

## Ultrasonic absorption studies in solutions of ortho and para hydroxy benzoic acid in dioxan

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**Abstract.** Ultrasonic absorption was measured in ortho and para hydroxy benzoic acid (OHBA and PHBA) in dioxan at room temperature for various solute concentrations. The variation of ultrasonic absorption in both solutions with the solute concentration showed two maxima, one at lower solute concentration and the other at higher solute concentration. The first maximum is explained as due to formation of hydrogen bonds between the O–H groups of OHBA and PHBA molecules and the oxygen of dioxan molecules and the second maximum as due to the COOH group of the OHBA/PHBA molecules and oxygen of dioxan molecules. In both systems the measured absorption is explained on the basis of Hall's two-state model.

**Keywords.** Ultrasonic absorption; hydrogen bond; volume viscosity; relaxation time.

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### 1. Introduction

Earlier studies carried out by Anbanandan *et al* (1976) in solutions of *o*-hydroxy benzoic acid (OHBA) and *p*-hydroxy benzoic acid (PHBA) in dioxan indicated the possibility of hydrogen bonding in these solutions. Ultrasonic velocity was studied by Sosamma *et al* (1988) in the same solutions at various solute concentrations ranging from 0·01–0·10 mole fraction at various temperatures. The variation of ultrasonic velocity in both solutions with solute concentration showed two velocity maxima, one at lower solute concentration and another at higher solute concentration. The maxima were explained as due to the formation of hydrogen bonds between the solute and solvent molecules. To obtain additional information on the molecular interactions in these systems we have carried out ultrasonic absorption studies in OHBA and PHBA solutions in dioxan and the results are reported in this paper.

### 2. Theoretical aspects

The classical absorption may be obtained from Stoke's–Kirchoff's equation as

$$(\alpha/f^2)_{cl} = \frac{8\pi^2\eta_s}{3\rho C^3} + \frac{2\pi^2 K(\gamma-1)}{\rho C^3 \gamma C_v}, \quad (1)$$

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where  $\rho$  is the density of the medium,  $C$  the sound velocity in the medium,  $\gamma$  the ratio of two specific heats,  $C_v$  the specific heat at constant volume,  $K$  the coefficient of thermal conductivity and  $\eta_s$  is the coefficient of shear viscosity. The contribution due to the second term in (1) is negligible for liquids of low thermal conductivity.

The measured ultrasonic absorption  $(\alpha/f^2)_{\text{obs}}$  is considered as the sum of classical absorption  $(\alpha/f^2)_{\text{cl}}$  and structural absorption  $(\alpha/f^2)_{\text{st}}$ . The excess absorption is defined as

$$(\alpha/f^2)_{\text{ex}} = (\alpha/f^2)_{\text{obs}} - (\alpha/f^2)_{\text{cl}}. \quad (2)$$

The excess absorption measured in water was explained using Hall's two-state model (Narayana *et al* 1975). The  $(\alpha/f^2)_{\text{ex}}$  value was theoretically calculated to be:

$$(\alpha/f^2)_{\text{ex}} = 2\pi^2 \rho C \beta_r \tau, \quad (3)$$

where  $\tau$  is the relaxation time,  $\beta_r$ , the relaxing part of the compressibility,  $C$  the velocity of sound and  $\rho$  the density of the liquid.

The structural relaxation time  $\tau$  was related to the molar volume ( $V$ ) and the free energy difference ( $\Delta F$ ) as follows

$$\tau = \frac{V \eta_s}{R_g T \left[ 1 + \exp \frac{\Delta F}{K_B T} \right]}, \quad (4)$$

where  $\eta_s$  is the shear viscosity,  $T$  the temperature,  $R_g$  the gas constant and  $K_B$  the Boltzmann constant.

The volume viscosity may be estimated from the relation

$$\eta_v = 4\eta_s/3 \left[ \frac{(\alpha/f^2)_{\text{obs}} - (\alpha/f^2)_{\text{cl}}}{(\alpha/f^2)_{\text{cl}}} \right], \quad (5)$$

where  $\eta_s$  is the shear viscosity.

