

Ultrasonic Velocity and Absorption Measurements for Polyacrylamide and Water Solutions

Jong-Rim Bae^{*}, Jeong-Koo Kim^{**}, Meyung-Ha Yi^{***}

^{*}Department of Physics, Taegu University

^{**}Department of Medical Ultrasonics, Hanseo University

^{***}Department of Ophthalmic, Seoul Health Junior College

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Abstract

Both ultrasonic velocity at 3 MHz and absorption coefficient for the frequency range of 0.2-2 MHz were measured in an aqueous solution of polyacrylamide for the concentration range of 0.5% to 2.5% by weight. Pulse echo overlap method was taken for measuring the ultrasonic velocity over the temperature range of 10-90°C and the high-Q ultrasonic resonator method was used for the absorption coefficient at 30°C. The velocity exhibited a maximum value at approximately 70°C, 71°C, 72°C, 73°C and 74°C in 2.5%, 2.0%, 1.5%, 1.0%, and 0.5% solutions, respectively. The velocity increased with the concentration at a given temperature. The ultrasonic absorption (α/f^2) at a given temperature increased linearly with the concentration for the concentration below 1.5%, but suddenly increased for the concentration above 1.5% concentration. The value of α/f^2 at 1 MHz was entirely due to the classical Stoke's viscous effect. The ultrasonic relaxation in polyacrylamide aqueous solutions, which may be the result of structural fluctuations of polymer molecules such as the segmental motion of the polymer chains, was observed, and at 2.5%, the value of α/f^2 was found to suddenly increase as frequency decreased.

Keywords: Polyacrylamide, Ultrasonic velocity, Absorption coefficient, Ultrasonic relaxation, Viscous effect

1. Introduction

Polyacrylamide may be used as a flocculant to clarify water and thus has a potential for practical use. Ultrasonic absorption and velocity may provide useful information on the behavior of the polyacrylamide in aqueous solution. The change of the absorption coefficients with frequencies might be explained by the relaxation of the structure fluctuation of polymer molecules. On the other hand the change of the velocity with temperatures behavior may be explained in terms of the structural change of water in the presence of polyacrylamide.

In the study, the finely powdered polyacrylamide was

taken which has an average molecular weight of 5 to 6 million. An polyacrylamide monomer has the chemical formula $\text{CH}_2\text{CHCONH}_2$ and a molecular weight of 71. For the different concentration of the polyacrylamide aqueous solutions, we measured ultrasonic velocity at 3 MHz using a pulse echo overlap method over the temperature range of 10-90°C and absorption over the frequency range of 0.2-2 MHz using a high-Q ultrasonic resonator method.

In previous years, the ultrasonic velocity has been studied in polyacrylamide[1] and other related polymer solutions[2]. M. F. Haque and F. B. Stumpf measured velocity at various concentrations and temperatures (25-45°C) in the solutions of polyacrylamide and water[1]. They suggested that the increase in velocity with concentration was related to the formation of a more rigid

Corresponding author: Jong-Rim Bae (jongrim@daegu.ac.kr)
Department of Physics, Taegu University, Jinryang, Gyeongsan,
Kyungpook, 713-714, Korea

structure of the solution due to the presence of a solute. However, they did not explain why the velocity increase with temperature. In addition, they did not observe velocity maxima in the solutions as their measurements were performed at temperatures below 45°C. The measurements in the solutions presented here may be a valuable addition to the previous studies.

II. Experiments

The polyacrylamide used in the study was obtained from Aldrich Chemical Company and was in the form of fine white powder. The powder had an average molecular weight of 5-6 million and a density of 1.302 g/cm³. Concentrations of 0.5%, 1.0%, 1.5%, 2.0% and 2.5% by weight were carefully measured. After the polymer was dissolved in distilled water, it was stirred for at least 24 h. The weights of water and polymer were carefully determined using a highly sensitive analytical balance. All concentration values were expressed in percent by weight.

