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The Rheological Study of Aqueous Solutions of Polyethylene Glycol at Ultrasonic Frequencies

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Ultrasonic investigations of aqueous solutions of polyethylene glycol solutions have been made by means of an ultrasonic pulse technique. Two samples of the polymer have been used, the molecular weights being 4000 and about 6000. The measurements of the sound velocity and of the absorption have been made on 5—30 wt% solutions of the polymers, together with an ethylene glycol - water mixture for the sake of comparison, over the frequency range of 5—45 Mc/sec. The temperature has been varied over the range of 10—70°C. It has been found that the velocity *vs.* temperature curve for each solution has a peak, and that the peak has a trend to shift to a lower temperature with the increase in the concentration. From the absorption data obtained, it has been found that a characteristic relaxation frequency appears near 40 Mc/sec at room temperatures. The magnitude of the absorption has been found to increase linearly approximately with the increase in the concentration, and to be independent of the molecular weight of the polymers at least in the range studied. From the temperature dependence of the relaxation frequency, the apparent activation energy of the relaxation process has been estimated to be not larger than 1 kcal/mol. It has been concluded from the results that the source of the relaxation process is not the hydrogen bonding between polymer molecules and water, as recently stated by G. G. Hammes *et al.* (*J. Phys. Chem.*, **70**, 1610 (1966)), but some intramolecular process.

The ultrasonic pulse method has been widely used recently for studies of various solutions. In our own previous papers[1,2] we have reported some results of ultrasonic investigations of aqueous solutions of polyvinyl alcohol. It has been found that aqueous solutions of the polymer have a characteristic relaxation frequency in the frequency region of the several tens of mega cycles, and the source of the relaxation process has been attributed to the hydrogen bonding between the

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[1] K. Arakawa and N. Takenaka, This Bulletin, **39**, 447 (1966).

[2] K. Arakawa, N. Takenaka, M. Watase and K. Kubota, *ibid.*, **37**, 559 (1964).

hydroxyl groups of the polymer and water molecules.

We will present here the results of some further work on aqueous solutions of polyethylene glycol. This polymer is well known to be easily soluble in water, and also to have both upper and lower consolute temperatures in aqueous solutions.3)

The relaxational behavior of polyethylene glycol solutions has been studied by the NMR method,4) the dielectric method,5) and the ultrasonic method.6) However, no conclusive result has yet been obtained. We will report in this paper the results of our study of the solutions of the polymer by means of the ultrasonic pulse technique, which is similar in its principle to that developed by Pinkerton.7)

Experimental

Samples. Two commercial samples, A and B, of polyethylene glycol obtained from the Wako Pure Chemical Industry Co., Ltd., were used in the present experiments. The intrinsic viscosity of the aqueous solutions are given in Table 1, together with the molecular weight. In the case of the sample A, the molecular weight was calculated using the data of Thomas and Charlesby.*1,8) The sample of ethylene glycol was also obtained from the same company, and was of a guaranteed grade.

The aqueous solutions of the polymer were prepared by mixing the calculated quantity of the polymer and water at room temperature, where the quantity of adsorbed water, which was determined by the dessication method, was taken into account, even though it was small.

Apparatus and Procedure for Measurements. The apparatus described in the preceding paper1) was used in the present work for the measurements of the ultrasonic velocity and the absorption of solutions. It is similar in its principle to that developed by Pinkerton.7) A block diagram of it is shown in Fig. 1, while it was explained in detail in the preceding paper.1)

TABLE 1. SAMPLES

Sample	Intrinsic viscosity (100 cc/g) 30°C	35°C	Molecular weight
A	0.104	0.102	4000
B	—	0.198	about 6000

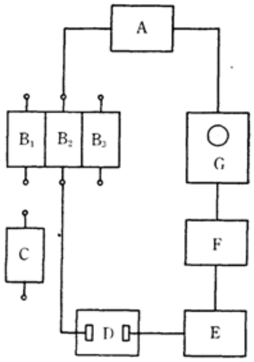

Fig. 1. Block diagram of the apparatus.

