

Dynamic Study of the Interaction between Diols and Water by Ultrasonic Methods

Part 3.—2-Methylpentane-2,4-diol Solution

BY SADAKATSU NISHIKAWA* AND NOBUYOSHI NAKAO

Department of Chemistry, Faculty of Science and Engineering,
Saga University, Saga 840, Japan

Received 5th November, 1984

Ultrasonic absorption, velocity, density and viscosity have been measured in aqueous solutions of 2-methylpentane-2,4-diol at 25 °C as a function of the concentration. A single relaxational absorption has been found whose cause has been attributed to the perturbation of an equilibrium associated with the solute–solvent interaction $AB \rightleftharpoons A + B$, where A is the solute and B the solvent. The forward and backward rate constants for this interaction have been evaluated from the concentration dependence of the relaxation frequency as $k_f = 1.1 \times 10^8 \text{ s}^{-1}$ and $k_b = 1.1 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The standard volume and enthalpy changes of the reaction have also been determined from the concentration dependence of the maximum excess absorption per wavelength as $\Delta V = 0.070 \text{ cm}^3 \text{ mol}^{-1}$ and $\Delta H = 1.7 \text{ kJ mol}^{-1}$. At high concentrations (above 5.5 mol dm^{-3}) another relaxation, which might be due to the inter-conversion of rotational isomers, has been also found in the same frequency range. This is confirmed from ultrasonic-absorption measurements in toluene mixtures.

In a series of investigations^{1, 2} on aqueous solution of diols by ultrasonic methods it has been reported that a relaxational excess absorption is observed in the MHz frequency range when the hydrophobicity of the solute is relatively large. Its cause has been attributed to the perturbation of an equilibrium associated with a solute–solvent interaction. In an aqueous solution of pentane-1,5-diol no absorption excess has been found because of the relatively small hydrophobicity. It is expected from the above experimental evidence that the relaxation process may occur when a methyl group is added to the compound and the hydrophobicity of the solute increases. In addition to this proposal, other relaxation process associated with the conformational change of the molecule, such as rotational isomerization, may also be expected to be present when the molecule has an antisymmetric structure. This has been the subject of many ultrasonic investigations.³

In this report we present ultrasonic-absorption and velocity results in aqueous solutions of 2-methylpentane-2,4-diol as a function of concentration together with those of density, thermal expansion and viscosity. Ultrasonic results for mixtures with toluene are also reported.

This kind of information is very important in understanding more complex reactions in biological systems because the preferential interaction of solvent components with proteins is well recognized.

EXPERIMENTAL

2-Methylpentane-2,4-diol was purchased from the Tokyo Kasei Co. Ltd and was distilled under reduced pressure. Toluene, from the Wako Chemical Co. Ltd, which was the purest grade obtainable, and doubly distilled water were used for preparing sample solutions. The desired concentrations were obtained by weight. The ultrasonic absorption coefficient, α , was measured by the improved pulse apparatus with a digital micrometer and a microcomputer. Details of the equipment have been described elsewhere.⁴ The sound velocity was measured by a sing-around meter operated at 1.92 MHz and interferometer at 2.5 MHz. Both errors are $< \pm 1 \text{ m s}^{-1}$. All ultrasonic measurements were carried out at 25 °C and the temperature was controlled within $\pm 0.005 \text{ °C}$. The solution density was measured using a pycnometer as functions of concentration and temperature (from 20 to 30 °C). The thermal expansivity, θ , was calculated from the relation

$$\theta = -(1/\rho)(d\rho/dT).$$

The viscosity coefficient was measured by an Ubbelohde viscometer at 25 °C.