The ultrasonic velocity was measured at 3 MHz using a pulse echo-overlap method[3] over the temperature range of 10-90°C. A block diagram of pulse-echo-overlap method was shown in Fig. 1. This system was, however, partially modified in our laboratory for the present study. Two transducers used were X-cut quartz with a fundamental ultrasonic pulse that was excited by sharp dc voltage with rise time shorter than 10 ns. The rf amplifier could be tuned to 3 MHz and monitored. Only the first arriving pulse and the second echo were visualized on CRT. The repetition rate of a CW oscillator was adjusted so that the two pulses were overlapped and matched cycle for cycle. The period of the oscillator which was measured by a counter gave a round-trip time of the pulse, and yielded the phase velocity with known path length. The sensitivities of the velocity measurements were 0.01%, respectively. This system was very convenient for simultaneous measurements of velocity, and suitable for the present experiments which were conducted at different temperatures.

The high-Q ultrasonic resonator method was employed

for absorption coefficients over 0.2-2 MHz[4]. A block diagram of the resonator method was shown in Fig. 2. A resonance cell which was composed of a quartz transducer and a slightly concave reflector was filled with a liquid sample, and standing sound waves were established in it. The amplitude of the standing waves was monitored, sweeping the sound frequency, by using Raman-Nath light diffraction and optical heterodyne detection. The bandwidth of the resonance curve provided a measure of acoustic dissipation caused by intrinsic absorption in the sample liquid and instrumental cavity loss. Relative measurement with a standard liquid with known absorption permitted to determine the absorption in the sample. The use of the concave reflector with a curvature radius of 200 mm decreased the instrumental loss and improved the Q factor of the resonator by two orders of magnitude at 300 kHz compared with a conventional resonator of the same diameter.

Water was used as the standard liquid because its acoustic impedance was close to that of polyacrylamide solutions. The viscosity was measured using a Brookfield rotating-cylinder viscometer and absorption measurements about 1 MHz using high-Q ultrasonic resonator method over the temperature range of 10-90°C were measured in

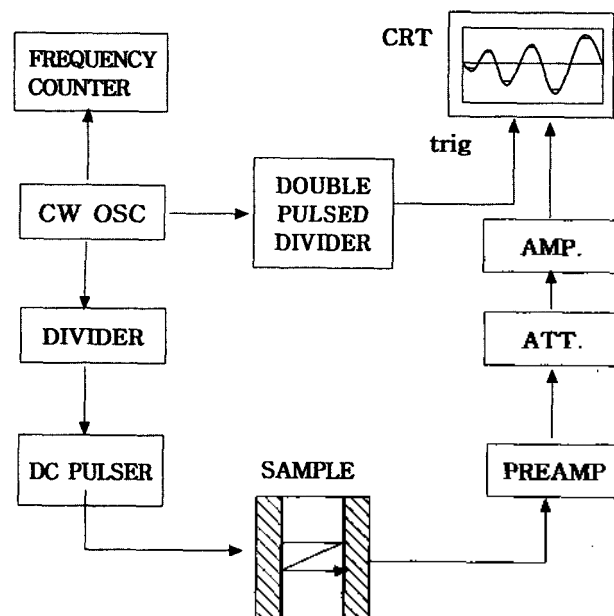


Figure 1. The block diagram of the pulse-echo-overlap method for measuring ultrasonic velocity.

polyacrylamide aqueous solutions.

III. Results and Discussion

Ultrasonic Absorption and Viscosity Measurements.

The results of the absorption coefficient of ultrasonic wave measurements at 1 MHz are shown in Figs. 3 and 4, as a function of temperature and concentration in percent by weight. Fig. 3 contains all the data points, whereas Fig.

4 has some omitted to avoid confusion. It is seen in Fig. 3 that α/f^2 decreases monotonically with increasing temperature at a given concentration. The magnitude of the slope of α/f^2 versus temperature tends to decrease more at higher temperatures. Also, the difference in α/f^2 between the solution and water decreases as temperature increases in Fig. 4, it is seen that α/f^2 at a given temperature increases almost linearly with concentration below to 1.5% concentration, but increase more rapidly in an exponential pattern for the concentration above 1.5%.