The relaxing part of compressibility ( $\beta_s$ ) is related to  $\eta_v$  and  $\tau$  by an expression developed by Litovitz and Davis (1965)

$$\eta_v = \beta_r \tau / \beta_0^2 \quad (6)$$

where  $\beta_0$  is the static compressibility. For viscoelastic liquids, the relaxation time may be related to the static compressibility ( $\beta_0$ ) and the two viscosities  $\eta_0$  and  $\eta_s$

$$\tau = \beta_0 \left[ \eta_v + \frac{4}{3} \eta_s \right] \quad (7)$$

### 3. Materials and methods

Ultrasonic absorption in OHBA and PHBA in dioxan was measured at a frequency of 10 MHz using a pulse echo interferometer at a temperature of  $30 \pm 0.1^\circ\text{C}$ . A cylindrical cell fabricated by the author (Balasubramanian 1988) in this laboratory was used for this purpose. The accuracy in the measurement of velocity is 0.1% and absorption is 0.03% respectively. The absorptions are represented as  $\text{Npm}^{-1} \text{s}^2$ . The

**Table 1.** Ultrasonic absorption and related parameters for the solution of *o*-hydroxy benzoic acid in dioxan.

X M.F	C ms <sup>-1</sup>	$\rho \times 10^{-3}$ kg.m <sup>-3</sup>	$\beta_s \times 10^{10}$ m <sup>2</sup> N <sup>-1</sup>	$(\alpha/f^2)_{\text{obs}}$ $(\alpha/f^2)_{\text{cl}}$ $(\alpha/f^2)_{\text{ex}}$			$\eta_s$ Poise	$\eta_v$ Poise	$\tau \times 10^{11}$ s	$\Delta F$ k <sub>cal</sub> /M	$\beta_r \times 10^{10}$ m <sup>2</sup> N <sup>-1</sup>
				$\times 10^{15}$ Npm <sup>-1</sup> s <sup>2</sup>							
0.01	1326.1	1.027	5.537	175.92	12.62	163.30	0.01148	0.19815	1.182	1.527	5.140
0.02	1323.7	1.029	5.547	175.92	13.14	162.78	0.01192	0.19679	1.180	1.633	5.131
0.03	1322.0	1.032	5.546	175.92	13.77	162.15	0.01247	0.19581	1.178	1.106	5.113
0.04	1327.9	1.033	5.490	230.89	13.64	217.25	0.01253	0.19966	1.188	1.107	5.065
0.05	1335.6	1.039	5.395	282.19	13.94	268.25	0.01311	0.33645	1.909	0.546	5.130
0.06	1334.7	1.042	5.387	250.46	14.27	236.19	0.01344	0.29645	1.694	1.007	5.078
0.07	1325.3	1.045	5.449	230.89	16.35	214.54	0.01511	0.26432	1.550	1.526	5.063
0.08	1342.2	1.051	5.284	300.71	17.32	283.39	0.01679	0.36611	2.053	1.102	4.979
0.09	1328.4	1.055	5.374	255.74	20.90	234.84	0.01963	0.29409	1.713	1.990	4.958
0.10	1330.2	1.058	5.342	249.58	25.11	224.47	0.02376	0.28315	1.682	2.489	4.804

For explanation of symbols, see text

**Table 2.** Ultrasonic absorption and related parameters for the solution of *p*-hydroxy benzoic acid in dioxan.

X M.F	C ms <sup>-1</sup>	$\rho \times 10^{-3}$ kg.m <sup>-3</sup>	$\beta_s \times 10^{10}$ m <sup>2</sup> N <sup>-1</sup>	$(\alpha/f^2)_{\text{obs}}$ $(\alpha/f^2)_{\text{cl}}$ $(\alpha/f^2)_{\text{ex}}$			$\eta_s$ Poise	$\eta_v$ Poise	$\tau \times 10^{11}$ s	$\Delta F$ k <sub>cal</sub> /M	$\beta_r \times 10^{10}$ m <sup>2</sup> N <sup>-1</sup>
				$\times 10^{15}$ Npm <sup>-1</sup> s <sup>2</sup>							
0.01	1346.7	1.037	5.317	219.02	12.66	206.36	0.01219	0.26479	1.494	1.049	5.011
0.02	1345.7	1.039	5.312	220.56	13.23	207.33	0.01274	0.26612	1.509	1.068	4.973
0.03	1348.1	1.042	5.280	225.28	14.57	210.71	0.01414	0.27253	1.539	1.396	4.922
0.04	1359.9	1.044	5.179	229.87	15.22	214.65	0.01518	0.28551	1.588	1.514	4.823
0.05	1354.4	1.045	5.214	216.18	17.53	198.65	0.01729	0.26143	1.483	2.015	4.792
0.06	1366.3	1.047	5.116	219.94	18.28	201.66	0.01855	0.27283	1.522	2.128	4.692
0.07	1366.9	1.052	5.087	218.46	20.33	198.13	0.02076	0.26970	1.513	2.403	4.613
0.08	1386.8	1.056	4.924	230.98	21.81	209.17	0.02334	0.29847	1.623	2.523	4.458
0.09	1377.1	1.060	4.974	223.37	24.38	198.99	0.02564	0.27908	1.558	2.829	4.433
0.10	1380.1	1.065	4.929	224.28	25.39	198.89	0.02701	0.28209	1.528	2.935	4.372

For explanation of symbols, see text

viscosities of the solutions were determined using ostwalds viscometer with an accuracy of 0.04% in a constant temperature bath at 30+0.1°C. The densities were measured using a pycnometer with an accuracy of 0.005%. All the measured and calculated parameters are shown in tables 1 and 2. The variation of the parameters with concentration is shown in figures 1-4.

