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Ultrasonic Relaxation of Water-Dioxane System

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Ultrasonic investigations of the water-dioxane system were made by means of an ultrasonic pulse technique. The ultrasonic velocity and absorption of the solutions were measured in the frequency range from 5 to 45 Mc/sec. The temperature was varied from 20 to 60°C. It was observed in the velocity *vs.* concentration curves obtained at various temperatures that all curves converged at 0.03—0.04 mol fraction of dioxane. The ultrasonic absorption of pure dioxane was found to increase with the rise of temperature, which might be ascribed to the vibrational relaxation. From the ultrasonic absorption data obtained for the solutions of the water-dioxane system in various compositions and temperatures it was observed that at 0.3—0.4 mol fraction of dioxane an absorption peak was present in the absorption *vs.* concentration curve, and also that there was no shift of the concentration at the peak with the variation of temperature. Some discussion on the structure of the water-dioxane system was given from the ultrasonic data obtained.

Dioxane is completely miscible with water. The water-dioxane system is of considerable interest, since the dielectric constant of the system varies from the magnitude of about 80 for pure water to the magnitude of about 2 for pure dioxane with the variation of its composition. Also, the strong interactions, which are supposed to consist mainly of hydrogen bonding, are present between dioxane and water molecules, though dioxane molecules have no ability to form hydrogen bonding between themselves.

The physical properties of water and dioxane are similar in several respects. For example, the difference between their boiling points is within 15°C, and that between their freezing points is within 12°C, *etc.* The size and shape of molecules are however, fairly different.

From the view-points described above, the water-dioxane system has long been the object of thermodynamical,[1-5] viscometric,[6] dielectric,[7-9] NMR,[10] spectroscopic,[11] and ultrasonic studies.[12] However, no decisive conclusion has been obtained at present. We have measured the ultrasonic velocity and absorption of the water-dioxane system by means of an ultrasonic pulse technique, and discussed the structure of the solutions.

Experimental

Apparatus and Procedures for Measurements. The ultrasonic velocity and the absorption were measured according to the pulse method developed by Pinkerton[13] and others. The apparatus and the procedures for the measurements were described in the preceding paper.[14] The sound velocity was measured at a fixed frequency of 5 Mc/sec. The absorption was measured over the frequency range of 15—45 Mc/sec. All measurements in this experiment were made in the range of temperature from 20°C to 60°C with 10°C intervals, and the temperature was controlled to within ±0.1°C.

Materials. For the measurements of dioxane-water mixtures, the reagent-grade dioxane, obtained from Wako Pure Chemicals, was mixed with freshly distilled water. In the case of the measurements of pure dioxane the dioxane sample was further purified according to the following procedure:[15] after being treated with hydrochloric acid and thereafter with potassium hydroxide, the dioxane sample was refluxed with metallic

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sodium and was fractionally distilled. The fraction in boiling range of 101.3—101.7°C was used for the measurement.

Results

Sound Velocity. The ultrasonic velocity at 5 Mc/sec obtained for the water-dioxane system of various compositions is plotted against temperature in Fig. 1. The accuracy of the data obtained is within 2 m/sec. As is seen in Fig. 1, the sound velocity of water-dioxane mixtures and also that of pure dioxane decrease linearly with the increase in temperature, being in sharp contrast with the increasing trend in the velocity *vs.* temperature curve for pure water which is given for comparison.

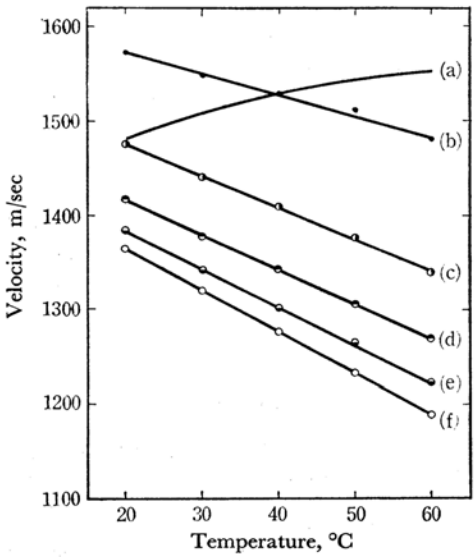

Fig. 1. Temperature dependence of ultrasonic velocity for the dioxane-water system.
dioxane mol%: (a) pure water, (b) 17.5 mol%, (c) 40 mol%, (d) 60 mol%, (e) 80 mol%, (f) pure dioxane

In order to investigate the concentration dependence of ultrasonic velocity, the velocity is plotted against dioxane concentration by mole % for each temperature in Fig. 2. It is seen that at about 3—4 mol% of dioxane (about 15 vol% of dioxane) all curves converge, and that the trend of the temperature dependence of sound velocity is reversed after passing through that concentration.

