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Ultrasonic Study on Solute-Solvent Interaction in Aqueous Systems of Ethers

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Ultrasonic velocity and absorption were measured for binary mixtures of water and ethers (1,2-dimethoxyethane, bis(2-ethoxyethyl)ether, bis(2-methoxyethyl)ether, ethylether, diethoxymethane, 1,1-diethoxyethane and 1,2-diethoxyethane) in the frequency range 15—45 MHz at 10—30 °C. Vibrational relaxation was observed in the pure liquid of 1,2-dimethoxyethane. For each solution of 1,2-dimethoxyethane and bis(2-methoxyethyl)ether, the maximum absorption at the intermediate composition was ascribed to the formation of dihydrate and trihydrate, respectively. The difference between the behavior of ethyl group in water and that of methyl group was discussed from the absorption data.

It has been accepted that hydrocarbon-water interaction (hydrophobic interaction) plays an important role in the conformation of biopolymers in aqueous solutions. For the elucidation of the nature of the interaction, we have studied the aqueous solutions of polyethyleneoxide,[1] dioxane,[2,3] alkyl-substituted urea,[4] amino acid,[5] diamine,[6] tetraalkylammonium salt[7] *etc.* in relation to the structure theory of water.[8–10]

Ultrasonic studies of the aqueous solution of polyethyleneoxide have been carried out by several workers.[1,11–15] It was concluded that "the local water structure formation around the polymer consists of water molecules hydrogen-bonded to oxygen atoms of the chain and hydrophobic water structure around the $-CH_2CH_2-$ groups",[12] and also that it is the origin of the ultrasonic relaxation in the MHz region in the solution. From a study on the aqueous solution of dioxane,[2,3] the presence of dioxane dihydrate was proposed. It was concluded that, concerning the water structure, the structure-breaking ability due to two etheral oxygens is diminished in part by the structure-forming ability due to two $-CH_2CH_2-$ groups.

Many problems concerning the interaction between water and alkyl groups with polar groups remain nusolved.

An ultrasonic measurement is one of the most useful methods for studying the structure of liquids and solutions.[16–18] We have undertaken a comprehensive study of aqueous solutions of ethers by means of an ultrasonic pulse technique with the intention to investigate ethyleneoxide-water and alkyl group-water interactions.

Experimental

Apparatus and Procedures. The ultrasonic pulse method was used for the measurement of absorption coefficient and velocity. The apparatus and procedures were described previously.[1,19] The sound velocity and absorption coefficient were measured at 5 MHz and in the frequency range 15—45 MHz, respectively at temperatures 10—30 °C. The data of the absorption coefficient were reproducible within ±2% and sound velocity data ±1 m/s.

Samples. The samples of ethers were obtained from Wako Pure Chemical Ind. Co. Ltd. (Table 1). Before purification, ethylether was treated with a saturated potassium permanganate solution containing 5% sodium hydroxide, with 50% sulfuric acid and then with water.[20] To bis(2-ethoxyethyl)ether and bis(2-methoxyethyl)ether, a small amount of water was added and the mixture was distilled. Impurities such as xylene were azeotropically removed.

All the samples were refluxed over potassium-sodium alloy after desiccation with potassium hydroxide, and then fractionally distilled through a Widmer column. Distillation was carried out under reduced pressure for 1,2-diethoxyethane and bis(2-ethoxyethyl)ether and for bis(2-methoxyethyl)ether under nitrogen atomsphere. The boiling points observed are given in Table 1.

Results

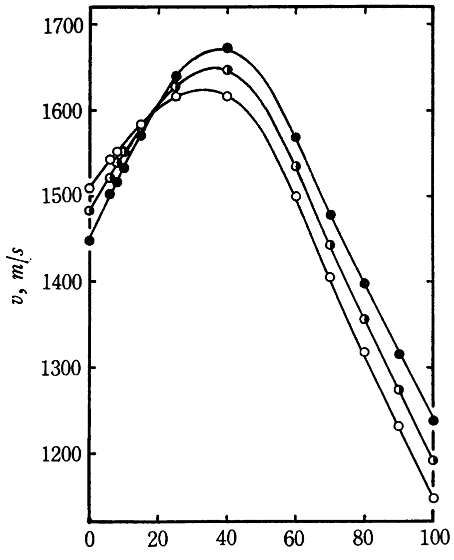
Sound Velocity. 1,2-Dimethoxyethane, bis(2-ethoxyethyl)ether and bis(2-methoxyethyl)ether are miscible with water in all compositions, while other ethers are partially miscible at room temperature. The aqueous solution of bis(2-ethoxyethyl)ether has a lower critical solution temperature (L.C.S.T., 28 °C, 63.5% ether).[25] The sound velocity *vs.* concentration curves for aqueous solutions of 1,2-dimethoxyethane, bis(2-ethoxyethyl)ether and bis(2-methoxyethyl)ether are shown in Figs. 1(a)—(c), where the concentration is given in vol %.[26] The sound velocity data for dilute aqueous solutions of ethylether, diethoxymethane,