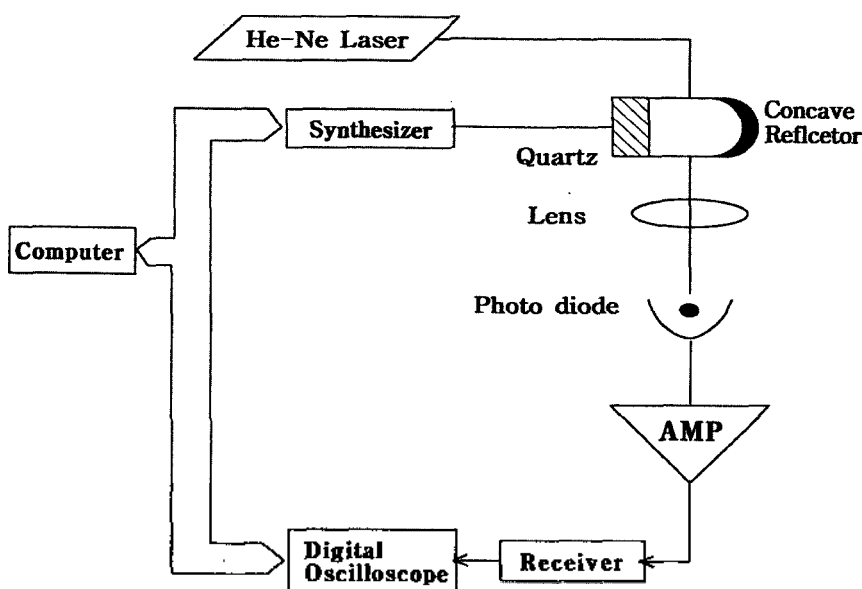


Figure 2. Block diagram of high-Q ultrasonic resonator method for measuring absorption coefficients.

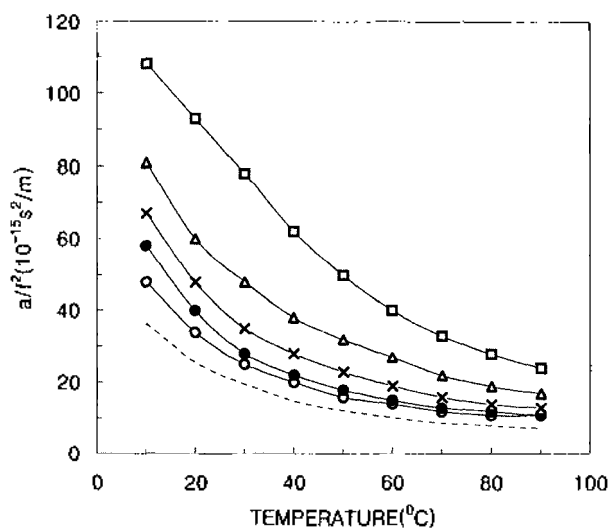


Figure 3. The absorption α/f^2 versus temperature for polyacrylamide with water. The symbols \circ , \bullet , \times , Δ , \square and $-$ represent concentration 0.5, 1.0, 1.5, 2.0 and 2.5% by weight and pure water, respectively.

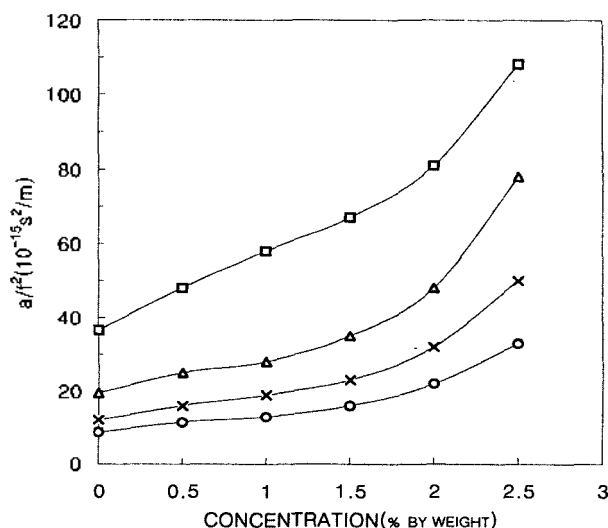


Figure 4. The absorption α/f^2 versus concentration for polyacrylamide with water. The symbols \square , Δ , \times and \circ represent temperature 10.0, 30.0, 50.0, and 70.0°C, respectively.