It is well known that the increasing trend of sound velocity in pure water with the increase of temperature in this temperature range is ascribed to the presence of the "open structure" in liquid water.[16-18] The disappearance of that trend after

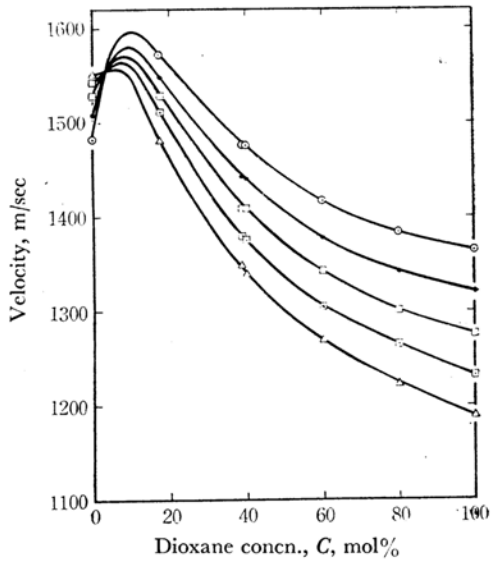

Fig. 2. Concentration dependence of ultrasonic velocity.
⊙ 20°C, ● 30°C, □ 40°C, ⊡ 50°C, △ 60°C

the addition of about 3—4 mol% of dioxane to water is supposed to occur from the strong interaction of dioxane molecules to the structure in water, where dioxane molecules behave as the hydrogen bonding acceptor and water molecules as the hydrogen bonding donor.

Ultrasonic Absorption of Dioxane. The absorption coefficient, α, was measured for the sample of pure dioxane over the frequency range from 15 to 45 Mc/sec. The data obtained are given in Fig. 3, which are plotted against frequency in a logarithmic scale. The accuracy of α obtained is within $\pm 2\%$. As is clearly seen in Fig. 3, no characteristic relaxation frequency is observed in this frequency range. The magnitude of the absorption is found to increase with the increase of temperature. From these observations the

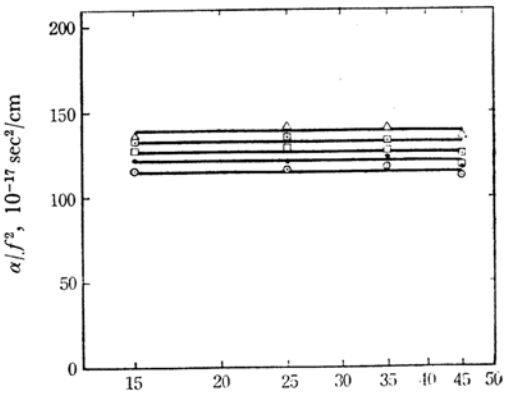

Fig. 3. Ultrasonic absorption of dioxane.
⊙ 20°C, ● 30°C, □ 40°C, ⊡ 50°C, △ 60°C

16) L. Hall, *Phys. Rev.*, **73**, 775 (1948).
17) G. Nénethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3382 (1962).
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source of the ultrasonic absorption in dioxane in this frequency range might be ascribed to the vibrational relaxation. The temperature dependence of α is also shown in Fig. 4. The value reported by Heasell and Lamb[19] is also given which is slightly smaller than our data in spite of the fairly large difference in the frequency used. We might say that no characteristic relaxation frequency should be present in the frequency range including the measurement of Heasell *et al.*

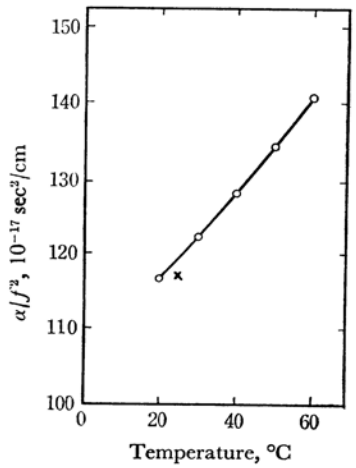

Fig. 4. Temperature dependence of ultrasonic absorption for dioxane.
× Heasell anb Lamb's data[19] at 24.6°C and 104 Mc/sec