## 4. Results

### 4.1 OHBA in dioxan

It can be seen from figure 1A that in solutions of OHBA in dioxan, the ultrasonic absorption initially increases with increase in solute concentration, attains a maximum value at solute concentration of 0.05 mole fraction (cm<sub>1</sub>), then decreases with further increase of solute concentration attaining a second maximum at a solute concentration of 0.08 mole fraction (cm<sub>2</sub>). The excess absorption calculated for these solutions also

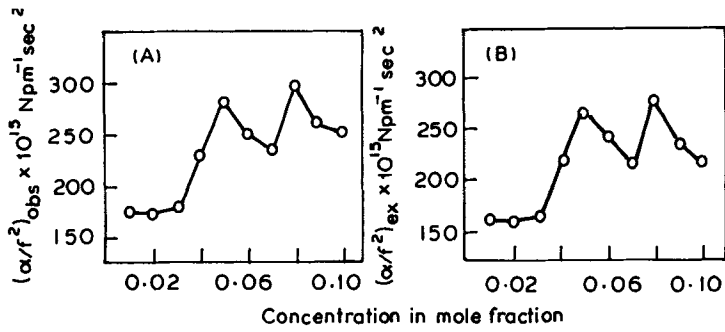


Figure 1.

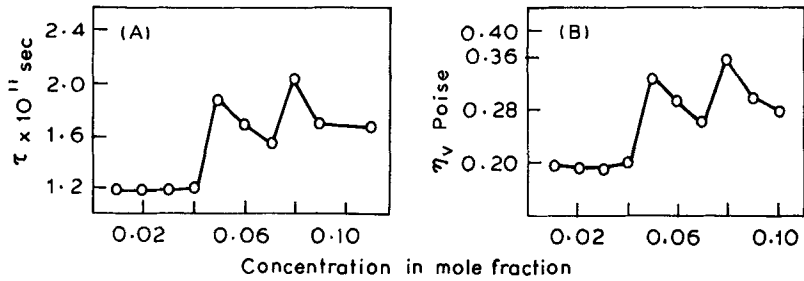


Figure 2.

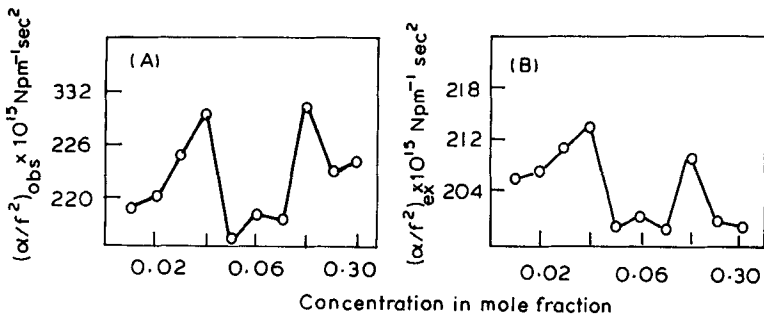


Figure 3.

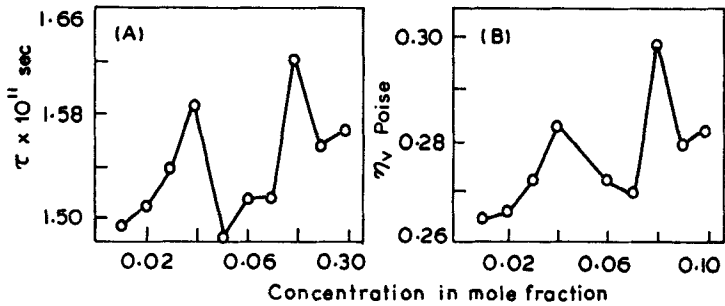


Figure 4.

shows two maxima at 0.05 mf ( $cm_1$ ) and at 0.08 mf ( $cm_2$ ) with increase in concentration of OHBA in dioxan (figure 1B).

