The Ultrasonic Velocity and Absorption of Aqueous Solutions of Polyvinyl Alcohol[*]

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A number of rheological studies of polymer solutions have been made by various authors. However, for the aqueous solution of polyvinyl alcohol we do not have much information concerning the rheological properties of the solution except for those obtained by the method of stationary flow viscosity. At audio frequencies an extensive study of the dynamic mechanical properties of the solution has been made recently by Onogi and his co-workers.[1] At ultrasonic frequencies several studies by means of ultrasonic interferometers have been made,[2] but with limited success.

Recently, an ultrasonic pulse technique has been developed as the most convenient and standard means for the study of the rheological properties of liquids and solutions at ultrasonic frequencies.[3] In the present experiment we measure the velocity and absorption of the longitudinal sound wave which propagate through an aqueous solution of polyvinyl alcohol.

The oscillational displacement, ξ, at a distance, x, from a source of a sound wave is:

$$\xi=\xi_0 \exp(-\alpha x) \exp\{i\omega(t-x/c)\} \tag{1}$$

where c is the sound velocity, ω the angular frequency, ξ_0 the amplitude of oscillation, α the absorption coefficient, and t time.

The complex longitudinal wave modulus, M^*, in an infinitely spread medium is:

$$M^*=M_1+iM_2=K^*+(4/3)G^* \tag{2}$$

where K^* is the complex bulk modulus and G^* is the complex shear modulus.

The real part, M_1, and the imaginary part, M_2, of the complex modulus, M^*, are respectively, expressed as follows;

$$M_1=K_1+\frac{4}{3}G_1=\rho c_l^2 \frac{1-\left(\frac{\alpha_l c_l}{\omega}\right)^2}{\left\{1+\left(\frac{\alpha_l c_l}{\omega}\right)^2\right\}^2} \tag{3}$$

$$M_2=K_2+\frac{4}{3}G_2=\rho c_l^2 \frac{2\left(\frac{\alpha_l c_l}{\omega}\right)}{\left\{1+\left(\frac{\alpha_l c_l}{\omega}\right)^2\right\}^2} \tag{4}$$

where ρ is the density and where the suffix l refers to a longitudinal wave.

According to Eqs. 3 and 4 described above, we can obtain the dynamic elastic modulus, M_1, and the loss modulus, M_2, from the values of c_l and α_l.

Experimental

Apparatus and Procedure.—The apparatus used in this experiment for the measurement of the velocity and absorption of a longitudinal ultrasonic wave, is basically similar to that reported previously by Pinkerton and others.[3] A block diagram of it is shown in Fig. 1.

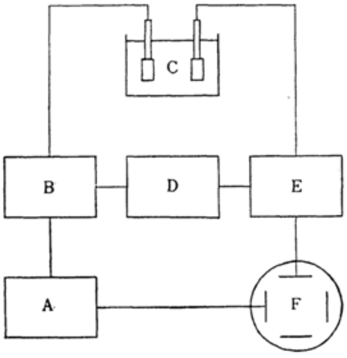

Fig. 1. Block diagram of the apparatus.

A: Pulse generator	B: Oscillator
C: Cell	D: Attenuator
E: Amplifier	F: Synchroscope

A pulse generator supplies an electric pulse of about 10 μ sec. duration and with a repetition rate of 2～5 kc./sec. into a high-frequency oscillator, which operates as an oscillator only during the loading period of the pulse. The pulse-modulated high frequency voltage from the oscillator is led

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1) S. Onogi, I. Hamana and H. Hirai, *J. Appl. Phys.*, **29** 1503 (1958).

2) T. Soeya and R. Kono, *J. Phys. Soc. Japan*, **12**, 950 (1957); H. Shiio and H. Yoshihashi, *J. Phys. Chem.*, **60**, 1049 (1956); T. Yasunaga, K. Iwata and M. Miura, The 7th Annual Symposium of Sound Chemistry, Hiroshima, 1962.