Ultrasonic Absorption of Water-Dioxane System. The data of the ultrasonic absorption of the water-dioxane sytem are given in the form of α/f^2 *vs.* $\log f$ relation, where f is frequency, in

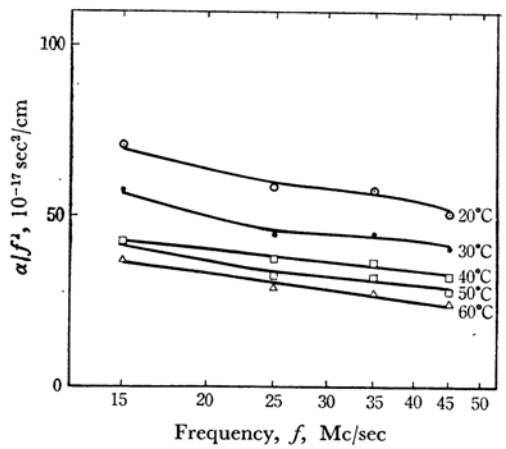

Fig. 5(a). Ultrassonic absorption of the water-dioxane system (17.5 mol% of dioxane).

19) E. L. Heasell and J. Lamb, *Proc. Phys. Soc.*, **B69**, 869 (1956).

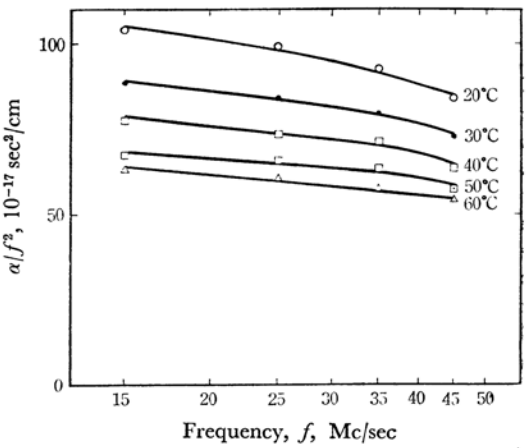

Fig. 5(b). Ultrasonic absorption of the water-dioxane system (40 mol% of dioxane).

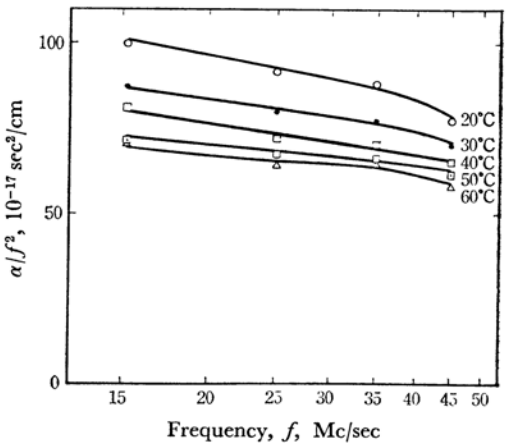

Fig. 5(c). Ultrasonic absorption of the water-dioxane system (60 mol% of dioxane).

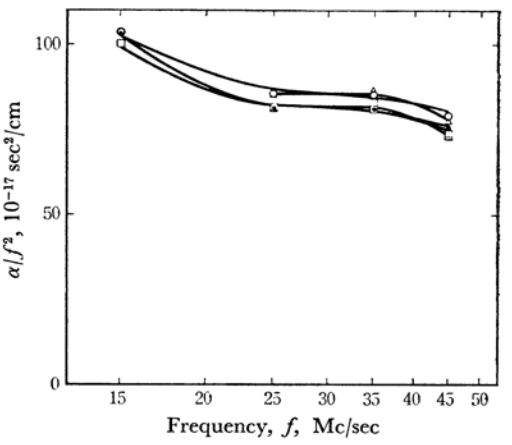

Fig. 5(d). Ultrasonic absorpption of the water-dioxane system (80 mol% of dioxane).
⊙ 20°C, ● 30°C, □ 40°C, ⊡ 50°C, △ 60°C

Fig. 5(a)—(d). The molar concentration of dioxane is 17.5, 40, 60, and 80 mol% respectively. As for the ultrasonic absorption of the water-dioxane system, the data obtained by means of an optical diffraction method was reported previously by Burton.[12] However, Burton's values are much larger than ours.

