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The Rheological Study of Aqueous Solutions of Polyvinyl Alcohol at Ultrasonic Frequencies

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The ultrasonic velocity and the absorption have been measured over the 5—45 Mc./sec. frequency range for aqueous solutions of polyvinyl alcohol by means of an ultrasonic pulse technique which was similar in principle to that used by Pinkerton (*Proc. Phys. Soc.* **B62,** 286 (1949)). The temperature varied over the 3—70°C range. The velocity-versus-temperature curves have been found to be convex upwards, like that of pure water, but the peak shifts upwards and to the lower-temperature side with an increase in the concentration. The ultrasonic absorptions of aqueous solutions of partly-saponified polyvinyl alcohol have been found to be larger than those of perfectly-saponified alcohol at the same concentrations. Two relaxation mechanisms have been found for each sample. For the solutions of the perfectly-saponified sample, the first relaxation frequency, f_1, is 35 Mc./sec. at 12°C, while the second relaxation frequency f_2 is 40 Mc./sec. at 60°C, for example. On the other hand, these values have been found to be nearly equal for the solutions of the partly-saponified sample. The activation energy, ΔH_2, obtained from the temperature dependence of f_2 is about 4 kcal./mol., irrespective of the quantity of resuidal acetate groups, and the ΔH_1 value for f_1 is of the order of 10 kcal./mol.

In a previous paper[1] some results of rheological investigations of concentrated aqueous solutions of polyvinyl alcohol using an ultrasonic pulse technique have been reported; the adiabatic compressibility of polymer molecules in solutions have been discussed elsewhere.[2] However, the previous data concern one ultrasonic frequency in the mega cycle region; therefore, we have attempted in the present experiment to obtain ultrasonic data on the solutions of polyvinyl alcohol over a wider range of frequencies using a newly-constructed apparatus for the measurement of the ultrasonic velocity and the absorption by the pulse method.[1,3]

The oscillational displacement, ξ, in a longitudinal wave through the solution at a distance, x, from a source of sound 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, the time. We will here obtain c and α values for various frequencies and temperatures.

Experimental

Apparatus and Procedure.—The apparatus used in this experiment is similar to that reported in the previous paper,[1] but this apparatus can be used for a wider range of frequencies. A block diagram of it is shown in Fig. 1.

A pulse generator supplies an electric pulse of about 5—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 oscillator is constructed from three independent parts, each of which is used for each available frequency range between 1—50Mc./sec.; for the measurement in the range of 50—100 Mc./sec., a frequency doubler unit[4] is inserted in a position series to the oscillator. The pulse-modulated high-frequency voltage from the oscillator is led to a transmitter quartz in a cell which contains a sample solution; there it is transduced into an ultrasonic pulse. The pulse which has been propagated through the solution is again transduced into an electric pulse by a receiver quartz and then led to an attenuator. The pulse from the attenuator is amplified and supplied into a vertical axis of a synchroscope.

The velocity of sound, c, is measured according to the procedure described in the previous paper.[1] The amount of attenuation is determined by the compensation method, using the attenuator. That is, the difference in the attenuator reading gives the amount of attenuation for the given path length between the two positions of the movable receiver quartz when attenuator is adjusted so that the pulse pattern in the synchroscope screen has the same height for the two positions of the receiver quartz. The absorption coefficient, α, is determined from the tangent of a linear plot of the amount of attenuation against the length of the ultrasonic path.

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[1] K. Arakawa, N. Takenaka, M. Watase and K. Kubota, This Bulletin, **37**, 559 (1964).

[2] Y. Miyahara and Y. Masuda, *Science* (*Kagaku*), **30**, 588 (1960); Y. Masuda, T. Hasegawa and Y. Miyahara, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **82**, 1131 (1961); H. Shiio and H. Yoshihashi, *J. Phys. Chem.*, **60**, 1049 (1956).

[3] J. M. Pinkerton, *Proc. Phys. Soc.*, **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); J. H. Andreas and P. L. Joyce, *Brit. J. Appl. Phys.*, **13**, 462 (1962).