3) J. M. M. Pinkerton, *Proc. Phys. Soc.* (*London*), **B62**, 86 (1949); L. Melchor and A. A. Petrauskas, *Ind. Eng. Chem.*, **44**, 716 (1952); D. G. Ivey, B. A. Mrowca and E. Guth, *J. Appl. Phys.*, **20**, 486 (1949).

to a transmitter quartz crystal in a cell which contains a sample solution and is there transduced into an ultrasonic pulse. At the same time, the electric pulse is led also to an attenuator. An ultrasonic pulse which has propagated through the solution is again transduced into a pulse-modulated high frequency voltage by a receiver quartz crystal. The two pulses from the receiver quartz and the attenuator are amplified and, thereafter, supplied into the vertical axis of a synchroscope.

The velocity of the sound wave in a solution is obtained from the amount of the shift of the pulse which has propagated through the solution on the synchroscope screen when the separation of two quartz crystals is varied by the rotation of a micrometer screw.

The absorption coefficient α is obtained by comparing the pulse which has passed through the solution with that which has passed through the attenuator on the synchroscope screen. That is, α is obtained from the tangent of the linear plot of the attenuator reading against the distance between two quartz transducers, when the ultrasonic path is varied and when the height of the two pulses is kept equal by adjusting the attenuator. The separation of two quartz transducers is designed to be always within the Fresnel region.③

Samples.—Two commercial samples of polyvinyl alcohol were used. The specification of each sample is given in Table I.

TABLE I. SAMPLES

Sample	Intrisic viscosity $[\eta]_{30°C}$ (100 cc./g.)	Residual acetate groups (mol. %)
A	0.91	<0.7
B	1.00	12.2

The intrinsic viscosity of each aqueous solution at 30°C, $[\eta]_{30}$ was obtained by mean of an Ostwald-type viscometer. The amounts of residual acetate groups were determined by the titration method. The viscosity average molecular weight of sample A, $\overline{M}_V$, was found to be 8×10^4 from the value of $[\eta]_{30°C}$ according to the following formula reported by Nakajima and Furutate:④

$$[\eta]_{30°C}=6.66\times10^{-4}\,\overline{M}_V^{\,0.64} \tag{5}$$

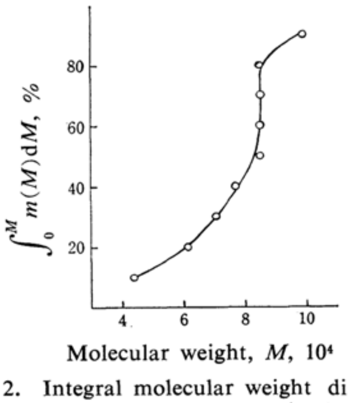

Fig. 2. Integral molecular weight distribution function for sample A obtained from the solution component by Spencer's method.

The integral molecular weight distribution function of sample A was determined by using Spencer's method according to the procedure reported by M. Matsumoto.⑤ The integral distribution curve thus obtained is given in Fig. 2.

From the curve it may be seen that the distribution function, $m(M)$, has a sharp peak at 8.5×10^4.

Aqueous solutions of polyvinyl alcohol were prepared as follows. The aqueous solutions were prepared by heating a mixture of a powder sample and a calculated quantity of water, (where the quantity of adsorbed water in a powder sample as determined by the dessication method was taken into account) on a boiling water bath for more than two hours. The solution was poured into a cell which was held in a temperature bath directly after the sample had been completely dissolved, and then the measurement was begun as soon as the thermal equilibrium in the cell was reached.

Measurement. — In this experiment the sound velocity and the absorption were measured for solutions of sample A in which the range of concentration was over 5~15% by weight and also for solutions of sample B in which the range of concentration was 5 and 10% by weight. The temperature was varied within the range of 3~70°C at 10°C intervals. The temperature in the cell was controlled to an accuracy of ±0.1°C for lower temperatures and ±0.2°C for higher temperatures. The frequency of the ultrasound was 1.42 Mc./sec. for all measurements throughout this experiment.

Results and Discussions

Data of Sound Velocity and Absorption.—In

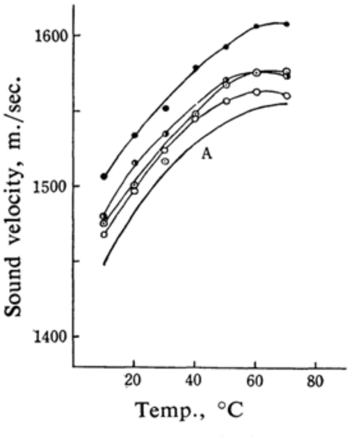

Fig. 3. Sound velocity of the aqueous solutions of sample A.
Concn., wt.%
○ : 5.0, ⊙ : 7.5, ◑ : 10.0, ● : 15.0
(A) Pure water

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④ A. Nakajima and K. Furutate, *Chem. High Polymers* (*Kobunshi Kagaku*), **6**, 460 (1949).

