity of propagation and absorption coefficient characteristic of aqueous solutions of macromolecules are of interest in the fields of physical chemistry and biophysics to the extent that these properties are useful in studying the kinetic behavior of chemical and structural equilibria having reaction rate constants between  $10^{-9}$  and  $10^{-4}$  sec.<sup>2a</sup> These equilibria may be perturbed by changes in temperature, pressure, or density produced by the sound wave. The molecular process whose characteristic time determines the rate at which equilibrium is restored, after the perturbation, is referred to as a relaxation process.<sup>2b</sup> It has been observed that perturbations of configurational equilibria may result in significant acoustic absorption<sup>3</sup> and definite changes in absorption and velocity that correlate with structural alterations have also been reported.<sup>4,5</sup> This study was undertaken to continue the investigation of the ultrasonic absorption spectra of aqueous solutions of macromolecules which assume similar configurations but which differ chemically. Polyethylene glycol (PEG), a synthesized long-chain flexible macromolecule, was chosen for this purpose since it assumes a random coil configuration in aqueous solution as does another macromolecule, dextran, which has already been studied.<sup>6,7</sup> In addition, since PEG is readily obtainable in several narrow molecular weight fractions, the effect of polymerization on the acoustic properties of the solution could be studied.

## Theory

The adiabatic propagation of a longitudinal acoustic wave through a fluid medium results in time-varying localized perturbations in thermodynamic equilibria at rates which depend on the sound frequency,  $f$ , and maximum interaction for any particular equilibrium occurs when  $f = f_0 = (2\pi\tau)^{-1}$ , where  $\tau$  is the characteristic relaxation time of the reaction being perturbed. This leads to a time lag between an applied pressure and the resulting change in density. Consequently, molecular energy level populations are perturbed at the expense of

acoustic wave energy, and the process results in absorption. The absorption that is experimentally observed may result from multiple independent or coupled relaxation processes which can yield a spectrum of relaxation times.

Shear viscosity was one of the first properties to be recognized as responsible for the absorption of sound in fluids.<sup>8</sup> Although it was realized at the time that a liquid may possess bulk viscosity as well, this was not considered, as no direct method was available for its measurement. The well-known equation describing the absorption of sound by a viscous liquid is

$$\alpha = \frac{2\pi^2 f^2}{\rho V^3} (\eta_v + \frac{4}{3}\eta_s) \quad (1)$$

where  $\rho$  and  $V$  are the undisturbed density and the low-frequency speed of sound, and  $\eta_v$  and  $\eta_s$  are the bulk and shear viscosities, respectively. Variation in the viscosity with frequency is due to relaxation; however, for water the viscous relaxation times are thought to be of the order  $10^{-12}$  sec,<sup>9,10</sup> which is almost two orders of magnitude beyond the currently attainable range of acoustic measurements.

(1) (a) Portions of this work were extracted from the thesis submitted by L. W. K. in partial fulfillment of the requirements for the Ph.D. degree in Electrical Engineering, University of Illinois, 1968. (b) To whom correspondence should be addressed at Research Department, Zenith Radio Corp., 6001 W. Dickens Avenue, Chicago, Ill. 60639.

(2) (a) F. Dunn, P. D. Edmonds, and W. J. Fry, "Absorption and Dispersion of Ultrasound in Biological Media" in "Biological Engineering," H. P. Schwan, Ed., McGraw-Hill Book Co., New York, N. Y., 1969; (b) M. Eigen and L. deMayer, "Relaxation Methods" in "Technique of Organic Chemistry," Vol. 8, part 2, S. L. Friess, et al., Ed., Interscience, New York, N. Y., 1963.

(3) G. Schwarz, *J. Mol. Biol.*, **11**, 64 (1965).

(4) L. W. Kessler and F. Dunn, *J. Phys. Chem.*, **23**, 4526 (1969).

(5) R. Zana, R. Cerf, and S. Candau, *J. Chim. Phys.*, **60**, 869 (1963).

(6) S. A. Hawley and F. Dunn, *J. Chem. Phys.*, **50**, 3523 (1969).

(7) S. A. Hawley, L. W. Kessler, and F. Dunn, *J. Acoust. Soc. Amer.*, **38**, 521 (1965).

(8) G. G. Stokes, *Trans. Cambr. Phil. Soc.*, **8**, 287 (1845).

(9) L. Hall, *Phys. Rev.*, **73**, 775 (1948).

(10) H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957).