TABLE 1. BOILING POINTS OF ETHERS

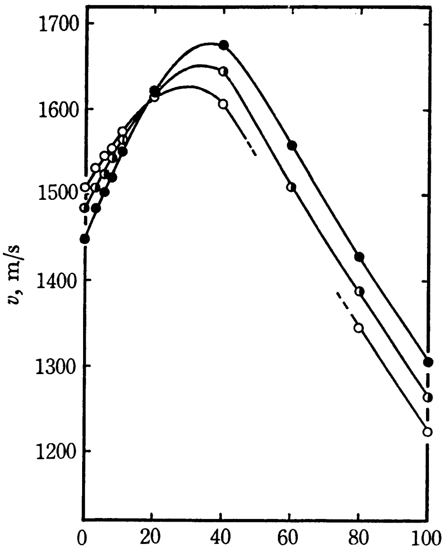
Sample		Bp (°C) Present work	Ref.
Ethylether	$C_2H_5OC_2H_5$	34.4	34.55[20]
Diethoxymethane	$C_2H_5OCH_2OC_2H_5$	87.9	87.9[21]
1,1-Diethoxyethane	$(C_2H_5O)_2CHCH_3$	103.5	103.6[20]
1,2-Diethoxyethane	$C_2H_5OC_2H_4OC_2H_5$	43.5 (47.5 mmHg)	
Bis(2-ethoxyethyl)ether	$(C_2H_5OC_2H_4)_2O$	70.9 (10 mmHg)	
1,2-Dimethoxyethane	$CH_3OC_2H_4OCH_3$	85.1	85.2[22] 84.6[23]
Bis(2-methoxyethyl) ether	$(CH_3OC_2H_4)_2O$	163.0	162[24]

1,1-diethoxyethane and 1,2-diethoxyethane at 20 °C are shown in Fig. 2, including those for 1,2-dimethoxyethane, bis(2-ethoxyethyl)ether and bis(2-methoxyethyl)ether solutions. We see that the velocity *vs.* concentration relation is similar to each other in dilute aqueous solutions of all these materials, and that the relation is represented by a single curve for all the solutions.

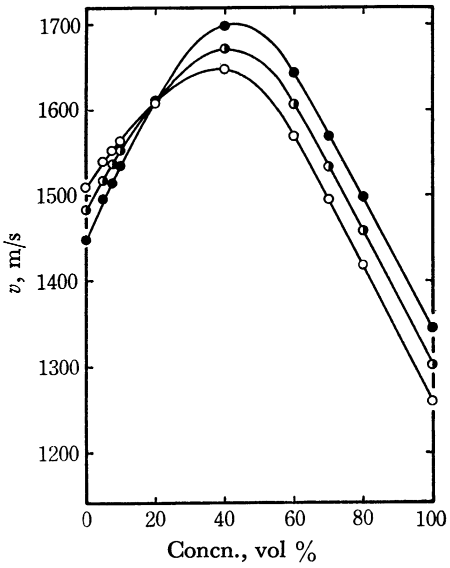
Ultrasonic Absorption. Ultrasonic absorption, α/f^2, where α is absorption coefficient and f frequency, is plotted against temperature for pure 1,2-dimethoxyethane, bis(2-ethoxyethyl)ether and bis(2-methoxyethyl)ether (Fig. 3). In the frequency range studied, no relaxation was observed. The absorption of bis(2-ethoxyethyl)ether and bis(2-methoxyethyl)ether decreases and that of 1,2-dimethoxyethane increases with temperature rise. This indicates the presence of a vibrational relaxation mechanism in the pure liquid of 1,2-dimethoxyethane like dioxane.[2)]



(a)



(b)



(c)

Fig. 1. The plot of ultrasonic velocity *vs.* concentration of ethers (vol %) in aqueous systems of ethers, (a): 1,2-dimethoxyethane, (b): bis(2-ethoxyethyl)ether, (c): bis(2-methoxyethyl)ether, ●: 10 °C, ◑: 20 °C, ○: 30 °C.