An important factor to be considered for polymer solutions is shear viscosity. Fig. 5 shows that the measured shear viscosity decreases with temperature for all concentrations. The rate of the decrease in the shear viscosity were greater at lower temperatures than higher temperatures. The largest value of the shear viscosity shown at 10°C for the 2.5% solution is nearly 7,000 times than the value for pure water. While the shear viscosity is almost four orders of magnitude greater than pure water, the value of a/f^2 for the solution is just greater by a factor of 3 than that of pure water as shown in Fig. 3. The relaxation effects at 1 MHz may be observed in Fig. 6. But the contribution of the relaxation to ultrasonic absorption is relatively small at 1 MHz. Therefore the ultrasonic absorption for the solution is entirely due to the classical Stoke's viscous effect.

The plot of a/f^2 versus temperature at a given concentration shows the same general trend as the viscosity versus temperature. Furthermore, the measurements of a/f^2 versus temperature show that at 10°C the difference in

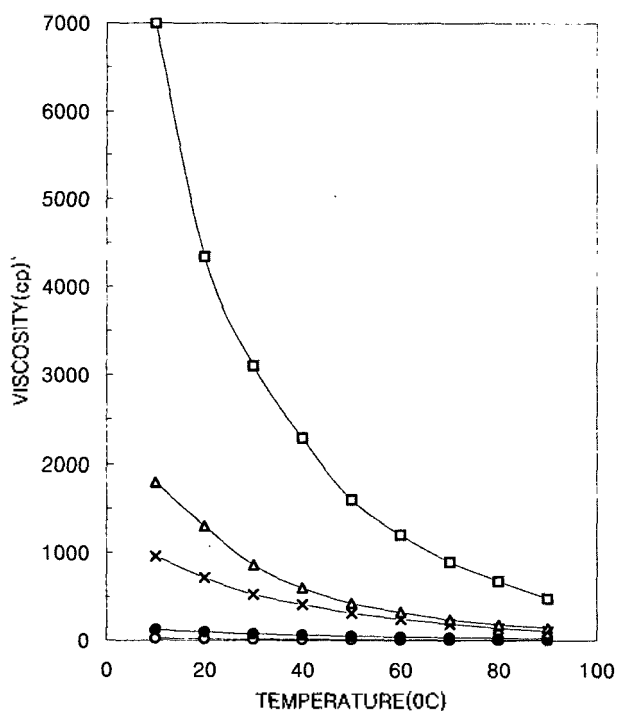


Figure 5. Shear viscosity versus temperature for polyacrylamide with water. The symbols \circ , \bullet , \times , Δ , \square and \dots represent concentration 0.5, 1.0, 1.5, 2.0 and 2.5% by weight and pure water, respectively.

values for the 2.5% solution and water is three to two times the difference at 90°C. This may be related to the fact that the viscosity shows a stronger temperature dependence for the higher concentrations as seen in Fig. 5. The reason for any increase in viscosity upon adding the polymer to water may be due to the interaction of polymer molecules with water molecules. Specifically this might involve the association of water molecules with the amide group (CONH_2) of the polyacrylamide. The association by hydrogen bonding with water can take place at the O, N, and H sites in the amide group. The similar bonding of metal ions and other ions possible at the N and O sites of the amide group, gives polyacrylamide importance as a flocculating agent.

Fig. 6 shows the measured absorption coefficients of ultrasonic waves at 30°C over the frequency range from 0.2 to 2 MHz in polyacrylamide aqueous solutions. In Fig. 6, at 0.1-1.5% concentration, a/f^2 changes little with frequency. In Fig. 6 absorption coefficients for the concentration 1.0% were omitted to avoid confusion. However at 2.5%, a/f^2 rapidly increases with decreasing frequency. As seen in Fig. 6 the relaxation of polyacrylamide aqueous solutions result in the corresponding absorption spectra which cannot be described in terms of