[4] H. J. McSkimin, *J. Acoust. Soc. Am.*, **34**, 404 (1962).

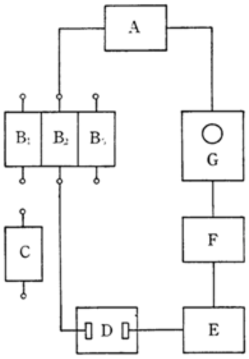


Fig. 1. Block diagram of the apparatus.
A: Pulse generator
B_1, B_2, B_3,: Oscillator
B_1, 1—15 Mc./sec.
B_2, 15—30 Mc./sec.
B_3, 30—50 Mc./sec.
C: Doubler, 60—100 Mc./sec.
D: Cell
E: Attenuator
F: Amplifier
G: Synchroscope

Samples.—The two samples, A and B, used were the same as those reported in the preceding paper.[1)] The average molecular weight was 8.0×10^4 for the perfectly-saponified P.V.A. sample A and about 9×10^4 for the sample B, which is the partly saponified P. V. A. and which has 12.2 mole % of the residual acetate groups. The preparation procedure of the aqueous solution is similar to that reported previously.[1)]

Measurement.—In this experiment the sound velocity and absorption were measured for 5 and 10 wt. % solutions of the two samples. The temperature was varied within the range of 3—70°C. The frequency range used was 5—45 Mc./sec.

Results and Discussion

The Effect of Aging on Ultrasonic Absorption.—Concentrated polymer solutions are often found to exhibit an aging behavior. In Fig. 2 the absorption coefficient, α, which was measured for the 10 wt.% solution of sample A is plotted against the standing time after the thermal equilibration of the solution has been reached at room temperature. As may clearly be seen in Fig. 2, the

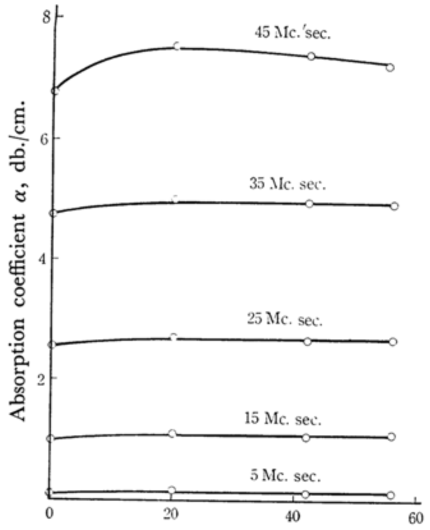


Fig. 2. Aging curve for the 10 wt.% solution of sample A.

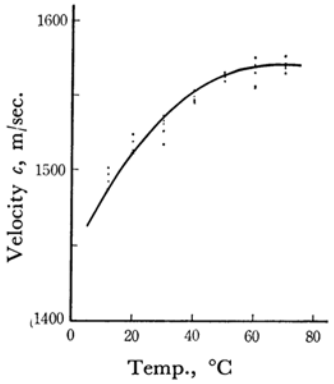
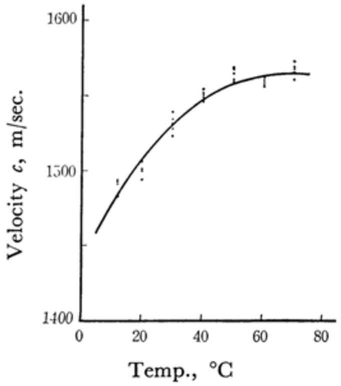


Fig. 3(a). Sound velocity, sample A, 5%.
Horizontal shift Δh: -5°C
Vertical shift Δv: $+15$ m/sec.



Eig. 3(b). Sound velocity, sample B, 5%.
Δh: -5°C, Δv: $+10$ m/sec.

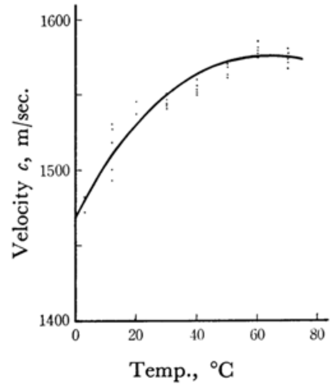


Fig. 3(c). Sound velocity, sample A, 10%.
Δh: -10°C, Δv: $+20$ m/sec.