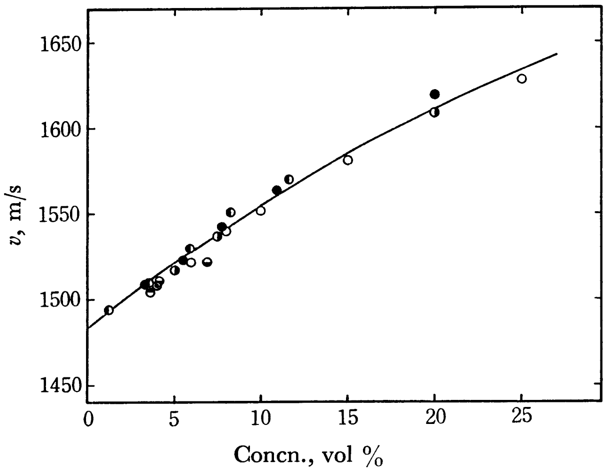


Fig. 2. Ultrasonic velocity in aqueous solutions of ethers at 20 °C, ○: 1,2-dimethoxyethane, ●: bis(2-ethoxyethyl)ether, ◑: bis(2-methoxyethyl)ether, ⊖: ethylether, ⊙: diethoxymethane, ◓: 1,1-diethoxyethane, ◐: 1,2-diethoxyethane.

The absorptions of aqueous solutions of these ethers at 15 MHz are plotted against concentration (Figs. 4(a)—(c)). They are also plotted at various frequencies at 20 °C for the 1,2-dimethoxyethane–water system (Fig. 5). The absorption *vs.* concentration curves have a peak at about 60—80 vol %. The maximum value decreases with increasing frequency. In the aqueous solutions of 1,2-dimethoxyethane and bis(2-methoxyethyl)ether, the maximum value decreases with increasing temperature, while in the solutions of bis(2-ethoxyethyl)ether it increases. In Fig. 6, the absorption of the aqueous solutions of 1,2-dimethoxyethane and that of bis(2-methoxyethyl)ether at 10 °C and at 35 MHz are plotted against concentration

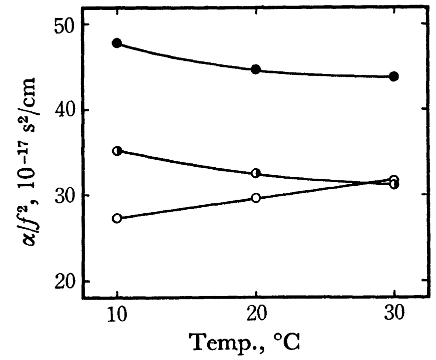
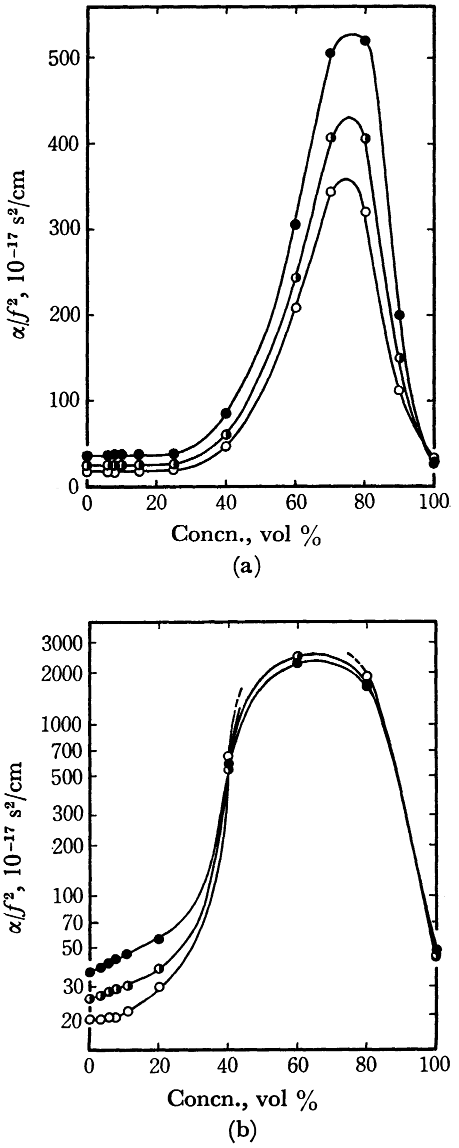


Fig. 3. Ultrasonic absorption in pure ethers,
○: 1,2-dimethoxyethane, ●: bis(2-ethoxyethyl)ether,
◑: bis(2-methoxyethyl)ether.