The shear viscosity exhibited by a dilute solution of long-chain flexible polymers results from the frictional resistance opposing the flow of solvent molecules past polymer segments and the resistance to perturbation of the configurational equilibrium of the polymer. Further, the bulk viscosity is due to resistance of the polymer molecules against changing the volume they occupy in the solvent in response to a pressure change, and it is dependent on solvent-polymer interactions which may not affect the shear viscosity. Adequate physical models which would predict the observed frequency dependence of bulk viscosity have not yet been developed for aqueous systems because of the inadequate knowledge of the specific solvent-polymer interactions. The polymer model used to calculate the dynamic shear viscosity consists of a linear arrangement of  $N + 1$  identical beads each having mass  $m$  connected alternately by  $N$  massless link segments.<sup>11</sup> If complete flexibility is allowed at each bead, the mean-squared distance between the ends of the chain,  $\bar{L}^2$ , is given by the statistical random walk result for large  $N$ <sup>11</sup>

$$\bar{L}^2 = \bar{b}_0^2 N \quad (2)$$

where  $\bar{b}_0^2$  is the mean-squared segment length. Since complete flexibility cannot be allowed,  $\bar{b}_0^2$  is replaced by  $\bar{b}_{\text{eff}}^2$ .

The dynamic shear viscosity of an infinitely dilute solution of Gaussian coiled polymers is given by<sup>12,13</sup>

$$\eta^* = \eta_0 + \frac{CN_A}{M_w} KT \sum_{k=1}^N \frac{\tau_k}{1 + i\omega\tau_k} \quad (3a)$$

$$\eta^* = \eta' + i\eta'' \quad (3b)$$

where  $\eta_0$  is the shear viscosity of the solvent,  $C$  is the concentration of polymer molecules,  $M_w$  is the weight-average molecular weight of the polymer,  $N_A$  is Avogadro's number,  $T$  is the absolute temperature,  $K$  is Boltzmann's constant, and the summation is carried out over all  $N$  segments of the polymer. In eq 3b,  $\eta''$  can be considered as elasticity. The relaxation time,  $\tau_k$ , depends on hydrodynamic interactions<sup>12-15</sup> which may be taken into account by the expansion parameter<sup>12</sup>  $\epsilon$  by

$$\frac{\bar{b}_{\text{eff}}^2}{\bar{b}_0^2} = N^\epsilon \quad (4)$$

The relaxation times are given by

$$\tau_k = \frac{M_w \eta_0 [\eta]_0}{\left( \sum_{k=1}^N \lambda^{-1} \right) N_A K T \lambda_k} \quad (5)$$

where  $[\eta]_0$  is the intrinsic viscosity of the solution at  $\omega = 0$ , given by<sup>12</sup>

$$[\eta]_0 = (2.84 \times 10^{23}) \frac{\bar{L}^3}{M_w} \quad (6)$$

and the  $\lambda_k$ 's are tabulated as a function of  $\epsilon$  in ref 14.

### Ultrasonic Technique

The amplitude of a plane, progressive sinusoidal wave decays exponentially as it propagates through a lossy, homogeneous, infinitely extended medium according to

$$P(x,t) = P_0 \exp(-\alpha x) \exp[i(\omega t - kx)] \quad (7)$$

where  $P$  is the instantaneous value of the acoustic pressure amplitude as a function of distance  $x$  and time  $t$ , and  $k$  is the wave number. The pulse technique employed in this study to measure the absorption coefficient in liquids simulates the free field condition expressed by eq 7 for finite sample sizes, provided that the pulse length in the medium is short compared with the acoustic path length. In addition, the error in the absorption coefficient due to the spectrum of frequencies associated with a pulse train is negligible if the pulse is at least  $30\pi/\omega$  sec in length.<sup>16</sup>

Two techniques were employed in the present study to measure the absorption coefficient over the frequency range from 1.5 to 163 MHz. The first technique,<sup>17,18</sup> an automated version of that originally described by Pellam and Galt,<sup>16</sup> can be employed into the low megahertz frequency range depending on the magnitude of the absorption relative to the attenuation due to diffraction. For example, for a 1-in. diameter transducer the above considerations limited operation to 9 MHz. Over the frequency range from 9 to 69 MHz two matched 3-MHz fundamental frequency X-cut quartz transducers are set parallel and coaxial to each other in the liquid to be studied. Each transducer is edge-mounted with its front face in direct contact with the liquid and its back face exposed to an air-filled cavity. One transducer emits pulses of ultrasonic energy, while the other transducer is employed as a detector. The acoustic path length is varied by displacing one transducer relative to the other at constant velocity. The amplitude of the received acoustic pulse varies according to eq 7, and the amplitude of the electrical signal from the receiving transducer is recorded on a logarithmic recorder whose chart displacement is synchronized to the moving transducer. Over the frequency range from 75 to 165 MHz, a pair of 15-MHz fundamental, X-cut quartz transducers bonded to fused quartz delay rods are substituted for the 3-MHz transducers.

In this variable path length technique, the absorption could be determined to within  $\pm 3\%$  in water over the approximate frequency range from 15 to 100 MHz.