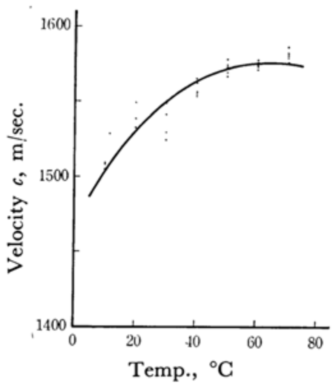


Fig. 3(d). Sound velocity, sample B, 10%. Δh: −10°C, Δv: +20 m/sec.

effect of aging is not very large, but it has a tendency to increase with the frequency; the primary effect of aging is confined within 20 hr., while after more than 20 hr. the absorption coefficient is found to reach a constant value. Therefore, in the present experiment the measurements were made after the prepared solution had been allowed to stand at room temperature for more than 20 hr. after its preparation.

Data of Ultrasonic Velocity.—In Figs. 3(a), (b), (c), and (d) the sound velocities obtained for solutions of samples A and B are plotted against the temperature for each concentration; here the frequency dependence is not very clear. All the data for the 5—45 Mc./sec. frequency range are also plotted together against the temperature. Each solid line is one which is obtained by the parallel shift of the velocity vs. the temperature curve for pure water[5] (the amount of the shift is given in each figure). The sound velocity in pure water is found to have a maximum value, 1555.5 m/sec., at 74°C.[5] It may be seen in Fig. 3 that the peak in the velocity vs. the temperature curve shifts toward a temperature lower than that for pure water; it may also be seen that the amount of shift increases with the increase in the concentration.

Data of Sound Absorption.—In Figs. 4(a), (b), (c), and (d) the absorption coefficient, α, is plotted against the temperature; the frequency is varied within the 5—45 Mc./sec. range. It is found that the absorption of aqueous solutions of sample B is larger than that of sample A at the same concentration. It may be seen especially in Figs. 4(c) and (d) that absorption curves have two characters, that is, a peak or shoulder at about the 0—20°C range and a shoulder at about the 30—40°C range; it may also be seen that the two peaks or shoulders shift to a higher temperature region with the increase in frequency. It is well known that the ultrasonic absorption of pure water decreases monotonously with the increase in temperature in this frequency range. Therefore, from these two characteristics we may

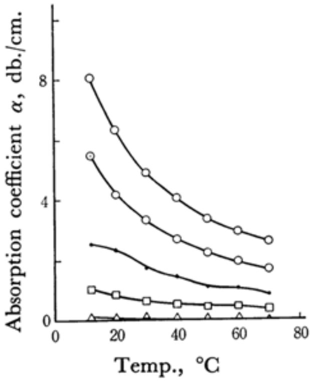


Fig. 4(a). Absorption coefficient, sample A, 5% solution.
○ 45 Mc. ⊙ 35 Mc. • 25 Mc. □ 15 Mc.
△ 5 Mc.

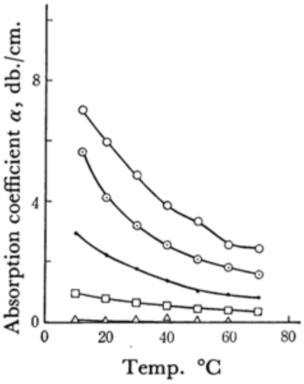


Fig. 4(b). Absorption coefficient, sample B, 5% solution.

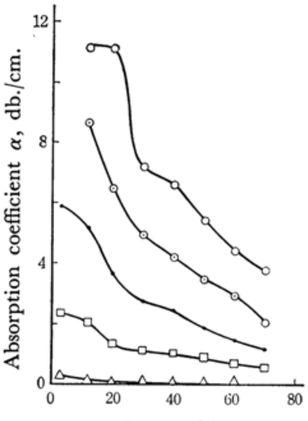


Fig. 4(c). Absorption coefficient, sample A, 10% solution.