⑤ M. Matsumoto, ibid., **9**, 137 (1952).

Fig. 3 the sound velocity obtained for solutions of sample A is plotted against the temperature, while the velocity for solutions of sample B is similarly treated in Fig. 4. The velocity versus temperature curve for pure water reported by Greenspan and Tschiegg6) is also shown in Figs. 3 and 4 for the sake of comparison. Figures 5 and 6 give, respectively, data of sound absorption for solutions of samples A and B.

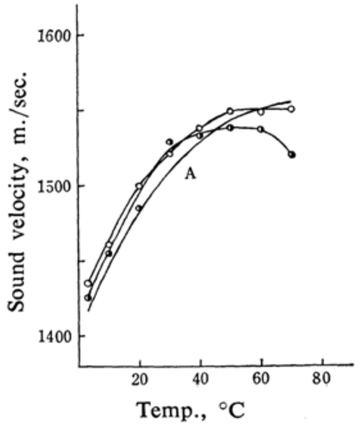

Fig. 4. Sound velocity of aqueous solutions of sample B.
Concn., wt.%
○ : 5.0, ◑ : 10.0
(A) Pure water

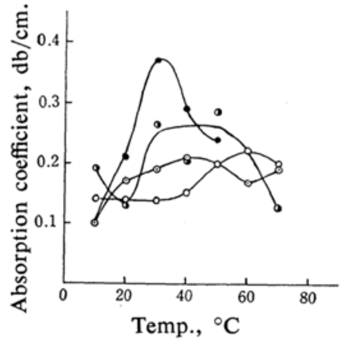

Fig. 5. Sound absorption of the aqueous solutions of sample A.
Concn., wt.%
○ : 5.0, ⊙ : 7.5, ◑ : 10.0, ● : 15.0

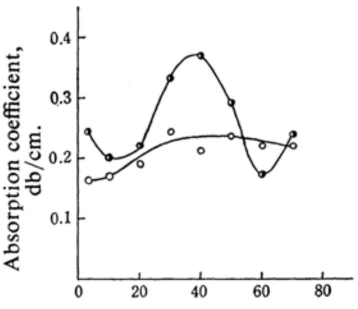

Fig. 6. Sound absorption of the aqueous solutions of sample B.
Concn., wt.%
○ : 5.0, ◑ : 10.0

The values of M_1 and M_2 were calculated according to Eqs. 3 and 4 for all the solutions used in this experiment. Two examples of M_1 and M_2 versus T curves are given in Figs. 7 and 8, where values of M_2/ω are plotted in place of those of M_2 for the convenience of further discussions.

It is well known that the sound velocity versus temperature curve for pure water at ultrasonic frequencies has a peak at 74°C, and that the maximum value of velocity is 1555.5

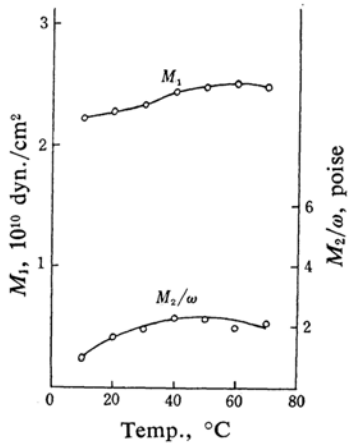

Fig. 7. M_1 and M_2/ω versus T curves of the aqueous solution of sample A.
(7.5 wt.%)

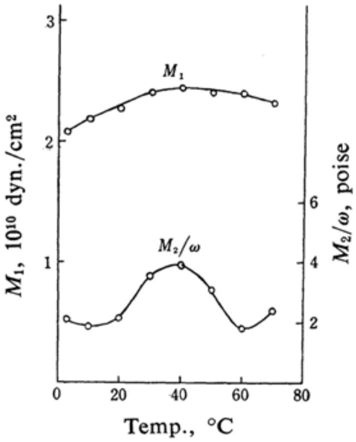

Fig. 8. M_1 and M_2/ω versus T curves of the aqueous solution of sample B.
(10 wt.%)