(11) C. Tanford, "Physical Chemistry of Macromolecules," Wiley, New York, N. Y., 1961.

(12) B. H. Zimm, *J. Chem. Phys.*, **24**, 269 (1956).

(13) P. E. Rouse, *ibid.*, **21**, 1272 (1953).

(14) V. Bloomfield and B. H. Zimm, *ibid.*, **44**, 315 (1966).

(15) A. Peterlin, *J. Polym. Sci., Part A2*, **5**, 179 (1967).

(16) J. R. Pellam and J. K. Galt, *J. Chem. Phys.*, **14**, 608 (1946).

(17) S. A. Hawley, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1966.

(18) L. W. Kessler, S. A. Hawley, and F. Dunn, *J. Acoust. Soc. Amer.*, **41**, 1591 (1967).

This decreased to about  $\pm 4\%$  at 9 MHz due to the diffraction corrections, and to about  $\pm 8\%$  at 165 MHz due to limitations of the instrumentation in maintaining parallelism between the two transducers. In PEG solutions, where the absorption coefficients exceeded that of water, the diffraction corrections became less important. Velocity measurements are performed by electronically measuring the length of time required to change the acoustic path length by 100 wavelengths of sound. Details of this system can be found in ref 19 and 20.

At lower frequencies a comparison technique described by Carstensen<sup>21</sup> minimizes diffraction effects by determining the acoustic properties of the sample liquid relative to those known of a reference liquid. In the present study, water served as a convenient reference liquid since its absorption coefficient and velocity of sound have already been determined accurately.<sup>22,23</sup> The two compartments of a double chamber tank are separated by an acoustically transparent window and filled, respectively, with the reference liquid and the sample liquid. One 3-in. diameter, 0.3-MHz ceramic transducer is placed in each chamber, and the pair face each other through the window. The transducers are mounted coaxially parallel and are supported a fixed distance apart on a sliding carriage. The acoustic measurements are made by moving the carriage along the axis of sound propagation, which results in changes in the relative amounts of sample and reference liquids in the acoustic path. If the velocity of sound in the sample liquid is within a few per cent of that in the reference liquid, then varying the relative amounts of each within the acoustic path produces little change in the overall acoustic path length and consequently only a negligible diffraction effect. Due to the negligible diffraction corrections necessary with the comparison technique, the absorption coefficient could be determined to within  $\pm 3\%$  in situations where the measured attenuation exceeded about 4 db, for example, at 2 MHz in a 0.2 g/cc solution of PEG. Details of this technique can be found elsewhere.<sup>19</sup>

## Results

The ultrasonic absorption coefficient was determined in aqueous solutions of six molecular weight fractions of polyethylene glycol over a frequency range from 1.5 to 163 MHz and over a temperature range from 4.2 to 32.2°. PEG samples,  $M_w$  20,000 and  $M_w$  4500, were obtained through the courtesy of Dow Chemical Co., Midland, Mich. Molecular weight fractions 1450, 400, and 150 were obtained from Matheson Coleman and Bell, Cincinnati, Ohio, and the monomer was obtained from Allied Chemical Co., Morristown, N. J. Solutions were prepared by dissolving the polymer in singly distilled water and filtering twice through type A glass fiber filters. The concentrations of the polymer solutions of  $M_w$  1450 and above were determined by

evaporation, and volumetric solutions were prepared for the three remaining fractions. All concentrations were determined within  $\pm 0.5\%$  at 20.0°.

A common method for presenting acoustic absorption data for solutions is to plot the excess frequency free absorption per unit concentration

$$A = \Delta\alpha/Cf^2 \quad (8)$$

as a function of frequency where  $C$  is the mass concentration of solute and  $\Delta\alpha$  is the difference in the observed absorption coefficients between the solution and the solvent. For PEG the relationship between  $\Delta\alpha$  and  $C$  is linear up to a concentration of about 0.21 g/cc<sup>19,24</sup> and all measurements reported are within this range, where polymer-polymer interactions are not significant acoustically.

Repeated investigations failed to reveal any statistically significant difference in the ultrasonic absorption coefficient between solutions of  $M_w$  20,000 and  $M_w$  4500 over the entire frequency range, and therefore these data were combined and averaged at each frequency. The excess absorption parameter  $A$  is plotted in Figure 1 as a function of frequency at 20.7° for all molecular weight fractions investigated and in Figure 2 the absorption for the two largest molecular weight fractions is shown for other temperatures. Evidence of relaxation is prominent for  $M_w \geq 1450$  and may also be present for lower molecular weights in the frequency range covered by this investigation. If relaxation phenomena were not present,  $A$  would be a constant