A: Pulse generator
B₁, B₂, B₃: Oscillator
B₁, 1—15 Mc/sec
B₂, 15—30 Mc/sec
B₃, 30—50 Mc/sec
C: Doubler
D: Cell
E: Attenuator
F: Amplifier
G: Synchroscope

The sound velocity was obtained by counting the number of carrier waves of a calibrated frequency which passed over the marked vertical line of a synchroscope screen when the ultrasonic path in the solution was varied by the rotation of a micrometer screw. The magnitude of attenuation was determined by the compensation method, using the attenuator. The details of the procedure were described in the preceding paper.1) The temperature was varied over the range of 10—70°C, with 10°C intervals, and was maintained within a fluctuation of 0.1°C at ordinary temperatures and one of 0.2°C at the upper and lower extremes of the temperature range. The absorption data were reproducible to within ±3%, and the velocity data of within ±0.1%.

Results and Discussion

Sound Velocity. The data of sound velocity obtained for solutions of the sample B with various

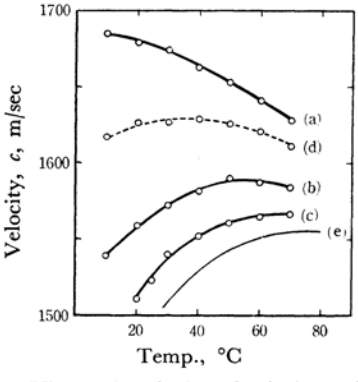

Fig. 2. Ultrasonic velocity of solutions of sample B at 5 Mc/sec.
(a) 30 wt%, (b) 12 wt%, (c) 5 wt%.
(d) Ethylene glycol - water mixture
(e) Pure water

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3) G. N. Malcolm and J. S. Rowlinson, *Trans. Faraday Soc.*, **53**, 921 (1957).

4) T. M. Connor and K. A. McLauchlan, *J. Phys. Chem.*, **69**, 1888 (1965).

5) M. Davies, G. Williams and G. D. Loveluck, *Z. für Elektrochemie*, **64**, 575 (1960).

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

7) J. M. M. Pinkerton, *Proc. Phys. Soc.*, **B62**, 86 (1949).

[*1] The formula given by Thomas and Charlesby concerning the $[\eta]$ *vs.* M relation of aqueous solutions at 35°C is found to be incorrect or missprinted; we have therefore modified their formula as follows:

$$[\eta]_{35^\circ\mathrm{C},\ \mathrm{water}}=(1.13\times10^{-4})\,M^{0.82}$$

We used this formula for the calculation of the molecular weight of the sample A.

8) D. K. Thomas and A. Charlesby, *J. Polymer Sci.*, **52**, 195 (1960).

concentrations are plotted against the temperature in Fig. 2, together with the data for an ethylene glycol - water mixture with the composition of 3 : 7. It may clearly be seen in Fig. 2 that the peak found in the velocity *vs.* temperature curve shifts to a lower temperature with an increase in the concentration. This may be ascribed to the effect of solute molecules, which destroy the "open structure" or the "flickering clusters"[9] with a density lower than that of unbonded water molecules.

Time Effect of Absorption. In order to investigate the time effect of sound absorption, we have measured the change in absorption with the lapse of standing time for a 20 wt% solution of the sample A at 30°C. The data are given in Fig. 3 in the form of an α/f^2 *vs.* $\log f$ curve, where α is the absorption coefficient, and f, the frequency. It may be seen in Fig. 3 that, with the lapse of time, the magnitude of α/f^2 increases on the whole, and also that the inflection point which appeared in the α/f^2 *vs.* $\log f$ curve shifts to a lower frequency with the lapse of time. Therefore, it may be tentatively said that some aggregation process occurs in an aqueous solution of polyethylene glycol with the lapse of standing time.

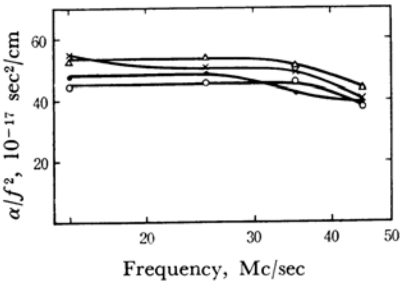

Fig. 3. Time effect of absorption for 20 wt% solution of sample A at 30°C.
○ directly after the preparation, ● 24 hr
× 6 days, △ 10 day

Data of Sound Absorption. The ultrasonic absorption of the solutions of the samples A and B, and, also, that of the ethylene glycol-water mixture has been measured. The measurements have been made directly after the preparation of the solutions in order to avoid the time effect as much as possible. The data obtained are given in Fig. 4(a)—(e) for each solution in the form of an α/f^2 *vs.* $\log f$ relation. Concerning the data at 5 Mc/sec, the contribution from the diffraction effect[10] to the total attenuation has been calculated and excluded from the total attenuation. In the frequency region higher than 5 Mc/sec, it is very small and is within the extent of the fluctuation of the observed value.