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[5] M. Greenspan and C. E. Sschiegg, *J. Res. Natl. Bur. Std.*, **58**, 249 (1957); *J. Acoust. Soc. Am.*, **31**, 75 (1959).

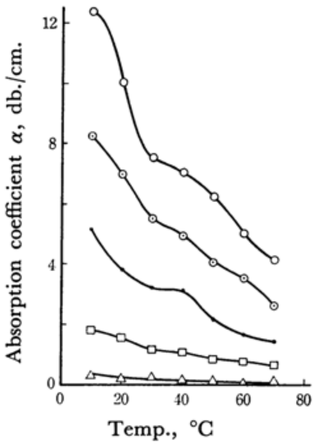

Fig. 4(d). Absorption coefficient, sample B, 10% solution.

say that in this range of temperature and frequency the ultrasonic absorption of aqueous solutions of polyvinyl alcohol is approximately composed of three parts. The first one is, of course, to be attributed to free water, which is the greater part by weight in these solutions. The contribution from this part to the total absorption is, however, not necessarily the greater part of the total absorption. In the case of a 10% solution it is about one-third of the total absorption. The second and the third parts are to be attributed to polymer molecules, including the contribution from hydrated bound water. The second corresponds to the peak or shoulder at about the 0—20°C range, and the third, to the shoulder at about 30—40°C, as has been described above.

In Figs. 5(a) and (b), the excess absorption, Δ, for the 10 wt.% solution;

$$\Delta=\left(\frac{\alpha}{f^2}\right)_{\text{solution}}-0.9\left(\frac{\alpha}{f^2}\right)_{\text{water}} \tag{2}$$

is plotted against the temperature. The dashed lines are the values (α/f^2) for pure water,[6] which may be, so to speak, regarded as back ground curves in the total absorption. The amount of Δ is the part of the absorption attributed to polymer molecules in solutions, including the excess contribution of hydrated water molecules, that is, the difference between the amount of the absorption of hydrated water molecules and the amount of the absorption of the water molecules when they are allowed to be free. The presence of the two absorption mechanisms may clearly be seen in Figs. 5(a) and (b). Therefore, it may safely be said that the ultrasonic absorption of a polyvinyl alcohol solution in this temperature range is approximately given by the summation of three parts, as is shown in Fig. 6, for example, where, however, the proportion of the absolute amount of each component is, of course, somewhat arbitrary.

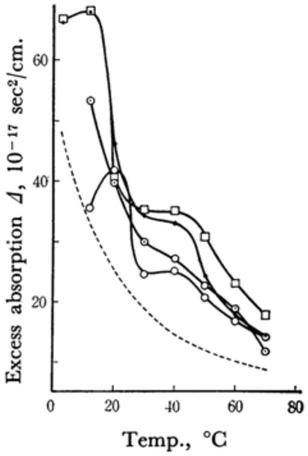

Fig. 5(a). Excess absorption, sample A, 10%.
○ 45 Mc ⊙ 35 Mc • 25 Mc □ 15 Mc.

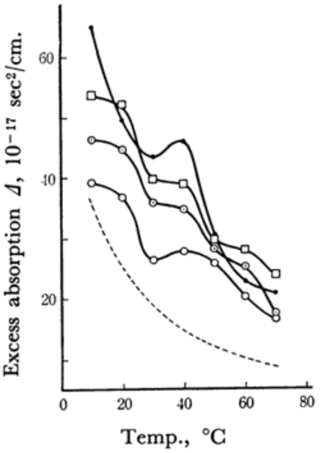

Fig. 5(b). Excess absorption, Sample B, 10%.

Frequency Dependence of Ultrasonic Absorption.—In order to obtain the frequency dependence of the ultrasonic absorption we have given here, in Figs. 7(a) and (b), the α/f^2 vs. f curve, and also the $\alpha\lambda$ vs. f curve in Figs. 8(a) and (b), where λ is the wavelength, obtained from the data shown in Figs. 4(c) and (d).