#### 4.2 PHBA in dioxan

The variation of ultrasonic absorption with solute concentration in the solutions of PHBA in dioxan is shown in figure 3A and it can be seen that the behaviour is similar to the one observed in the solution of OHBA in dioxan, with the exception that the absorption maxima occur at different solute concentrations. The first maximum ( $cm_3$ ) occurs at 0.04 mf and the second ( $cm_4$ ) at 0.08 mf of solute concentration. The excess absorption calculated for these solutions also shows two maxima at 0.04 mf and at 0.08 mf with increase in concentration of PHBA in dioxan (figure 3B).

### 5. Discussion

The ultrasonic absorption in both the systems initially increases with increase in solute concentration and reaches a maximum value and then decreases (figures 1A and 2A). The mole fraction of the solute which corresponds to the maximum absorption may be called the critical concentration. The maximum absorption at critical concentration indicates that the solution is highly structured. The present study confirms the two maxima observed in the velocity studies in the same systems by Sosamma *et al* (1988). The first maximum is explained as due to the formation of hydrogen bond between the O-H groups of OHBA/PHBA molecules and the oxygen atom of the dioxan molecules. A similar explanation may also hold good for the first maximum observed in the absorption vs concentration curves. The formation of hydrogen bonds is likely to make the solution highly structured and such a solution generally absorbs more ultrasound energy (Srinivasa Manja and Srinivasa Rao 1986). The second maximum is explained as due to the formation of hydrogen bond between COOH monomers of OHBA/PHBA molecules and oxygen of the dioxan molecules. The same explanation may also hold good for the second maxima observed in the present curves.

In both the systems of OHBA and PHBA in dioxan, the experimentally observed ultrasonic absorptions are higher than the classical absorption for all concentrations (tables 1 and 2). The values of  $(\alpha/f^2)_{ex}$  are found to be 4–6 times the value of classical absorption. This indicates that the absorption of ultrasonic waves in the solution of OHBA in dioxan is not only due to shear viscosity but also due to some other effects. Probably the major contribution comes from structural effects.

The decrease in the absorption above 0.05 mole fraction in both systems can be explained as follows. Formation of strong hydrogen bonds generally increases the inter proton distance between adjacent hydrogen bonds, thereby weakening the intermolecular forces of the bulk solutions (Lippincott and Srinivasa Rao 1964). This may be the reason for the decrease of ultrasonic absorption above 0.05 mole fraction of solute concentration in both the systems studied.

To obtain further confirmation that the ultrasonic absorption maximum at  $cm_1$  is due to the phenolic hydroxyl groups, the ultrasonic absorption was experimentally measured in solutions of benzoic acid in dioxan in the solute concentration range 0.01 to 0.1 mole fraction. In this solution only one maximum is observed at 0.07 mole

fraction of solute concentration. The absence of velocity maximum at the lower solute concentration is due to the fact that benzoic acid molecules do not possess any phenolic hydroxyl group. This confirms that the absorption maximum observed in both solutions of OHBA/PHBA in dioxan ( $cm_1$ ) is due to the formation of hydrogen bonds between phenolic O–H groups of the above acid and the oxygen of dioxan molecules.

The decrease in ultrasonic absorption above the solute concentration of 0.08 mole fraction in both systems may be interpreted as due to weakening of hydrogen bonds in solutions formed between monomers and dioxan molecules. It is probable that at concentration  $cm_2$  all the molecules are broken into monomers and hydrogen bonds are formed. It is also likely that the solute molecules above the critical concentration ( $cm_2$ ) may stay in dimer form. These dimers are fairly large in size compared to dioxan molecules and have to be accommodated in the liquid and this may cause some structural changes resulting in weakening of intermolecular forces. This is probably the reason for the decrease in ultrasonic absorption observed above the concentration  $cm_2$  in both the system studied.

The concentration at which first maximum was observed is at 0.05 mole fraction for OHBA and at 0.04 mole fraction for PHBA at 307K. This difference in value of concentration may be due to the fact that the phenolic group in PHBA is not chelated and hence it is more free to form hydrogen bonds than the phenolic group of *o*-hydroxy benzoic acid. Hence the hydrogen bonds are likely to be formed in solutions of PHBA in dioxan at a lower solute concentration as compared to OHBA in dioxan.

The two state model of Hall was applied by Srinivasa Manja *et al* (1985) to the solutions of certain carboxylic acids in dioxan. The two states in these solutions are: (1) dimer carboxylic acid molecules and (2) carboxylic acid monomers hydrogen bonded to dioxan molecules.

There will be an equilibrium between dimers and monomers hydrogen bonded to dioxan molecules at a given temperature. A compression during the wave propagation will produce a change in the number of molecules in both the states caused by the breaking of intermolecular hydrogen bonds. This structural change lags behind the acoustical pressure which is the cause of the absorption. The model was applied to methanol and ethanol at elevated pressures to explain the excess absorption (Narayana *et al* 1975).