Concentration Dependence of Ultrasonic Absorption. In order to investigate the concentration dependence, the magnitude of absorption at 30°C and 25 Mc/sec has been plotted in Fig. 5 in the form of an α/f^2 *vs.* C relation, where the contribution from the solvent is eliminated.[1]

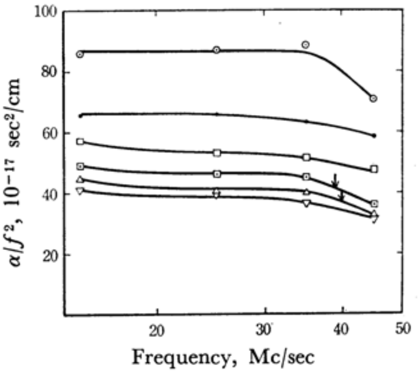

Fig. 4(a). Ultrasonic absorption for 30 wt% solution of sample B.
⊙ 20°C, ● 30°C, □ 40°C, ⊡ 50°C, △ 60°C, ▽ 70°C

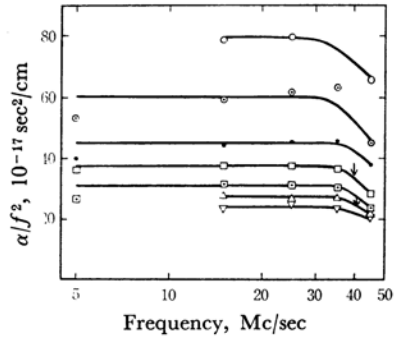

Fig. 4(b). Ultrasonic absorption for 20 wt% solution of sample A.
○ 10°C, ⊙ 20°C, ● 30°C, □ 40°C, ⊡ 50°C, △ 60°C, ▽ 70°C

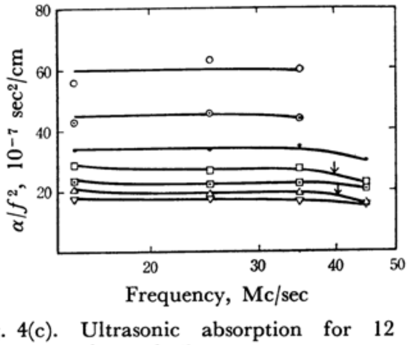

Fig. 4(c). Ultrasonic absorption for 12 wt% solution of sample B.
○ 10°C, ⊙ 20°C, ● 30°C, □ 40°C, ⊡ 50°C, △ 60°C, ▽ 70°C

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[9] G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3382 (1962).

[10] K. Seki, A. Granato and R. Truel, *J. Acoust. Soc. Am.*, **28**, 230 (1956).

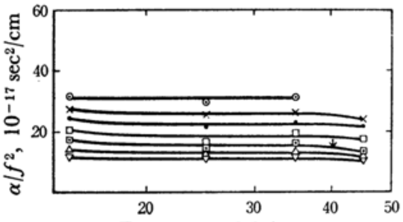

Fig. 4(d). Ultrasonic absorption for 5 wt% solution of sample B.
⊙ 20°C, × 25°C, ● 30°C, □ 40°C, ⊡ 50°C, △ 60°C, ▽ 70°C

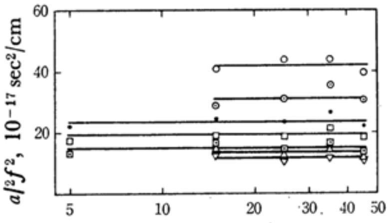

Fig. 4(e). Ultrasonic absorption for ethylene glycol-water mixture with composition of 3 : 7.
○ 10°C, ⊙ 20°C, ● 30°C, □ 40°C, ⊡ 50°C, △ 60°C, ▽ 70°C

As may clearly be seen, the relation is approximately linear, though a small trend to a higher-order dependence on the concentration appears in concentrated solutions. From this fact it may be said that mutual interactions among polymer molecules are not the primary source of the ultrasonic absorption in the frequency range of the present experiment.