As has been stated before on the basis of a consideration of the temperature dependence of the absorption, the presence of two relaxation mechanisms may be concluded. They are characterized by two relaxation frequencies, f_1 and f_2, each, which are numbered in order from the low temperature side in the α vs. T curve. For example, in the case of the 10 wt.% solution of the sample A, the value of f_1 and f_2 is determined from the

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[6] J. M. M. Pinkerton, *Proc. Phys. Soc.*, **B62**, 129, 286 (1949); *Nature*, **160**, 68 (1947); M. Pancholy, *J. Acoust. Soc. Am.*, **25**, 1003 (1953); T. Kishimoto and O. Nomoto, *J. Phys. Soc. Japan*, **9**, 1021 (1954).

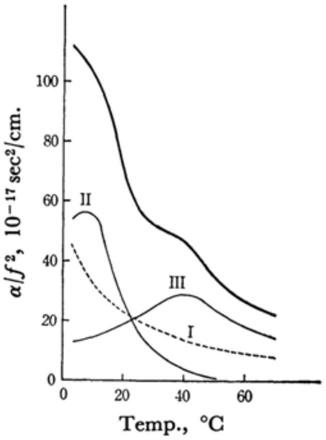

Fig. 6. Three parts of the absorption curve for the 10% solution of sample A at 25 Mc./sec.
I: 1st part (free water), II: 2nd part
III: 3rd part

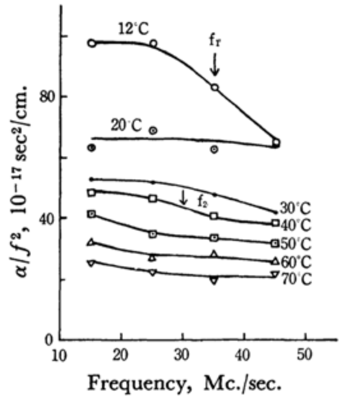

Fig. 7(a). Frequency dependence of the absorption, 10% solution of sample A.

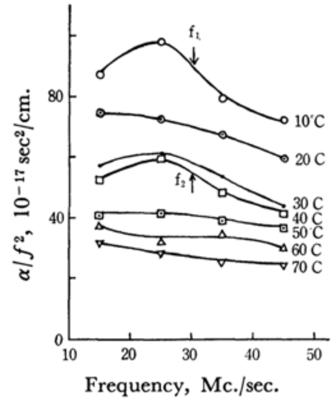

Fig. 7(b). Frequency dependence of the absorption, 10% solution of sample B.

curves in Fig. 7(a) and Fig. 8(a). In Fig. 8(a) the large peak in the curve at 12°C, which is characterized by the relaxation frequency f_1, is

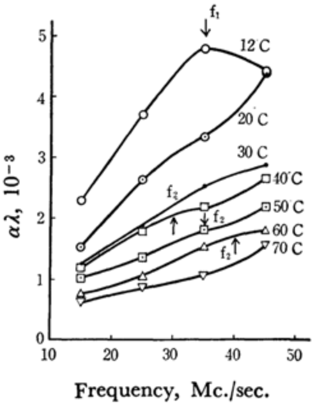

Fig. 8(a). $\alpha\lambda$ vs. f curve for the 10% solution of sample A.

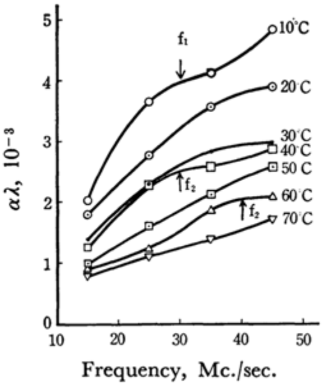

Fig. 8(b). $\alpha\lambda$ vs. f curve for the 10% solution of sample B.

found to correspond to the peak at 0—20°C in Fig. 5(a), while this peak is found to be shifted at the high frequency end at 20°C in Fig. 8(a). The shoulder[7] found at 30 Mc./sec. in the 40°C curve in Fig. 8(a), which corresponds to the shoulder near 40°C in Fig. 5(a), seems to shift gradually to the high frequency side with the increase in temperature; this shoulder is thought to be characterized by the relaxation frequency f_2. A similar consideration holds for the 10 wt.% solution of the sample B.