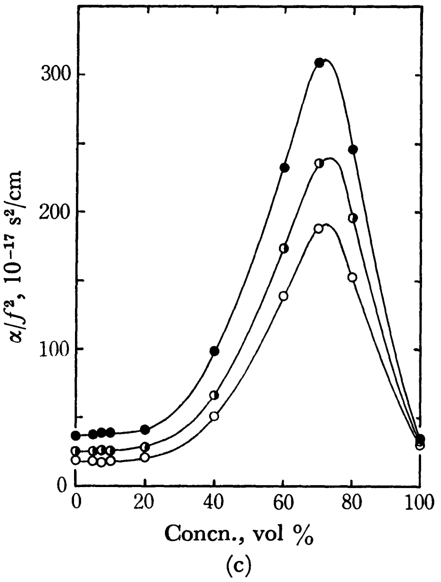
(mol %), including that of 1,2-ethanediol-water mixtures reported by Blandamer *et al.* (at 0 °C, 70 MHz).[27]

The ultrasonic absorption for all solutions at low concentrations is plotted against concentration by vol% in Fig. 7. No relaxation has been observed in the frequency range measured. The absorption *vs.* vol % relations in these solutions are classified into two groups, each of which is represented by a single curve. The upper curve is for the ethers with ethyl groups at each end of a molecule, the lower curve for those with methyl groups at each end.



(a)

(b)



(c)

Fig. 4. The plot of ultrasonic absorption *vs.* concentration of ethers (vol %) in aqueous systems of ethers, (a): 1,2-dimethoxyethane, (b): bis(2-ethoxyethyl)ether, (c): bis(2-methoxyethyl)ether, ●: 10 °C, ◑: 20 °C, ○: 30 °C.

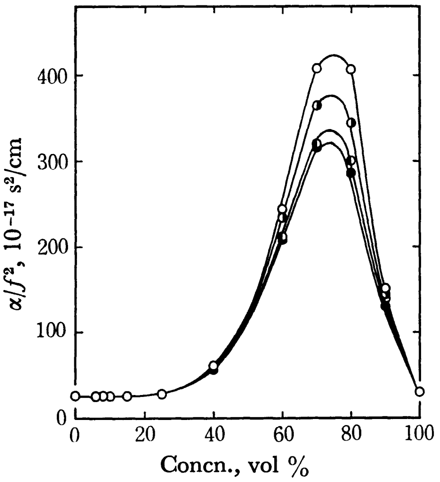


Fig. 5. The plot of ultrasonic absorption *vs.* concentration of ether (vol %) in the 1,2-dimethoxyethane-water system, ○: 15 MHz, ◑: 25 MHz, ◐: 35 MHz, ●: 45 MHz.

Partial molar volume has been calculated graphically[28] from the density data obtained for the bis(2-ethoxyethyl)ether-water system and is plotted in Fig. 8.

Discussion

The Origin of the Maximum in Ultrasonic Absorption. A marked peak appears at an intermediate composition in each absorption *vs.* composition curve. The behavior of the curve for bis(2-ethoxyethyl)ether (Fig. 4(b))

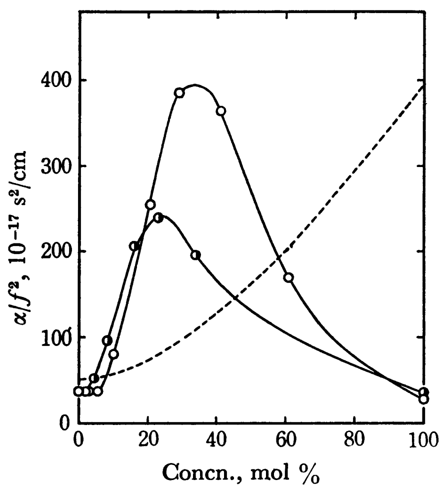


Fig. 6. The plot of ultrasonic absorption *vs.* concentration of ethers (mol %) in aqueous systems of ethers at 10 °C and 35 MHz, ○: 1,2-dimethoxyethane, ◑: bis(2-methoxyethyl)ether, dashed line: 1,2-ethanediol (at 0 °C 70 MHz, ref. 27).

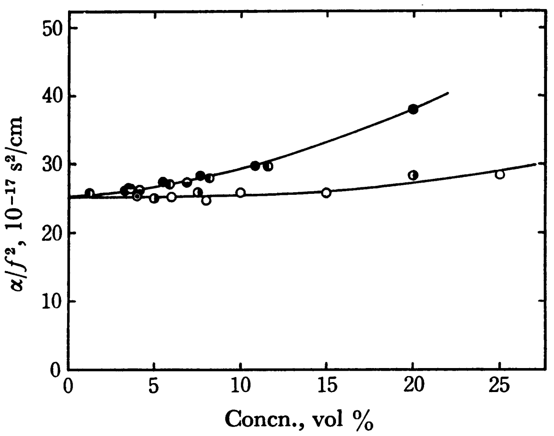


Fig. 7. Ultrasonic absorption in aqueous solutions of ethers at 20 °C. ○: 1,2-dimethoxyethane, ●: bis(2-ethoxyethyl)ether, ◑: bis(2-methoxyethyl)ether, ◒: ethylether, ⊙: diethoxymethane, ◓: 1,1-diethoxyethane, ◐: 1,2-diethoxyethane.