The concentration dependence of α/f^2 is shown in Fig. 6, where the absorption data for pure water reported by Pinkerton[13] and also our data for the solutions of 75 vol% (38.9 mol%) dioxane are added. A maximum of α/f^2 is seen in Fig. 6 at about 0.4 mol fraction of dioxane at lower temperatures. At higher temperature the maximum is found to deform into a shoulder, but the mole fraction at the shoulder is seen to be constant. The characteristic in the α/f^2 *vs.* mole fraction curve is found to be more discriminate, after the value of α/f^2 obtained according to the proportional calculation to the mole fraction of two components, $(\alpha/f^2)_{lin}$, has been subtracted from the observed value of $(\alpha/f^2)_{obs}$.

The value of the excess absorption,

$$\Delta = (\alpha/f^2)_{obs} - (\alpha/f^2)_{lin}$$

is plotted against the mol% of dioxane in Fig. 7.

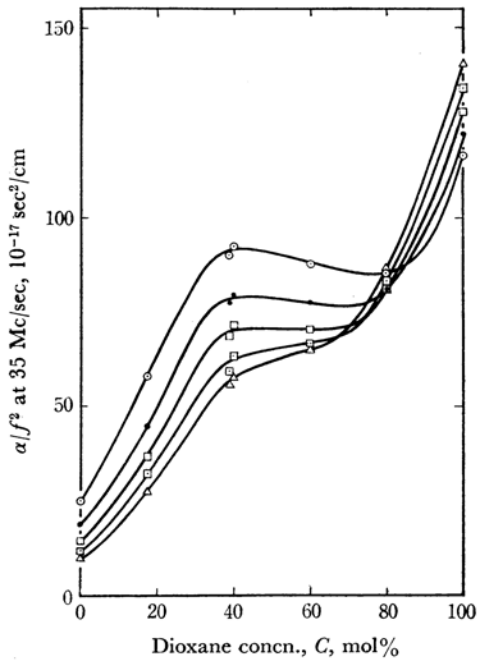

Fig. 6. Concentration dependence of ultrasonic absorption.
⊙ 20°C, ● 30°C, □ 40°C, ⊡ 50°C, △ 60°C

From Fig. 7 it is observed that a maximum of Δ is present always at about 0.35 mol fraction of dioxane irrespective of the variation of temperature though the magnitude of Δ becomes smaller with the increase in temperature.

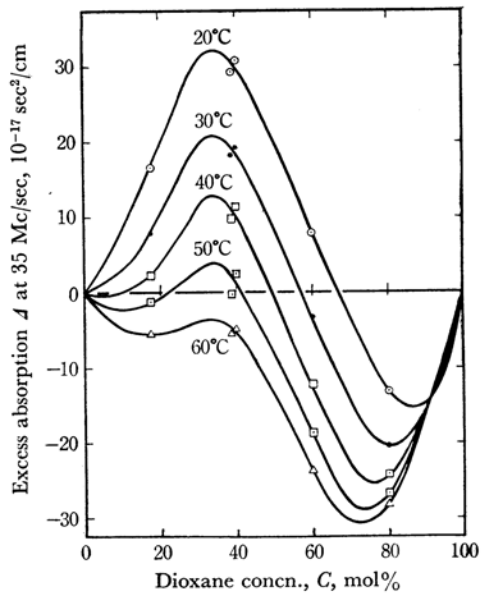

Fig. 7. Concentration dependence of excess absorption.

The temperature dependence of α/f^2 in each solution is shown in Fig. 8. As is clearly seen, the α/f^2 *vs.* temperature curves go downwards with the increase in temperature up to the 60 mol% solutions. In the solution of 80 mol% dioxane