RESULTS AND DISCUSSION

In aqueous solutions of 2-methylpentane-2,4-diol the value of α/f^2 , the absorption coefficient divided by the square of the sound-wave frequency, increases monotonically with concentration at a given frequency. This means that the so-called peak sound absorption concentration is not found within a limited frequency range, although it is a characteristic feature of sound behaviour in aqueous solutions of non-electrolytes. However, relaxational absorption has been observed in solutions at concentrations $> 1.59 \text{ mol dm}^{-3}$. Representative ultrasonic-absorption plots are shown in fig. 1, and all spectra observed are well described by the following equation for a single relaxation process:

$$\alpha/f^2 = A/[1 + (f/f_r)^2] + B \quad (1a)$$

or

$$\mu = (\alpha/f^2 - B)fv = Afv/[1 + (f/f_r)^2] \quad (1b)$$

where A is the amplitude of the excess absorption, B is the background absorption, f_r is the relaxation frequency, v is the sound velocity and μ is the absorption per unit wavelength. The ultrasonic parameters were determined by a non-linear least-mean-squares method using a microcomputer. The solid curves in the figure are those calculated using the determined values of A , f_r and B . These parameters are listed in table 1 as a function of the analytical concentration along with the density, sound velocity, thermal expansivity and viscosity coefficient. Fig. 2 and 3 show the concentration dependences of the relaxation frequency and of the amplitude of the excess absorption and the background absorption, respectively. When they are compared with those for aqueous solutions of butane-1,2-diol¹ and hexane-1,6-diol² a quite different dependence has been observed in the amplitude of the excess absorption: it tends to increase at concentrations above 6 mol dm^{-3} . Even in liquid 2-methylpentane-2,4-diol a clear single relaxation has been found, as seen in fig. 1. Meister *et al.*⁵ reported the existence of a relaxation process in this liquid at various temperatures, and their interpretation focussed on viscoelastic properties. There seem to exist two kinds of relaxational processes in high-concentration aqueous solutions.

In a first approximation we consider the relaxation processes independently. First, the relaxation observed in aqueous solutions below 5.5 mol dm^{-3} is analysed. The concentration dependences of the ultrasonic parameters in this concentration range

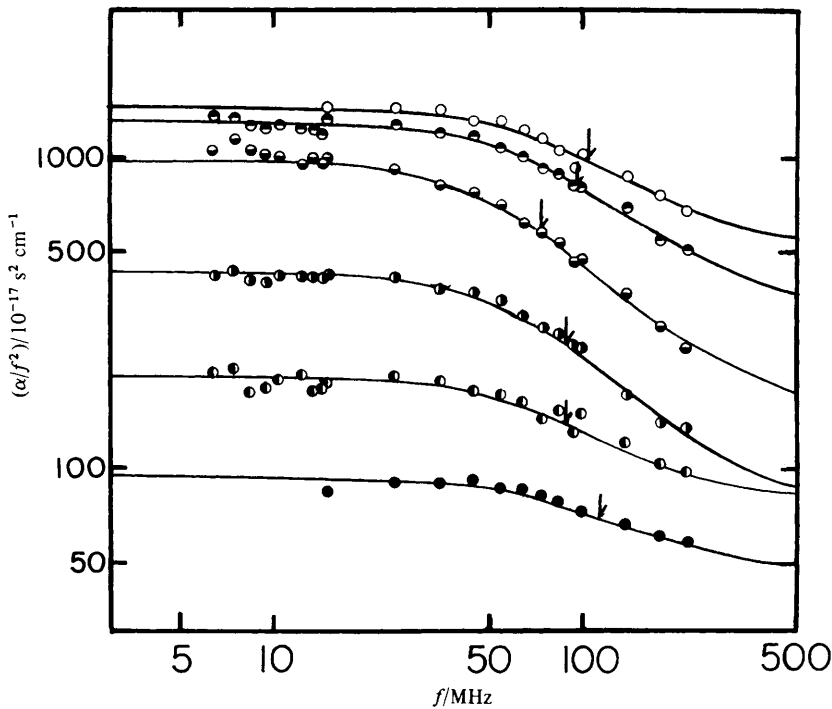


Fig. 1. Ultrasonic-absorption spectra for liquid 2-methylpentane-2,4-diol and its aqueous solutions at 25 °C. ○, pure liquid; ●, 6.05 mol dm⁻³; ◐, 3.07 mol dm⁻³; ◑, 2.34 mol dm⁻³; ◒, 1.94 mol dm⁻³ and ◓, 1.59 mol dm⁻³.