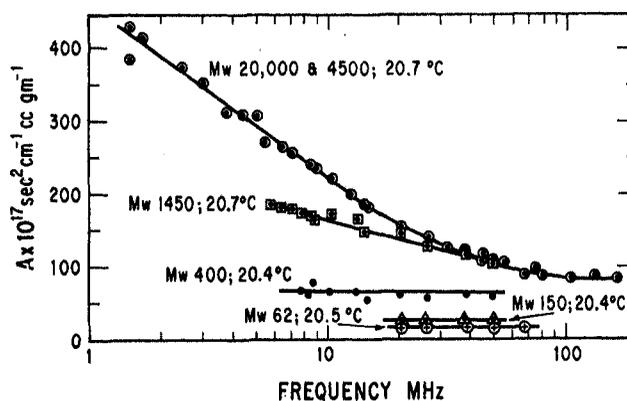


Figure 1. Ultrasonic absorption spectrogram for aqueous PEG solutions.

(19) L. W. Kessler, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1968.

(20) L. W. Kessler, S. A. Hawley, and F. Dunn, "Automatic Determination of Velocity and Absorption of Sound in Fluids," accepted for publication in *Acustica*.

(21) E. L. Carstensen, *J. Acoust. Soc. Amer.*, **26**, 858 (1954).

(22) J. M. M. Pinkerton, *Proc. Phys. Soc. (London)*, **B62**, 129 (1949).

(23) M. Greenspan and C. E. Tschiegg, *J. Acoust. Soc. Amer.*, **31**, 75 (1959).

(24) W. D. O'Brien, Jr., M.S. Thesis, University of Illinois, Urbana, Ill., 1968.

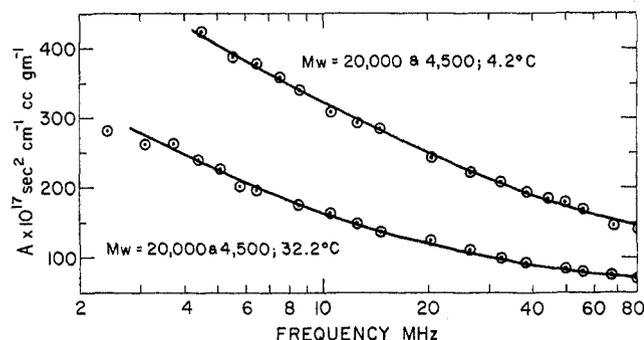


Figure 2. Ultrasonic absorption spectrogram for aqueous PEG solutions.

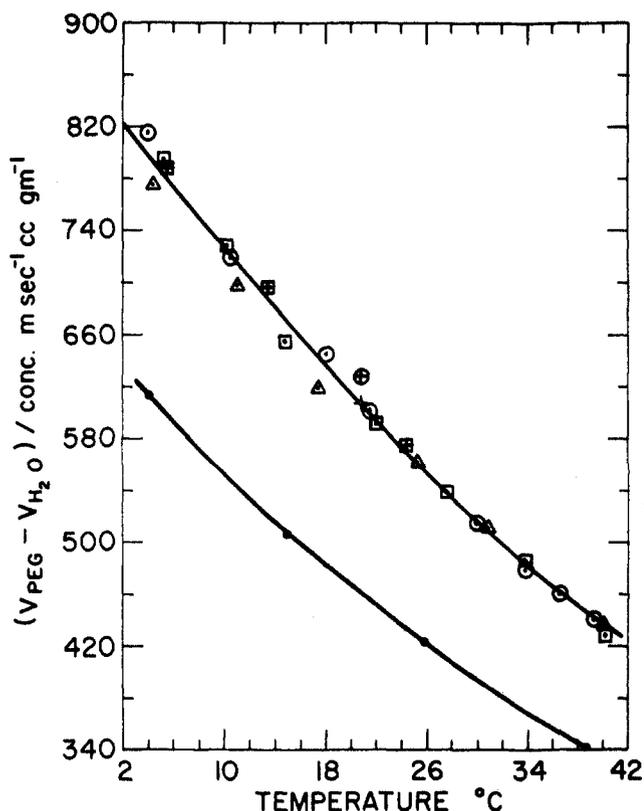


Figure 3. Normalized difference between the velocity of sound in aqueous solutions of PEG and that in water:  $\circ$ ,  $M_w$  20,000, 0.200 g cc<sup>-1</sup>;  $\Delta$ ,  $M_w$  20,000, 0.1034 g cc<sup>-1</sup>;  $\square$ ,  $M_w$  4500, 0.187 g cc<sup>-1</sup>;  $+$ ,  $M_w$  1450, 0.203 g cc<sup>-1</sup>;  $\oplus$ ,  $M_w$  400, 0.200 g cc<sup>-1</sup>;  $\boxplus$ , triethylene glycol, 0.200 g cc<sup>-1</sup>;  $\bullet$ , ethylene glycol, 0.195 g cc<sup>-1</sup>.

over the frequency range as indicated by eq 1. The velocity of sound was determined as a function of temperature for each solution as shown in Figure 3. With the exception of the monomer, the velocity of sound in aqueous solutions of PEG is proportional to concentration and independent of molecular weight to within the limits of the experimental data.