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6) M. Greenspan and C. E. Tschiegg, *J. Res. Nat. Bur. Standards*, **59**, 249 (1957); *J. Acoust. Soc. Am.*, **31**, 75 (1959).

m./sec.[6-7] Concerning the temperature dependence of the sound velocity, the curves given in Fig. 3 for solutions of sample A, which is completely saponified polyvinyl alcohol, are found to have, on the whole, characteristics similar to the curve for pure water, though the peaks of the curves of sample A seem to shift to a little lower temperature side than in those of the latter. For solutions of sample B which contain acetate groups and hydroxyl groups in a mole ratio of about one to eight, the situation appears quite different, as may be seen in Fig. 4.

The peak of velocity versus temperature curve becomes broader and shifts towards a lower temperature region than do the curves for solutions of sample A and for pure water.

Concerning the concentration dependence of the sound velocity, each curve shown in Fig. 3 may be clearly seen to ascend upon an increase in the concentration. In this respect also, the circumstances for solutions of sample B appear to differ considerably from those for sample A, as may be seen in Fig. 4. In the lower temperature region the concentration dependence of the sound velocity for solutions of sample B does not seem to differ much from that for solutions of sample A, but when temperature is raised above about 50°C, the concentration dependence is found to have a reverse tendency; that is to say, the sound velocity becomes smaller with an increase in the concentration for solutions of sample B. This fact suggests that the configuration of high polymers in aqueous solutions of sample B differs considerably from that in solutions of sample A, and that this different behavior may safely be attributed to the presence of acetate groups in the proportion of about one to eight by mole ratio.

The absorption of ultrasound is found to increase with the concentration for both groups of solutions, as may clearly be seen in Table II from the values of the absorption coefficient α_m averaged over the temperature range used in the present experiment. In Table II the values of $(M_2/\omega)_m$ which are averaged over the temperature range are also given, together with the values of the temperature, T_{max}, where the M_2/ω versus T curve has a peak.

TABLE II. DATA OF SOUND ABSORPTION

Sample	Concn., c wt.%	α_m db/cm.	$(M_2/\omega)_m$ poise	T_{max} °C
A	5.0	0.17	1.8	60
	7.5	0.18	1.9	50
	10.0	0.21	2.3	50
	15.0	0.24	2.8	35
B	5.0	0.21	2.1	50
	10.0	0.26	2.6	40

The values of $(M_2/\omega)_m$ are nearly all within the range of 2∼3 poises. According to the results reported by Onogi and his co-workers,[1] the values of (G_2/ω) are found to approach the value of about 10 poises or so for 15% solutions at audio frequencies, for example, as may be seen in Fig. 15 of their paper. Our values at the ultrasonic frequency may tentatively be said to be compatible with those of Onogi et al. at audio frequencyies, although our data with respect to M_2/ω, of course, include the contribution from the imaginary part of the bulk modulus, K^*.

The Compressibility of Polymer Molecules in Solutions.—Concerning the compressibility of polymer molecules in solutions, Miyahara, Shiio and others have made several studies by means of ultrasonic interferometers.[8]

We calculate the compressibility of polymer molecules in solutions as follows.

The volume of an aqueous solution V is

$$V = V_1 + V_2 + V_3 \qquad (6)$$

where V_1 is the volume of free water, V_2 the volume of bound water, and V_3 the volume of polymer molecules in the solution.

Therefore, the adiabatic compressibility, κ, of the solution may be represented as follows:

$$\kappa = (V_1/V)\kappa_1 + (V_2/V)\kappa_2 + (V_3/V)\kappa_3 \qquad (7)$$

where κ_1 is the adiabatic compressibility of free water, κ_2 the adiabatic compressibility of bound water, and κ_3 the adiabatic compressibility of polymer molecules in solutions.

We can obtain values of κ from the data of the sound velocity described above, ignoring the contribution from the shear elasticity, which is supposed to be much smaller than that from the bulk elasticity.[8-9] The values of κ_1 are calculated from the data for pure water reported by Greespan et al.[6] For the values of the compressibility of bound water, κ_2, the value 18×10^{-12} (c.g.s.) is substituted, following Hall and others;[8,10] this is assumed to be the value for the ice structure in water. As has previously been pointed out by Shiio;[11] bound water, which is attracted to solute molecules by a hydrogen bond, is supposed to be in a different state from ordinary water,

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[7] M. Greenspan, C. E. Tschiegg and F. Breckenridge, *J. Acoust. Soc. Am.*, **28**, 500 (1956).