Table 1. Ultrasonic and thermodynamic parameters in an aqueous solution of 2-methylpentane-2,4-diol at 25 °C

C_e /mol dm ⁻³	f_r /MHz	A B		v /m s ⁻¹	ρ /g cm ⁻³	θ /10 ⁻⁴ K ⁻¹	η_s /cP
		/10 ⁻¹⁷ s ² cm ⁻¹					
1.59	115	48.5	46.9	1616	0.9978	4.4	2.07
1.94	90.5	118.7	80.3	1629	0.9977	4.8	2.57
2.34	89.1	350.6	79.0	1631	0.9975	5.3	3.01
2.48	77.9	431.1	124.4	1625	0.9963	5.5	3.44
3.07	74.6	810.3	167.6	1606	0.9943	6.1	4.56
3.52	76.7	949.5	203.3	1586	0.9915	6.5	5.58
4.11	69.0	1221	260.9	1550	0.9855	7.0	7.62
4.59	76.0	1190	270.6	1524	0.9802	7.4	9.50
5.03	78.5	1196	310.1	1497	0.9741	7.6	11.9
5.55	82.7	1061	330.8	1474	0.9681	7.9	14.6
6.05	96.9	969.2	340.1	1444	0.9596	8.1	18.1
7.04	116	920.7	367.1	1382	0.9427	8.3	26.9
7.81	103	943.6	521.9	1315	0.9233	8.5	32.8

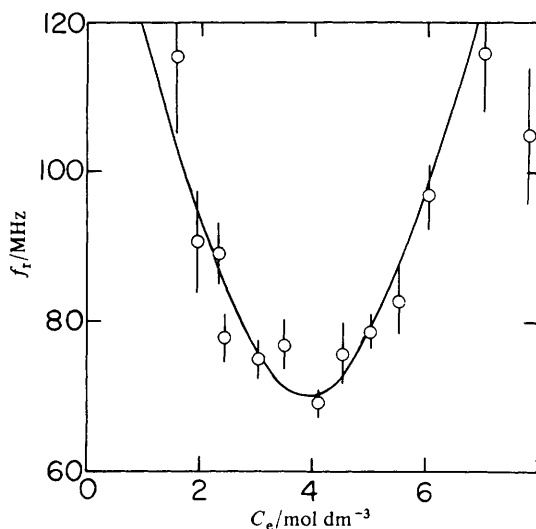


Fig. 2. Concentration dependence of the relaxation frequency for aqueous solutions of 2-methylpentane-2,4-diol.

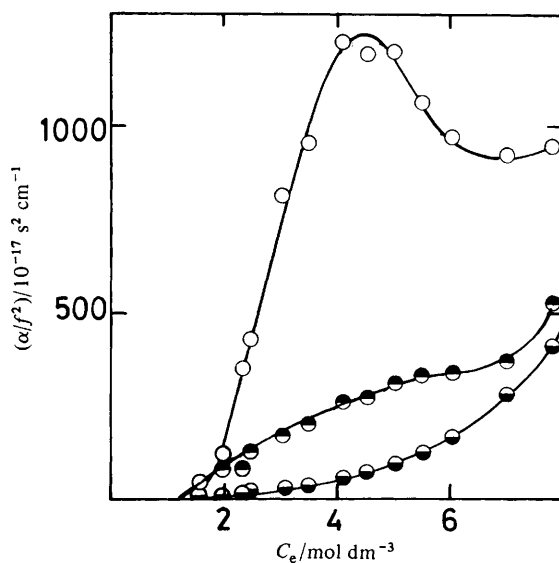


Fig. 3. Concentration dependences of the amplitude of the excess absorption (\circ), the background absorption (\bullet) and the classical absorption (\bullet) for aqueous solutions of 2-methylpentane-2,4-diol.