### Discussion

The ultrasonic absorption coefficients in aqueous solutions of PEG have been reported recently<sup>25,26</sup> to be

characterized adequately by single relaxation mechanisms for molecular weight fractions 20,000 and 7500 over the frequency range 10 to 200 MHz. On the other hand, a spectrum of relaxation times is necessary to characterize the absorption in aqueous solutions of dextran.<sup>6,27</sup> The absorption resulting from a single relaxation mechanism can be characterized by eq 9

$$\frac{\alpha}{f^2} = \frac{A\tau}{1 + \omega^2\tau^2} + B \quad (9)$$

where  $A$  and  $B$  are constants. Linear viscoelastic theories, however, predict a spectrum of relaxation times for long-chain flexible polymers in solution due to shear viscosity; *viz.*, combining eq 1 and the real part of eq 3 the shear viscosity contribution to the absorption becomes

$$\frac{\alpha}{f^2} = \frac{8\pi^2}{\rho V^3} \left[ \eta_0 + \frac{CN_A K T}{M_w} \sum_{k=1}^N \frac{\tau_k}{1 + \omega^2 \tau_k^2} \right] \quad (10)$$

To determine how well a single relaxation curve can describe the present data, a least-squares procedure was employed to select the optimum values for  $A$ ,  $B$ , and  $\tau$ . As shown in Figure 4, the somewhat linear dependence of  $A$  on  $\log f$  between 1.5 and 25 MHz is not compatible with the best-fit single relaxation curve. However, to confirm whether a single relaxation could provide a reasonable description of the data above 10 MHz, as reported by others,<sup>25</sup> the least-squares procedure was employed again with our data below 10 MHz omitted. This result is shown in Figure 5, and it is clear that a misleading conclusion about the nature of the relaxation can be reached easily if an insufficiently broad frequency range is considered.

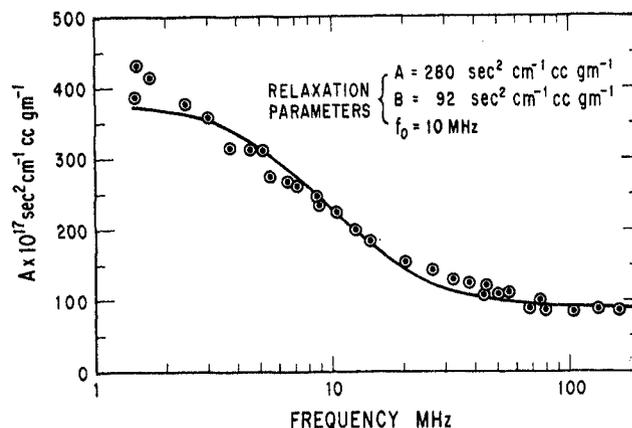


Figure 4. Best-fit single relaxation curve for  $M_w$  20,000 and  $M_w$  4500 (see eq 9).

(25) G. G. Hammes and T. B. Lewis, *J. Phys. Chem.*, **70**, 1610 (1966).

(26) T. B. Lewis, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1965.

(27) L. W. Kessler, M.S. Thesis, University of Illinois, Urbana, Ill., 1966.

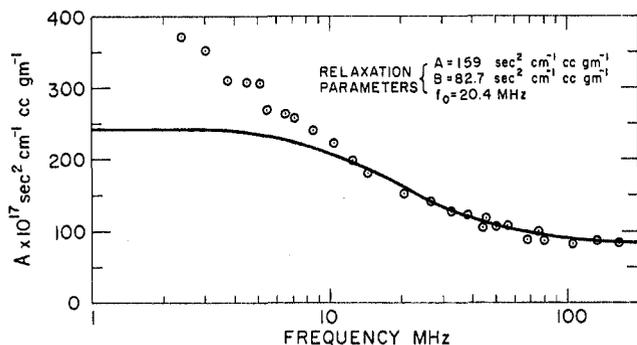


Figure 5. Best-fit single relaxation curve for  $M_w$  20,000 and  $M_w$  4500, above 10 MHz.