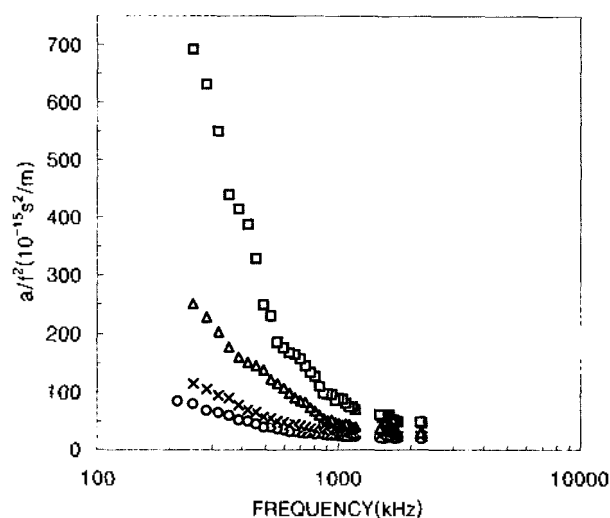


Figure 6. Frequency dependence of the absorption a/f^2 for polyacrylamide with water at 30°C divided by the square of frequency in the concentration range of 0.5%-2.5% by weight. The symbols \circ , \times , Δ , and \square represent concentrations 0.5%, 1.5%, 2.0% and 2.5% by weight, respectively.

a single relaxation.

The relaxation mechanisms in polyacrylamide aqueous solutions were associated with structural fluctuations of polymer molecules, proton transfer reaction of amide group, and hydration equilibrium (polyacrylamide-water interaction) by sound waves[5]. In general, the relaxation times which are related to hydration equilibrium (polymer-water interaction) are distributed over the frequency range from 2 GHz to 0.1 MHz[6]. And the relaxation frequencies which are related to proton transfer reaction of amide group exist around 1-5 MHz[5]. In Fig. 6, since α/f^2 is likely due to the classical Stoke's viscous effect at the frequency higher than 1 MHz, there is no relaxation above 1 MHz. Therefore relaxation mechanism in polyacrylamide aqueous solutions may be attributed to the structural fluctuations of polymer molecules, such as the segmental motion of the polymer chains. Shigeo Kato *et al* reported that the ultrasonic relaxation due to segmental motions in aqueous solutions of poly (acrylic

acid) was below 1 MHz[5] However, for the precise understanding of this mechanism, absorption coefficient measurements in the polyacrylamide solution should be performed over a wide frequency range, especially over a low-frequency range of 50 to 100 kHz.

Velocity Measurements. Fig. 7 shows the ultrasonic velocity in 0.5, 1.5, and 2.5% concentrations of the polyacrylamide aqueous solutions. We see that the ultrasonic velocity behavior in polyacrylamide aqueous solutions strongly reflects that in pure water. Fig. 8 magnifies the ultrasonic velocity in 0.5, 1.0, 1.5, 2.0, and 2.5% concentrations for the narrow temperature range of 60-90°C. Note that Fig. 8 contains all the data points, whereas in Fig. 7 some data points have been omitted to avoid confusion.

The velocity increases with increasing concentration at a given temperature. Also as the temperature increases at a given concentration, the velocity increase. Since the density should increase as more polyacrylamide is added, it means the compressibility decreases with concentration. This is seen from the fact that the velocity is equal to the