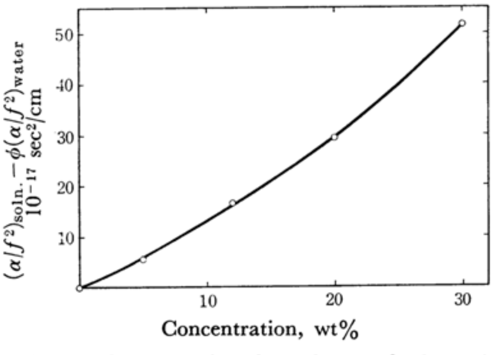

Fig. 5. Concentration dependence of absorption in 25 Mc/sec at 30°C.
ϕ: Volume fraction of solvent.

In Fig. 6 the temperature dependence of the absorption at 25 Mc/sec is given at each concentration, together with that for pure water for the sake of comparison. It may be seen that the α/f^2 *vs.* T curves are all similar in shape, irrespective of their concentration and molecular weights.

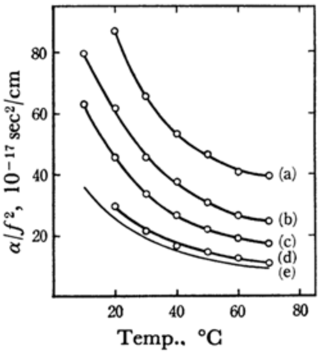

Fig. 6. Temperature dependence of absorption at 25 Mc/sec for polyethylene glycol solutions.
(a) 30 wt%, sample B; (b) 20 wt%, sample A;
(c) 12 wt%, sample B; (d) 5 wt%, sample B;
(e) Pure water

Discussion. As may be seen in Figs. 4(a)—(d), a relaxation frequency, f_r, is present near 40 Mc/sec at ordinary temperatures in the polymer solutions. It is clear that the relaxation frequency is kept nearly constant for different conditions of the molecular weight and concentration. As for the temperature dependence, a trend for the relaxation frequency to shift to a higher frequency with an increase in the temperature is seen, though the trend is small, as has been reported by Hammes and Lewis recently.[6] However, the data given by Hammes *et al.* have been confined to lower concentrations and lower temperatures, though the frequency range is fairly broad; further conclusive remarks have been difficult.

From the temperature dependence of f_r or τ(the relaxation time $\tau = 1/2\pi f_r$) the apparent activation energy, ΔH, for the relaxation process can be obtained. In the present data the shift of the inflection point, f_r, in the curves in Fig. 4(a)—(d), accompanied by the temperature increase, is very small, and we can not determine the magnitude of ΔH precisely from the shift of the inflection point in the α/f^2 *vs.* log f curves. However, it is sure that the magnitude of ΔH is not larger than 1 kcal/mol.

This is confirmed by another treatment, as in the following. When the process observed is represented by a single relaxation process, the absorption is given as follows:

$$\frac{\alpha}{f_2} = \frac{A\tau}{1+(\omega\tau)^2} + B, \qquad (1)$$

where A and B are constants and τ is a characteristic relaxation time.

As may be seen in Fig. 4(a)—(d), the α/f^2 *vs.* $\log f$ curves are found still to be decreasing at the higher extreme of the frequency region in the experiment; therefore, we can not obtain the magnitude of B experimentally. However, we can estimate it approximately as below. The

TABLE 2. MAGNITUDE OF PARAMETER B

Temperature °C	Hammes and Lewis's value 8 wt% (10^{-17} sec^2/cm)	Hammes and Lewis's value 5 wt% (10^{-17} sec^2/cm)	α/f^2 Pure water (10^{-17} sec^2/cm)	α/f^2 Ethylene glycol —water mixture (10^{-17} sec^2/cm)
10	43.2	39.8	35	42
20			25	31.5
25	25.8	24.1	22	28
30			19	23.5
40			14.5	19.0
50			12	15.0
60			10.5	13.0
70			8.5	11.5

magnitude of B used by Hammes *et al.* is slightly larger than the values of α/f^2 for pure water, and is found to increase linearly approximately with the increase in the concentration. However, it is difficult to consider that the increasing trend holds for larger concentrations as well, for the magnitude becomes too large. In Table 2 the values of B used by Hammes *et al.* and those of α/f^2 for pure water are given, together with those of α/f^2 of the ethylene glycol-water mixture, which are kept constant throguh the frequency region in the present experiment, as may be seen in Fig. 4(e). The values of α/f^2 for the ethylene glycol-water mixture with the weight compostition of 3 : 7 are found to be nearly equal to the B values of Hammes *et al.* for polyethylene glycol solutions of the lower concentration, 8 wt%. The increase in the B values from the values of α/f^2 for pure water is primarily to be ascribed to the change in the structure in water by the presence of solute molecules.