To elucidate the mechanism(s) responsible for the ultrasonic absorption, the contribution of dynamic shear viscosity must be considered. Heretofore it was thought that such a process was unimportant for this material for two reasons.<sup>25</sup> First, on the basis of their data (which were all above 10 MHz), the mechanism was concluded to be a single relaxation process, and second, the relaxation times predicted theoretically were more than an order of magnitude larger than those observed. Contributing to this last factor is an error in their calculation of  $\tau_k$  wherein the static viscosity of the solution  $\eta$  is used in place of that of the solvent,  $\eta_0$ .<sup>26</sup>

The dynamic shear viscosity contribution to the absorption coefficient is discussed below on the basis of the Bloomfield-Zimm theory.<sup>14</sup> Subsequent comparison with the contribution predicted by the Rouse theory<sup>13</sup> and the Zimm theory<sup>12</sup> resulted in only slight differences in the overall absorption. PEG molecules are assumed to be extended, nonfree-draining, flexible polymers and each structural unit is assumed to be the monomer unit, although larger segments could also have been used.<sup>11</sup> The effective segment length,  $b_{eff}$ , is calculated from the ratio of the intrinsic viscosity, predicted on the basis of  $b_0$  for nonfree-draining coils, to that observed, and from eq 6 and 2 the following relationship is obtained

$$\frac{[\eta]_0 \text{ theor}}{[\eta]_0 \text{ obs}} = \left[ \frac{b_0}{b_{eff}} \right]^3 \quad (11)$$

The intrinsic viscosity was reported in aqueous solutions of PEG at 20.0°<sup>28</sup> and found to be related to molecular weight by the following relationship

$$[\eta]_{\text{obs}} = 2.0 + 0.033(M_w)^{0.72} \quad (12)$$

Table I lists the properties of PEG polymer chains used to compute the relaxation times, and Table II lists the relaxation times for the first four modes of viscoelastic relaxation. The viscoelastic absorption is evaluated from the following equation where  $\Delta\alpha_s$  is the difference

$$A_s = \frac{\Delta\alpha_s}{Cf^2} = \frac{15.65 \times 10^{-5}}{M_w} \sum_{k=1}^N \frac{\tau_k}{1 + \omega^2 \tau_k^2} \quad (13)$$

Table I: Properties of PEG Polymer Chains

$M_w$	$N$	$[\eta]^a$ , cc/g	$[\eta]^b$ , cc/g	$b_{eff}$ , Å	$\epsilon$
20,000	455	43.2	11.7	6.78	0.14
4,500	102	16.1	5.48	6.30	0.15
1,450	33	8.23	3.16	6.07	0.184
400	9	4.47	1.63	6.16	0.306

<sup>a</sup> Intrinsic viscosity calculated from eq 12. <sup>b</sup> Intrinsic viscosity calculated from eq 6.

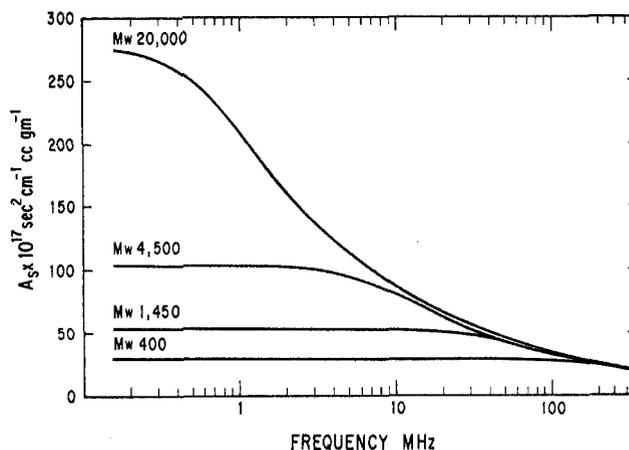


Figure 6. Computed absorption due to shear viscosity relaxation.

in the shear absorption coefficients between the solution and the solvent, and this result is plotted in Figure 6 for the three highest molecular weight fractions.

Comparison of Figure 6 with the experimentally observed results (Figure 1) suggests that the dynamic shear viscosity alone does not describe completely the observed ultrasonic absorption since the theoretical prediction accounts for only a fraction of that actually observed. For this comparison, the ordinates of Figures 1 and 6 are related by the equation  $A = A_s - 84 \times 10^{-17} \text{ sec}^2 \text{ cm}^{-1} \text{ cc g}^{-1}$  for a solution of concentration 0.2 g/cc. Since the frequency dependence of the absorption due to shear viscoelasticity may not be an unreasonable description of that observed, considering the high concentrations of the solutions employed, it appears possible, as suggested by Hawley and Dunn,<sup>6</sup> that the normal modes of the molecule determine the mode of coupling to other relaxation processes. The absorption, not accounted for by shear viscoelastic relaxation, can be accounted for by volume viscosity due to thermal or structural relaxation processes.<sup>29</sup> Thermal relaxation occurs if the temperature fluctuations which follow the sound wave perturb a molecular

(28) C. Sadron and P. Rempp, *J. Polym. Sci.*, **XXIX**, 127 (1958).

(29) J. Lamb in "Physical Acoustics," Vol. II, Part A, W. P. Mason, Ed., Academic Press, New York, N. Y., 1965, Chapter 4.