are similar to those observed in other diol solutions;^{1, 2} therefore we have analysed the excess absorption according to the model which relates to solute-solvent interactions. It is expressed as



Table 2. Rate and thermodynamic constants for aqueous solutions of diols

solute	k_f / 10^8 s^{-1}	k_b / $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	β	ref.
butane-1,2-diol	1.5	1.6×10^7	0.19	(1)
hexane-1,6-diol	1.6	1.7×10^8	0.11	(2)
2-methylpentane- 2,4-diol	1.1	1.1×10^8	0.141	this work

where k_f and k_b are the forward and backward rate constants, A is the solute, B is the solvent and AB is the solute-solvent complex. However, not all the solvent molecules may participate in the reaction. A good approximation is that the water molecules exist in two states, *i.e.* hydrogen-bonded and non-hydrogen-bonded. The latter should be expressed precisely as water capable of forming hydrogen bonds with the solute or with less structured water. Only these molecules may interact with the solute. The relationship between the relaxation frequency and the concentrations for the above reaction can be derived as follows:

$$2\pi f_r = k_b([A] + [B]) + k_f \\ = k_b[(C_d - \beta C_w + K_{12})^2 + 4\beta C_w K_{12}]^{1/2} \quad (2)$$

where C_d , C_w , β and K_{12} are the analytical concentrations of the solute and solvent, the molar fraction of the non-hydrogen-bonded water and the equilibrium constant (defined as $K_{12} = k_f/k_b$), respectively. The parameters k_b , β and K_{12} have been assumed to be independent of concentration and are determined so as to obtain a best fit to the experimental relaxation frequencies by a non-linear least-mean-squares method. In this determination the ultrasonic results in the concentration range $< 5.5 \text{ mol dm}^{-3}$ have been used because the experimental results at higher concentrations deviate from a smooth curve. The results are shown in table 2, along with those reported previously. The results for butane-1,2-diol and hexane-1,6-diol solutions are those at 20 °C. As the temperature dependences of the rate constants and the parameter β are small for the mechanism under consideration,⁶ they may be appropriate for comparison. The solid curve in fig. 1 is that calculated using these rate and thermodynamic constants and it fits the experimental data well. β is a good measure for estimating the structure of water in solution. In pure water it is estimated as > 0.24 .⁷ When a solute is added to liquid water the value of β decreases. This means that the solute acts as a water-structure promoter. The value of β for 2-methylpentane-2,4-diol falls between those of butane-1,2-diol and hexane-1,6-diol, showing that the hydrophobicity of 2-methylpentane-2,4-diol lies between those of the other two diols; this result is reasonable in terms of their structures.

Another parameter obtained from the ultrasonic-absorption and velocity results is the maximum excess absorption per wavelength, μ_m , which is related to the standard volume and enthalpy change of the reaction. It is expressed by the following equation for the reaction under consideration:

$$\mu_m = (\pi \rho v^2 \Gamma) (\Delta V - \Delta H \theta / \rho C_p)^2 / 2RT \quad (3)$$

$$\Gamma = ((1/[A]) + (1/[B]) + (1/[AB]) - \{1/([AB] + [B] + [AB])\})^{-1} \quad (4)$$

where ρ is the solution density, v is the sound velocity, ΔV is the standard volume change of the reaction, ΔH is the enthalpy change of the reaction, θ is the expansivity