The value of the activation energy, ΔH_2, may be determined to be 4.2 kcal./mol. for both samples, A and B, from the temperature dependence of f_2. The value of ΔH_1 for f_1 can not be determined, but it may be estimated to be larger than 10 kcal./mol. from the curves in Figs. 8(a) and (b).

In Fig. 7(b) it may be seen that the values of α/f_2 decrease with the decrease in frequency at low temperatures. This may be attributed to the presence of Rayleigh scattering because of the co-existence of some larger colloidal particles;

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7) M. Pancholy and S. P. Singal, ibid., **18**, 582 (1963).

this scattering follows the f^4 law. The fact that the decrease in α/f^2 with the decrease in frequency occurs at low temperatures only may be said to support this consideration.* Though the reason why this tendency is stronger for the sample B than for the sample A is not clear at present, it seems that it is to be attributed to the presence of residual acetate groups in the sample B which amount to about 1/8 in the mole fraction.

Longitudinal Wave Modulus.—From the values of the ultrasonic velocity and the absorption coefficient, the real part and imaginary part of the longitudinal wave modulus, M_1 and M_2, are obtained.

$$M_1=\rho c^2\frac{1-(\alpha c/\omega)^2}{\{1+(\alpha c/\omega)^2\}^2} \tag{3}$$

$$M_2=\rho c^2\frac{2(\alpha c/\omega)}{\{1+(\alpha c/\omega)^2\}^2} \tag{4}$$

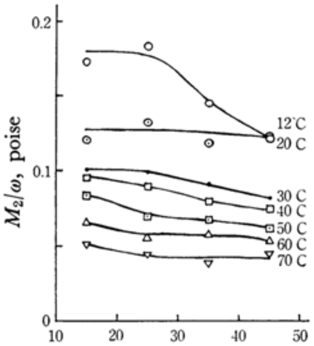

Fig. 9. Values of M_2/ω for the 10% solution of sample A.

From the values obtained in this work, the $(\alpha c/\omega)$ value is found to be very small compared with unity; therefore, the following relation is derived:

$$\frac{M_2}{\omega}=2\rho c^3\left(\frac{\alpha}{\omega^2}\right) \tag{5}$$

The M_2/ω quantity has the dimension of viscosity. In the preceding paper[1] it was found that the values of M_2/ω amount to 2—3 poises for the 10 wt.% solutions at 1.4 Mc./sec. From the present data we can determine the M_2/ω values to be of the order of 0.1 poises; these values are given in Fig. 9.

Summary and Conclusions

Data concerning ultrasonic velocity and absorption have been obtained by means of an ultrasonic pulse technique for aqueous solutions of polyvinyl alcohol.

1) The ultrasonic velocity and absorption have been measured over the temperature range of 3—70°C and the frequency range of 5—45 Mc./sec.

2) The ultrasonic absorption of aqueous solutions of partly-saponified polyvinyl alcohol is larger than that of perfectly-saponified polyvinyl alcohol at the same concentration.

3) Two relaxation mechanisms are present; one, which has been obtained from the temperature dependence of the relaxation frequency, is characterized by the activation energy of about 4 kcal./mol., and the other, by the activation energy of the order of 10 kcal./mol.

4) The value of the longitudinal wave modulus, M_2/ω, has been found to be of the order of 0.1 poises.

The authors wish to thank Miss Mitsuko Kobayashi for her cooperation in performing this study.

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* In Fig. 7(b) it may be seen that the curve at 20°C only is flat at low frequencies, in contrast to the above-described behavior of other curves at 10—40°C. This is because, if the Rayleigh dispersion is absent, the 20°C curve may be expected to go down rapidly with an increase in the frequency, while the 10, 30, and 40°C curves are more flat or slowly decrease on this low frequency side with an increase in the frequency.