**Table II:** Predicted Relaxation Times for Shear Viscoelastic Relaxation

$M_w$	$\tau_1$ , sec	$\tau_2$ , sec	$\tau_3$ , sec	$\tau_4$ , sec
20,000	$16 \times 10^{-8}$	$4.9 \times 10^{-8}$	$2.5 \times 10^{-8}$	$1.6 \times 10^{-8}$
4,500	$12 \times 10^{-9}$	$3.7 \times 10^{-9}$	$1.9 \times 10^{-9}$	$1.2 \times 10^{-9}$
1,450	$23 \times 10^{-10}$	$7.0 \times 10^{-10}$	$3.6 \times 10^{-10}$	$2.2 \times 10^{-10}$
400	$42 \times 10^{-11}$	$12 \times 10^{-11}$	$6.3 \times 10^{-11}$	$3.8 \times 10^{-11}$

equilibrium. Typical examples of such a process are chemical relaxation and rotational isomerism. Thus far, however, each thermal relaxation process observed has been best described by a single relaxation time. Structural relaxation occurs when the hydrostatic pressure or density fluctuations disturb a molecular level configurational equilibrium which results in a volume change, *i.e.*, a pressure-dependent arrangement of atoms in the solution. Structural relaxation is usually characterized by a broad spectrum of relaxation times<sup>29</sup> and is probably responsible for the excess absorption in aqueous solutions of PEG. At high frequencies, however, the nonzero limiting value of  $A_s$  of  $171 \times 10^{-17} \text{ cm}^{-1} \text{ sec}^2 \text{ cc g}^{-1}$  could also be due to an internal viscosity of the polymer chain,<sup>15</sup> but the data available do not permit the magnitude of this contribution to be calculated.

Two possible mechanisms of structural relaxation in aqueous PEG solutions are considered. First,  $\eta_v$  can be due to perturbation of the polymer-solvent complex by the sound wave. More specifically, either the structure of the hydration layer surrounding the polymer chain or the amount of hydration is pressure dependent. This mechanism has already been attributed to the excess absorption in aqueous solutions of dextran<sup>6</sup> and has also been proposed for PEG.<sup>28</sup> Second,  $\eta_v$  can be caused by a perturbation of the short-range structural configuration of the polymer chain which would result in a change in the radius of gyration of the flexible polymer. Two structural configurations exist for PEG, the zig-zag and the meandering forms,<sup>30</sup> for the low and the high molecular weight fractions, respectively. On the basis of entropy considerations the meandering form resides in a higher energy level, and it is possible that when the higher molecular weight fractions are subjected to ultrasonic stress, the structural equilibrium is shifted toward the zig-zag configuration. Suppose that each segment of the polymer chain that occupies the meandering form can be considered as a unit which is capable of structural relaxation in the ultrasonic range. Then, if interactions between units can be neglected, the ultrasonic absorption would be linearly dependent on the number of units present. Since the structure of all the high molecular weight PEG chains is predominantly the meandering configuration,<sup>30</sup> the number of relaxing units relative to the molecular weight of the polymer is constant. Therefore, on the assumption that the absorption is determined by the

presence of relaxing units, the absorption in aqueous solutions of high molecular weight fractions of PEG would depend on the mass concentration of the solution and not upon the molecular weight. This type of behavior is supported experimentally by Figure 7 which shows that above  $M_w$  4500,  $A$  is independent of molecular weight. Since the lower molecular weight fractions are composed of smaller percentages of meandering structures, the absorption per concentration decreases. This molecular weight dependence is similar to that observed for dextran<sup>6</sup> except that in that case the absorption approaches that of the monomer at higher frequencies,

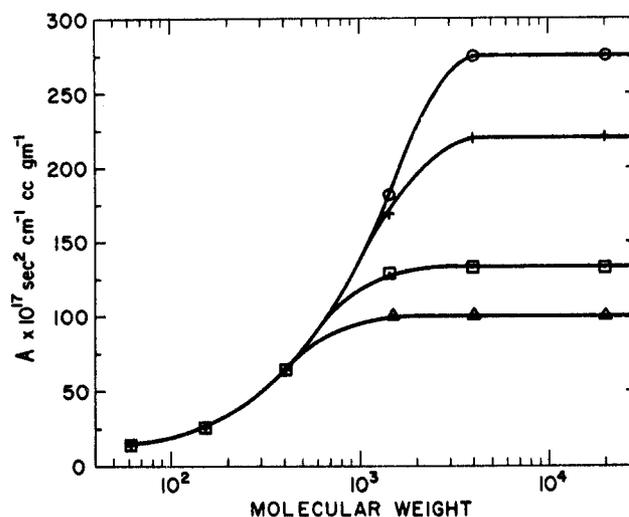


Figure 7. Dependence of absorption on molecular weight:  $\square$ , all frequencies;  $\circ$ , 6 MHz;  $+$ , 10 MHz;  $\square$ , 30 MHz;  $\triangle$ , 60 MHz.