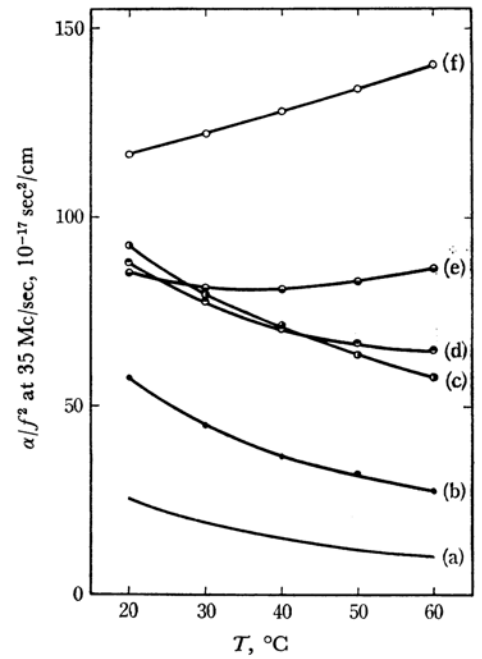

Fig. 8. Temperature dependence of ultrasonic absorption.
Dioxane mol%: (a) pure water, (b) 17.5 mol%, (c) 40 mol%, (d) 60 mol%, (e) 80 mol%, (f) pure dioxane

the cruve has a shallow minimum and is nearly flat.

Discussion

Vibrational Relaxation in Dioxane. As stated from the result given in Fig. 3, the source of ultrasonic absorption in dioxane is ascribed to the vibrational relaxation, which occurs from the time lag of energy transfer from the translational motion to the vibrational motion in dioxane molecules. When water is added to dioxane till the mole ratio of water to dioxane, 1 : 4 (the vol% of water in this composition is as small as about 5% since the dimension of dioxane molecule is larger than that of water molecule), this behavior practically disappears, as is seen in Fig. 8.

In the latter case some structure, which behaves as an energy bridge for the energy transfer from the external degree of freedom to the internal, may be formed in the solution as a result of the strong interaction, perhaps hydrogen bonding, between dioxane and water molecules.

Structure of Water-Dioxane System. It is observed in Fig. 6 and Fig. 7 that at 0.3—0.4 mol fraction of dioxane an absorption peak appears, and that the composition at the maximum absorption remains constant when the temperature is varied. The mole fraction at the maximum or shoulder corresponds to the composition of dioxane dihydrate. From the facts stated above the presence of dioxane dihydrate, which is proposed by Garg and Smyth on the basis of their dielectric measurements,[8] might be suggested.

The excess entropy of mixing, ΔS_E, reported by Vierk,[2] which was obtained from the data of the vapor pressure and the heat of mixing measured on the system, was found to have its maximum in the absolute magnitude at 0.35 mol fraction of dioxane at 20°C. Goates *et al.*[4] also reported from their calorimetric data that $|\Delta S_E|$ was maximum at about 0.3 mol fraction of dioxane at 25°C. According to the dilatometric data of Hovorka *et al.*,[5] the excess volume of mixing, ΔV_E at 25°C also was found to have its maximum value at 0.3—0.4 mol fraction of dioxane in its absolute magnitude at 20—50°C.

This thermodynamic data suggests the presence of some structure between water and dioxane molecules at the 0.3—0.4 mol fraction of dioxane, the composition of which approximately corresponds to dioxane dihydrate.

According to the dielectric relaxation measurements on the water-dioxane mixture reported recently by Garg and Smyth,[8] two relaxation times, τ_1 and τ_2, are present and the longer one, τ_1, which is of the order of 10^{-11} sec has its maximum value at 0.3—0.5 mol fraction of dioxane in the range of temperature, 10—55°C, where the mole fraction at its maximum is found to increase with the rise of temperature. Garg and Smyth have proposed the presence of dioxane dihydrate from their results according to the suggestion of Bak and Hynne.[8]

Geddes[6] proposed the presence of $C_4H_8O_2 \cdot 5H_2O$ from his viscometric results. According to Goates *et al.*[4] a dip in the mixing enthalpy was found at 0.15 mol fraction of dioxane and also in the case of the freezing point curve a sharp dip was found at the same mole fraction, which corresponded to the composition of $C_4H_8O_2 \cdot 6H_2O$. However in our ultrasonic relaxation data no feature is seen in that range of compsotion, and we can not state decisively the presence of hexahydrate or pentahydrate.

Summary and Conclusion

Ultrasonic investigations of the water-dioxane system have been made by the pulse method over the frequency range of 5—45 Mc/sec. The source of the ultrasonic absorption in this frequency range for pure dioxane has been ascribed to the vibrational relaxation. The ultrasonic absorption for the water-dioxane system has been found to have its maximum or shoulder at 0.3—0.4 mol fraction of dioxane and it has also been found that the mole fraction of maximum absorption is maintained to be nearly constant with the variation of temperature. The structure of the water-dioxane system has been discussed concerning the presence of dioxane dihydrate.

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