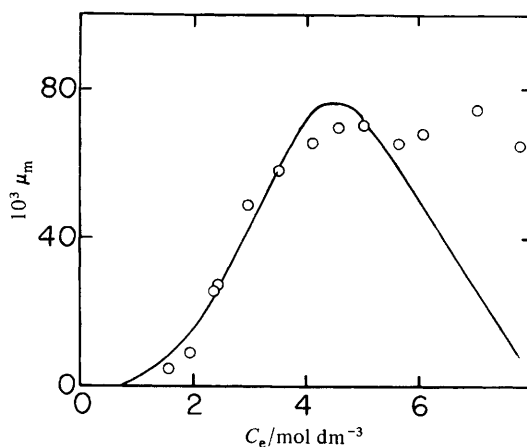


Fig. 4. Concentration dependence of the maximum excess absorption per unit wavelength for an aqueous solution of 2-methylpentane-2,4-diol.

of the solution and C_p is the specific heat at constant pressure. Using the procedure used in a study of aqueous solutions of butyl carbitol,⁸ the parameters ΔV and ΔH have been determined in the concentration range $< 5.5 \text{ mol dm}^{-3}$ to be $\Delta V = 0.070 \text{ cm}^3 \text{ mol}^{-1}$ and $\Delta H = 1.7 \text{ kJ mol}^{-1}$ from the intercept and slope of plots of $(2\mu_m RT / \pi \rho v^2 \Gamma)^{1/2}$ against $\theta / \rho C_p$. The solid curve in fig. 4 is calculated using these thermodynamic constants. At high concentrations it deviates remarkably from experiment.

A plausible explanation for the interaction between the solute and solvent may be hydrogen bonding, and the reaction site is thought to be the hydroxy group of the solute. The compound investigated here contains two hydroxy groups, so two reaction sites should be considered. We have considered¹ a reaction mechanism such as $\text{AB}_2 \rightleftharpoons \text{A} + 2\text{B}$. However, this does not explain the experimental results well. From the experimental evidence that the observed spectra can be well expressed by a single relaxational equation, we consider that the observed relaxation process may be attributed to a perturbation of the equilibrium associated with the 1:1 complex, although it is not certain which reaction site relates to the observed relaxation. The rate associated with the other hydroxy group might be on a different timescale than that used here. Another possible reason is the presence of an intramolecular hydrogen bond in the 2-methylpentane-2,4-diol molecule.

We next consider relaxation in the higher concentration range. In the present study and that of Meister *et al.* some relaxation is found in liquid 2-methylpentane-2,4-diol. In order to clarify the relaxation mechanism, absorption measurements in mixtures with toluene have been obtained as a function of the concentration of 2-methylpentane-2,4-diol, and a single relaxational absorption has been observed. The results of the ultrasonic parameters are shown in fig. 5. The relaxation frequency is almost independent of concentration and the amplitude of the excess absorption decreases very rapidly with increasing toluene content. At concentrations < 0.3 mole fraction the amplitude is too small to be observed. The cause of the relaxational absorption may be the perturbation of an equilibrium associated with a unimolecular reaction because of the concentration-independent relaxation frequency. A possible mechanism may be associated with rotational isomerization about the C(2)—C(3) bond. The

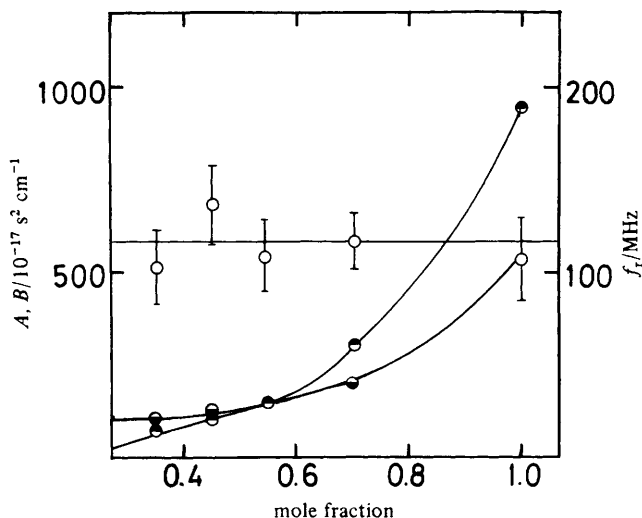


Fig. 5. Concentration dependences of the relaxation frequency (○), the amplitude of the excess absorption (●) and the background absorption (◐) for 2-methylpentane-2,4-diol + toluene mixtures at 25 °C.

concentration dependences of the ultrasonic parameters associated with rotational isomerization are different from those observed in the aqueous solutions.