whereas in PEG it does not. This could be due to additional relaxation processes that occur in a higher frequency range or due to an internal viscosity of the polymer. Also, with regard to the presence of relaxing units it is noteworthy that the absorption spectrum for  $M_w$  1450 approaches that for  $M_w$  4500 and  $M_w$  20,000 at about 35 MHz in both Figures 1 and 6. In contrast, viscoelastic theory predicts that the absorption spectra for  $M_w$  4500 and  $M_w$  20,000 should begin to diverge substantially in the neighborhood of 10 MHz, but this

(30) G. O. Curme, "Glycols," Reinhold, New York, N. Y., 1952, pp 180, 181.

is not observed experimentally. This implies the possibility of distinct relaxation processes occurring over the frequency range investigated.

*Acknowledgement.* The authors acknowledge grate-

fully the support of this research in part by a grant from the Institute of General Medical Sciences, National Institutes of Health, and in part by the Office of Naval Research, Acoustics Program.

## Electron Spin Resonance Spectra and Catalytic Activity of Molybdenum Oxide on Various Supports

by K. S. Seshadri and L. Petrakis

Gulf Research & Development Company, Pittsburgh, Pennsylvania 15230 (Received April 9, 1970)

Hexavalent molybdenum in the oxide form incorporated either by impregnation or coprecipitation into magnesium oxide, alumina, or magnesium aluminate, and subsequently reduced at elevated temperatures was investigated by electron spin resonance spectroscopy (esr), and its catalytic activity was tested by the vapor phase aldol condensation of *n*-butyraldehyde. The yield of certain products was found to correlate with the esr signal intensity, both showing the same functional dependence on molybdenum content that reached a maximum at 9 wt % in MoO<sub>3</sub>. The esr spectra showed considerable variation with preparation procedure, nature of support, pretreatment, and reduction temperatures. The species responsible for the esr signal were identified as Mo<sup>5+</sup>, and spectral parameters were extracted. No hyperfine structure components due to the odd isotopes of molybdenum were observed in the solid samples. However, such a hyperfine structure is observed in the isotropic spectra resulting from the acid solutions of the catalysts. When frozen, these acid solutions yield highly anisotropic spectra which are described by an axially symmetric spin Hamiltonian.

### Introduction

Catalytically active species are often paramagnetic and, therefore, can be studied by esr spectroscopy. Possible information that can be obtained about the active species includes qualitative identification of the valency and the nature of the site occupied, quantitative determination of the active species, and elucidation of the role of such variables as nature of support, calcination temperature, preparative procedure, reduction conditions, etc., on the appearance of the spectra. The availability of such information, of course, would be very significant in that it could provide some insight into fundamental aspects of heterogeneous catalysis. However, the extraction of the pertinent spectroscopic parameters from polycrystalline samples (catalysts) is seldom an easy task. For, unlike well-defined single crystals, powder spectra can have all the complications of the solid state (*e.g.*, anisotropy of *g* and hfs) for which there is little hope of separating these various complicating effects. When esr spectroscopy is used to study catalysts, a number of questions arise. Might not the spectroscopic parameters be expected to change radically with the nature of the support? How severe are changes that are introduced by variations in calcination temperatures, reduction temperatures, or in preparation

procedures such as coprecipitation and impregnation? Can the valence and nature of the active site be identified unambiguously? Can the various spectroscopic parameters be correlated with criteria of catalytic efficiency and selectivity of the systems for various reactions? We have studied the spectra of molybdenum oxide in a number of hosts in an attempt to answer some of these questions.

Molybdenum(V) in suitable media has been found to catalyze the polymerization of ethylene and has been studied by esr spectroscopy. A correlation between the esr spectra and the catalytic activity has been established.<sup>1</sup> Spin resonance of Mo(V) has also been reported in the host lattice of TiO<sub>2</sub><sup>2</sup> and in aqueous acid solutions.<sup>3</sup> The catalytic activity of molybdenum oxide, particularly of Mo<sub>2</sub>O<sub>5</sub>, has not been extensively explored. MoO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub>, and some nonstoichiometric Mo oxides have been used in the catalytic oxidation of 1-butene to butadiene.<sup>4</sup> The oxidation of

(1) V. A. Dz's'ko, E. M. Emel'yanova, Yu. I. Pecherskaya, and V. B. Kazanski, *Dokl. Akad. Nauk SSR*, **150**, 829 (1963).

(2) (a) R.-T. Kyi, *Phys. Rev.*, **128**, 151 (1962); (b) T.-T. Chang, *ibid.*, **136**, A1413 (1964).

(3) M. M. Abraham, J. P. Abriata, M. E. Foglio, and E. Pasquini, *J. Chem. Phys.*, **45**, 2069 (1966).