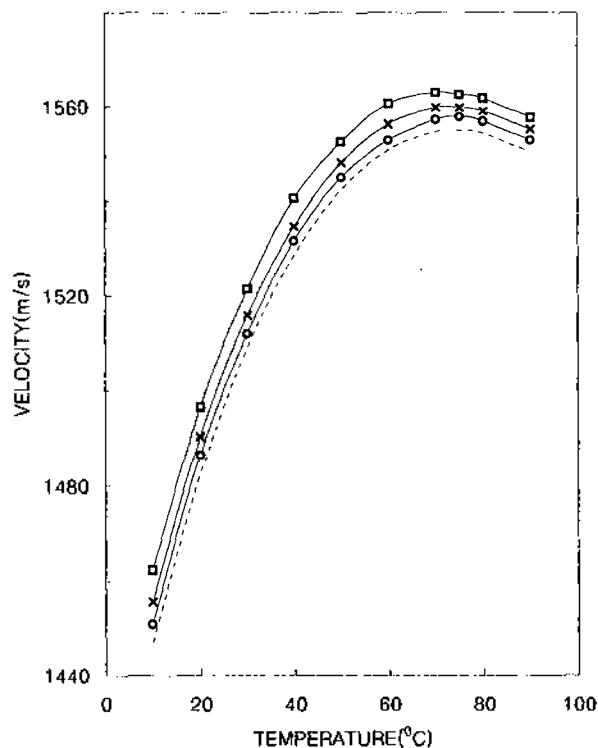


Figure 7. Ultrasonic velocity for polyacrylamide aqueous solutions at the different concentrations (0.5-2.5%) and the temperatures (10-90°C). The symbols \circ , \times , \square and $---$ represent concentration 0.5, 1.5, and 2.5% by weight and pure water, respectively.

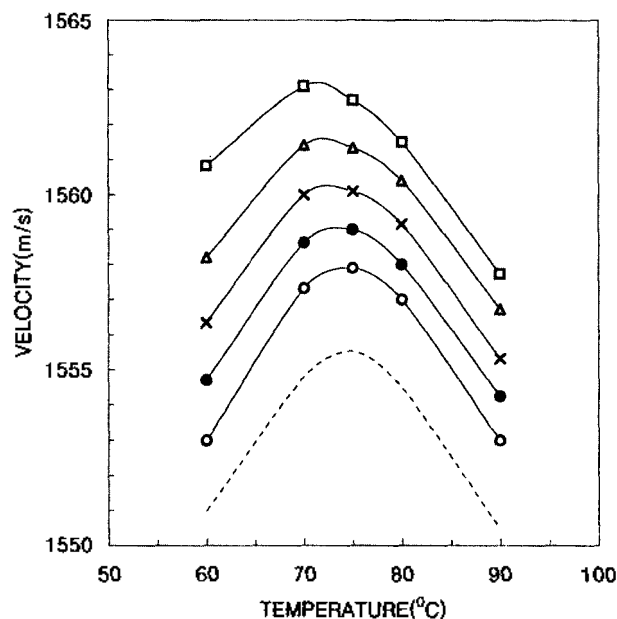


Figure 8. Ultrasonic velocity for polyacrylamide aqueous solutions at the different concentrations (0.5-2.5%) and the reduced temperatures (60-90°C). The symbols \circ , \bullet , \times , \triangle , \square and $---$ represent concentration 0.5, 1.0, 1.5, 2.0 and 2.5% by weight and pure water, respectively.

square root of the reciprocal of the product of density with compressibility. A physical interpretation for the solution is that its molecules may be more strongly bound which is polymer-water hydrogen bonding at sites on the polymer's amide (CONH₂) group as the concentration of polyacrylamide in water increases.

In Fig. 8, the maximum values of the velocity at these concentrations are found at a lower temperature than that in water. The maximum velocity in water is found at around 74°C [7]. The velocities in 0.5%, 1.0%, 1.5%, 2.0%, and 2.5% polyacrylamide aqueous solutions have maxima at about 70°C, 71°C, 72°C, 73°C and 74°C, respectively. The maximum velocity at each concentration tends to shift to higher temperatures with decreasing concentration. The maximum velocity in solutions is approximately 2-7 m/s less than that in pure water. However, the velocities at these concentrations show the same temperature dependence as that in water. This is interpreted in terms of changes in the structure of water and the interaction of the polymer and water.

IV. Conclusions

The present study on aqueous solutions of polyacrylamide carried out over a comparatively wide temperature range of 10-90°C gives a velocity maximum at each concentration. It is seen that the velocity's behavior in polymer solution strongly reflects that in pure water. The ultrasonic relaxation in polyacrylamide aqueous solutions, which may be the result of structural fluctuations of

polymer molecules such as the segmental motion of the polymer chains, was observed for the first time. The absorption α/f^2 at a given temperature increased linearly with concentration as it is below 1.5%, but, for the concentration above 1.5%, increased rapidly with concentration. It is more likely that the value of α/f^2 at 1 MHz is due to the classical Stoke's viscous effect.

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● Jong-Rim Bae

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