From the above two interpretations it may be expected that in aqueous solution above 5.5 mol dm^{-3} the two relaxations may be superimposed. However, it is not possible to distinguish the two relaxations in the ultrasonic spectra. If the relaxation frequencies for the two processes are close to each other the ultrasonic spectra look like a single relaxation from the equation for ultrasonic absorption [eqn (1a) or (1b)]. As may be seen from table 1, on increasing the concentration in aqueous solution the relaxation frequency tends to the value which is observed in toluene mixtures, *i.e.* *ca.* 103 MHz. In order to determine if these two processes exist in the higher concentration range, we have estimated the additivity of the two amplitudes of the excess absorptions at 6.05 and 7.04 mol dm^{-3} , corresponding to 0.308 and 0.535 mole fraction. At the same mole fractions in the toluene mixtures the amplitudes of the excess absorption are *ca.* 50×10^{-17} and *ca.* $130 \times 10^{-17} \text{ s}^2 \text{ cm}^{-1}$, respectively. On the other hand, the amplitude of the excess absorption due to the interaction may be estimated from the concentration dependences of the maximum excess absorption per unit wavelength and the relaxation frequency by extrapolating to higher concentrations. Their values are $710 \times 10^{-17} \text{ s}^2 \text{ cm}^{-1}$ at 0.308 mole fraction and $310 \times 10^{-17} \text{ s}^2 \text{ cm}^{-1}$ at 0.535 mole fraction. When these two estimated values are added at each concentration, they may come close to the values observed in aqueous solutions, although the latter are still higher. This means that the two relaxations exist in the high concentration range in aqueous solutions even if the absorption spectrum appears to be a single relaxation. In order to analyse the relaxation mechanisms quantitatively the coupled reaction processes should be taken into account. However, because of the absence of sufficient information concerning the reliability of equilibrium (I) in such a high concentration range, it is only shown that two such relaxations might exist in the high concentration range.

Finally, the classical absorption due to the solution viscosity is estimated by the Stokes equation:

$$(\alpha/f^2)_{\text{classical}} = 8\pi^2 \eta_s / (3\rho v^3) \quad (5)$$

where η_s is the shear-viscosity coefficient. The calculated classical absorption is also shown in fig. 3. It is smaller than the background absorption and the results indicate that other relaxation processes may exist at higher frequencies (above 300 MHz) in aqueous solution. Possible causes may be (i) relaxation associated with the solute-solute interaction *via* hydrogen-bonding and (ii) the reaction associated with formation of another complex between the solute and solvent.

¹ S. Nishikawa and M. Mashima, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 1249.

² S. Nishikawa, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 2651.

³ M. Blandamer, *Introduction to Chemical Ultrasonics* (Academic Press, London, 1983).

⁴ S. Nishikawa and K. Kotegawa, *J. Phys. Chem.*, in press.

⁵ R. Meister, C. J. Marhoeffer, R. Sciamanda, L. Cotter and T. Litovitz, *J. Appl. Phys.*, 1960, **31**, 584.

⁶ S. Nishikawa and T. Yamaguchi, *Bull. Chem. Soc. Jpn*, 1983, **56**, 1585.

⁷ C. M. Davis Jr and J. Jarzynski, *Adv. Mol. Relaxation Processes*, 1968, **1**, 155.

⁸ S. Nishikawa and M. Shibata, *Bull. Chem. Soc. Jpn*, 1984, **57**, 2357.

(PAPER 4/1883)