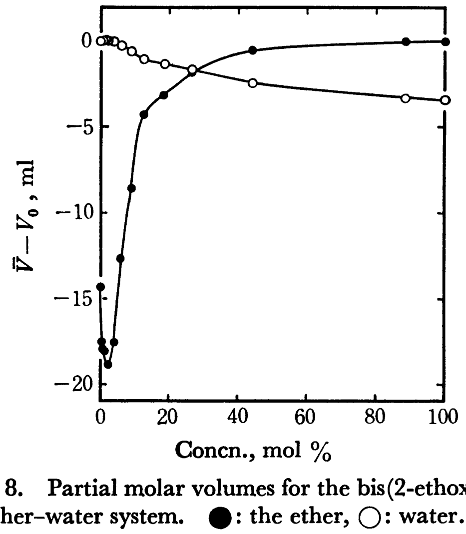


Fig. 8. Partial molar volumes for the bis(2-ethoxyethyl)-ether–water system. ●: the ether, ○: water.

differs from that for other ethers (Figs. 4(a) and (c)), the temperature dependence of absorption near the maximum being the reverse of that at each side. This is ascribed to the presence of L.C.S.T. It is well-known that ultrasonic absorption increases rapidly near L.C.S.T.[29]

In the aqueous solution of 1,2-dimethoxyethane and bis(2-methoxyethyl)ether the maximum of the ultrasonic absorption could be attributed to other sources. At the composition of each maximum (Figs. 4(a), (c), and 6) the molar ratio between ether and water is 1:2 and 1:3 for 1,2-dimethoxyethane and bis(2-methoxyethyl)ether, respectively. Thus, the molar ratio between etheral oxygen and water becomes 1:1 exactly at the composition for both ethers, because each ether has two and three etheral oxygen atoms per molecule, respectively. In the case of the dioxane–water mixture a similar feature was found and the formation of dioxane dihydrate was proposed.[2] Thus it is tentatively assumed that the origin of the maximum absorption is mainly attributed to the presence of hydrates (1,2-dimethoxyethane dihydrate and bis(2-methoxyethyl)ether trihydrate).

Absorption vs. Composition Curves for Low Concentrations. A deep minimum is found in the partial molar volume of the solute *vs.* composition curve for the bis(2-ethoxyethyl)ether–water system (Fig. 8), similar to other aqueous solutions of organic substance.[22,24,30] The composition of the minimum is about 2.5 mol % (about 20% by volume).

The sound velocity *vs.* concentration curves at various temperatures shown in Figs. 1(a)—(c) have a crossing point, where sound velocity is independent of temperature. The solute concentration at the point is about 15—20 vol % for every ether (Fig. 1). As to the ultrasonic absorption, each curve for the absorption *vs.* concentration relation has a flat region at low concentrations (below about 15—20 vol %) (Figs. 4, 5, and 7). The concentration at which the rapid increase of absorption begins is the same as that at the crossing point of velocity *vs.* concentration curves and nearly the same as that at the minimum of partial molar volume. This suggests that all these features are related to some common molecular process in dilute aqueous solutions. As regards the aqueous solutions of dioxane and other substances,[3] we proposed an explanation of a similar feature in absorption *vs.* concentration curves, based on a model of water structure. The underlying molecular process has been assumed to be the "cooperative formation" of the short-lived "ice-like structure" in liquid water.[10]

Difference between the Behavior of Ethyl and Methyl Groups in Water. As seen in Fig. 7, the absorption *vs.* concentration relation for ethers with ethyl groups at each end of a molecule is represented by a single curve (upper curve), and that for ethers with methyl group by another single curve (lower curve).

The difference between the upper and lower curves could be ascribed to the different behavior of ethyl and methyl groups in water. A methyl group at the end of a molecule is considered to rotate almost freely in water at room temperature.[31] Thus, from the large absorption of ethers with ethyl in comparison with that of ethers with methyl, the ethyl group at the molecular end is supposed to be hindered in its motion by the formation of the water structure about itself. The formation of "water structure" about ethyl group and its disruption by the direct contact of the hydrocarbon is considered to be the origin of "hydrophobic interaction" between hydrocarbons in general with exception of the methyl group.[10,32)]

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