From the above considerations, the magnitude of B for the ethylene glycol - water mixture, which is given in Table 2, may be used for obtaining the τ value at each temperature for the 30 wt% solution of polyethylene glycol from the peak of the $(\alpha/f^2-B)fc$ *vs.* $\log f$ curves. The $(\alpha/f^2-B)fc$ *vs.* $\log f$ curves obtained from the data shown in Fig. 4(a) are given in Fig. 7. The magnitude of ΔH obtained from the temperature dependence of the relaxation times, τ, thus obtained is found to be within the range of 0.5—1.0 kcal/mol.

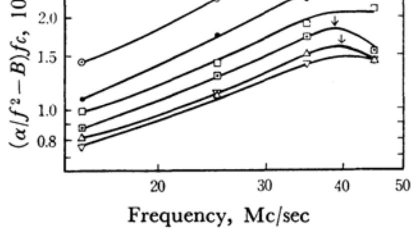

Fig. 7. Ultrasonic absorption per wavelength for 30 wt% solution of sample B.
⊙ 20°C, ● 30°C, □ 40°C, ⊡ 50°C, △ 60°C, ▽ 70°C

As has been stated above, the interaction between polymer molecules is not the primary source of the relaxation process observed. Therefore, the observed relaxation process must be attributed to either the intramolecular process of the polymer or the interaction between solute and solvent molecules, or to both. Hammes *et al.* ascribed the source of the relaxation to the solute-solvent interaction, that is, to the hydrogen bonding between the oxygen of the ether bond in the polymer and the OH of water molecules. However, the magnitude of the apparent activation energy, ΔH, obtained in the present study is too small to consider the source of the relaxation to be the hydrogen bonding. Therefore, it may be said that the relaxation process observed is to be attributed to the intramolecular process in the polyethylene glycol molecule.

The magnitude of the barrier potential for the internal rotation in the skeleton of the polyethylene glycol molecule may be supposed to be about 3 kcal/mol, considering the data concerning simple molecules.[11-13] For example, the magnitude has been determined to be 2.9 kcal/mol for the C–C bond rotation in the ethane molecule,[11] 2.7 kcal/mol for the C–C bond in the acetone molecule,[12] and 3.2±0.5 kcal/mol for the C–C bond rotation in the dichloroethane molecule in ether.[13] These values are too large to ascribe the source of the relaxation observed in this work to these internal rotations.

However, the polyethylene glycol chain is thought to have a greater flexibility.[5,14] Therefore, it is not unlikely that the small magnitude of the activation energy in aqueous solutions has some correlation with this greater flexibility of the

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[11] K. S. Pitzer, *Discussions Faraday Soc.*, **10**, 66 (1951).

[12] P. H. Kasai and R. J. Myers, *J. Chem. Phys.*, **30**, 1096 (1959).

[13] J. E. Piercy, *ibid.*, **43**, 4066 (1965).

[14] T. Uchida, Y. Kurita, N. Koizumi and M. Kubo, *J. Polymer Sci.*, **21**, 313 (1956).

polymer chain. In order to clarify the nature of the relaxation process further, more investigations are required.

Summary and Conclusions

Ultrasonic investigations of aqueous solutions of polyethylene glycol have been made by means of an ultrasonic pulse technique over the frequency range of 5—45 Mc/sec in the temperature range of 10—70°C.

1) In the ultrasonic velocity *vs.* temperature relation a trend is found for the peak in the curve to shift to a lower temperature with an increase in the concentration.

2) From the frequency dependence of the absorption data, a characteristic relaxation frequency is found within the range described above.

3) The relaxation frequency is found to be nearly independent of the concentration and molecular weight of the polymer.

4) From the temperature dependence of the relaxation frequency, the apparent activation energy has been found to be not larger than 1 kcal/mol.

5) The source of the relaxation process observed has been ascribed to the intramolecular process in the polymer molecules.

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