The two-state model of Hall was applied to the present system at the first critical concentration ( $cm_1$ ) where the phenolic O–H of hydroxy benzoic acid forms hydrogen bonds with dioxan. The two states are free OHBA molecules and hydrogen bonded OHBA – dioxan complexes through the O–H group.

The values of  $\beta_r$  and  $\tau$  are calculated using the theory of structural relaxation developed by Hall (1948) and these are shown in tables 1 and 2. The calculated values appear to be reasonable and this indicates that Hall's two-state model may also be applied for dilute solutions.

The two-state model can also be applied for the maxima obtained at higher concentration. The second maximum ( $cm_2$ ) at 0.08 mole fraction of solute concentration of OHBA is due to the formation of hydrogen bonds between carboxylic acid group (COOH) and the free oxygen atoms of the dioxan molecules. Since the situation is similar to the two state model of Hall which was proposed to explain the excess absorption in liquid water, the same model is extended here also to explain the excess absorption due to the formation of hydrogen bonds between the carboxylic acid of

*o*-hydroxy benzoic acid and dioxan at higher concentration. The two states assumed for the mixture at higher concentration are the dimeric state of the carboxylic acid (COOH) of the ortho hydroxy benzoic acid and the hydrogen bonded state between the monomeric carboxylic acid group with dioxan.

It is likely that the two states described for  $cm_1$  may also be present at this concentration, but their number may not be significant as the hydrogen bonds between monomeric carboxylic acid and dioxan are stronger as revealed in the velocity studies (Nambinarayanan 1981; Srinivasa Manja and Srinivasa Rao 1986; Sosamma *et al* 1988).

The variation of ultrasonic absorption with concentration for solutions of PHBA in dioxan and the other calculated parameters are shown in the table 2. It can be seen from figure 3A that in the solutions of PHBA in dioxan, the absorption co-efficient attains maximum at 0.04 and at 0.08 mole fraction. The two-state model of Hall was also applied to these cases.

Tables 1 and 2 show that in both cases of OHBA and PHBA in dioxan, the relaxation times increase with concentration, show a maximum at the critical concentration and then decrease. The same trend is observed in the second critical concentration (0.08) for *o*-hydroxy and *p*-hydroxy benzoic acid.

Tables 1 and 2 also show that the free energy difference for the two states are 0.56 kcal/mol at 0.05 mole fraction, 1.10 kcal/mol for 0.08 mole fraction of the OHBA in dioxan and 1.51 kcal/mol at 0.04 mole fraction at 2.52 kcal/mol at 0.08 mole fraction of PHBA in dioxan. The increase of free energy indicates that the hydrogen bonds formed at the higher concentrations ( $cm_1$ ) of *o*- and *p*-hydroxy benzoic acids are stronger (Glasstone 1956).

Finally it may be mentioned that the present absorption studies generally support the results obtained by Sosamma *et al* (1988) and indicate the usefulness of ultrasonic studies in the study of molecular interaction in liquid mixture. It is also possible to study chelation in these molecules by ultrasonic methods.

## References

- Anbanandan D, Krishnan B and Srinivasa Rao A 1976 *Indian J. Chem.* **14** 277  
Balasubramanian V 1988 *Molecular acoustical studies in some aqueous and non-aqueous solutions*, Ph.D thesis, University of Madras, Madras  
Glasstone 1956 *Text book of physical chemistry* (London: Macmillan)  
Hall L 1948 *Phys. Rev.* **73** 775  
Lippincott E R and Srinivasa Rao A 1964 *J. Chem. Phys.* **41** 3006  
Litovitz T A and Davis C M 1965 in *Physical acoustics, Principles and methods* (ed.) W P Mason (New York: Academic Press) Vol. 2  
Nambinarayanan T K 1981 *Ultrasonic studies on the nature of molecular interaction in some solution*, Ph.D thesis, University of Madras, Madras  
Narayana K L, Mallikarjuna Swamy K, Sriramamurthy J and Sitaramaswamy P 1975 *Nuovo Cimento*, **B25** 199  
Sosamma G, Nambinarayanan T K and Srinivasa Rao A 1988 *Indian J. Phys.* **B62** 31  
Srinivasa Manja K 1985 *Ultrasonic studies on the nature of molecular interactions in some aqueous, non-aqueous solutions and liquid crystals*. Ph.D. thesis, Madras University, Madras  
Srinivasa Manja K and Srinivasa Rao A 1985 *Pramāna – J. Phys.* **26** 459