[8] Y. Miyahara and Y. Masuda, *Science* (*Kagaku*), **30**, 588 (1960); *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 692 (1960); Y. Masuda, T. Hasegawa and Y. Miyahara, ibid., **82**, 1131 (1961); Y. Masuda and Y. Miyahara, ibid., **83**, 878 (1962); H. Shiio and H. Yoshihashi, *J. Phys. Chem.*, **60**, 1049 (1956); H. Shiio, T. Ogawa and H. Yoshihashi, *J. Am. Chem. Soc.*, **77**, 4980 (1955).

[9] E. Rouse and L. Sittel, *J. Appl. Phys.*, **24**, 690 (1953).

[10] L. Hall, *Phys. Rev.*, **73**, 775 (1948).

assumed, that is to say, to be already in a kind of "solid state" at ordinary temperatures. Therefore, it may be reasonable to assign the same value as that of the compressibility of ice to the value of the compressibility of bound water, κ_2. The value of V_2 is estimated from the amount of bound water, for which the value of 0.45 cc. per gram solute is assigned, as reported by Shiio et al.*[2] The value of V_3 is calculated from the value of concentration by weight in solutions without much error, where the density of solute molecules is assumed to be 1.3 g./cc., which is the value of the density of polyvinyl alcohol in the solid state. The value of V_1 is calculated from the values of V_2 and V_3 according to Eq. 6. The values of κ_3 for solutions of sample A may now calculated from Eq. 7 as in Table III.

TABLE III. VALUES OF κ_3 AT 25°C

Concn., wt.%	5.0	7.5	10.0	15.0	Mean value
κ_3, 10^{-12} c.g.s.	29.5	28.7	23.7	24.0	26.5

In Table III the values of κ_3 may be seen to decrease gradually with the increase in concentration. On the other hand the tendency to decrease is small, and we will not discuss it here. Rather, the fact that the values of κ_3 are nearly equal in spite of a fairly large difference in concentration has been noted; this finding may be said to support the adequacy of employing the concept, "compressibility of solute molecules in a polymer solution," as proposed by Masuda, Hasegawa and Miyahara.[8] In the present case where polymer molecules are supposed to be spread throughout a solution, a polymer solution is regarded as a hypothetical mixture of segments of polymer molecules and solvent molecules, and the compressibility, κ_3, which we discuss here may be regarded as that of the segments in the solution. It may be said that the term "segment" employed here is not always identical with "segment" in the ordinary sense. The values of κ_3 we obtained here are larger than that reported by Shiio et al.[2] However, the discrepancy does not matter at present considering the difference in the procedure for the determination of κ_3.

Summary and Conclusions

An ultrasonic pulse technique has been applied to measure the velocity and absorption of the longitudinal sound wave in aqueous solutions of polyvinyl alcohol at ultrasonic frequencies. Two samples of polyvinyl alcohol have been used: sample A, completely saponified polyvinyl alcohol, and, sample B, partially saponified Polyvinyl alcohol (including residual acetate groups by 12.2 mol.%). The following results have been obtained.

1) Ultrasonic velocity and absorption have been measured over the temperature range of 3～70°C in the concentration range of 5～15% by weight.

2) For sample A the temperature dependence of velocity is similar to that for pure water, but for sample B the velocity vs. temperature curves have been found to have a broader peak.

3) Concerning the concentration dependence of the velocity, in sample A the sound velocity increases with the increase in the concentration, but in sample B a reverse dependence of velocity on concentration has been found at higher temperatures.

4) The value of M_2/ω amounts to about 2～3 poises on the average for both samples.

5) The compressibility of polymer molecules in solutions has been calculated to be 26.5×10^{-12} c.g.s.u. on the average for completely saponified polyvinyl alcohol.

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* Yasunaga et al. have recently reported that the amount of bound water is 0.46 cc./g.[2]

11) H. Shiio, *Kagaku no Ryoiki*, **11**, 440 (1957).