

Ultrasonic absorption studies in some solutions of carboxylic-acids in dioxan

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Abstract. Ultrasonic absorption studies are carried out in carboxylic acid-dioxan mixtures for various concentrations at $30 \pm 0.1^\circ\text{C}$. The measured absorption is much higher than the classical absorption. The excess absorption initially increases with increase of carboxylic acid concentration, attains a maximum and then decreases with further increase in concentration. The related parameters such as volume viscosity, relaxation time and free energy difference between the two states (ΔF) have also been calculated. The results can be explained satisfactorily using Hall's two-state model.

Keywords. Ultrasonic absorption; hydrogen bond; dimer acids; volume viscosity.

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1. Introduction

Ultrasonic absorption studies in liquids provide an insight into the nature of molecular interactions in them (Blandermer 1973). In associated liquids the measured ultrasonic absorption is generally higher than the classical absorption and it is explained on Hall's two state model (Hall 1948; Narayana *et al* 1975). Ultrasonic velocity studies carried out in this laboratory in solutions of oxalic acid dihydrate, benzoic acid and succinic acid in dioxan (Nambinarayanan 1981) indicated that the solute molecules are broken into monomer form thus forming hydrogen bonds with the free oxygen atom of the solvent dioxan molecule. The association through hydrogen bonding increases with increase in the concentration of the solute reaching a maximum at a particular concentration (C_m). The association decreases with further increase in the concentration of the solute. However, to understand the molecular dynamics completely, ultrasonic absorption studies were carried out for these solutions. Parameters such as volume viscosity (η_v), ultrasonic relaxation time (τ) and free energy difference (ΔF) between the states were determined to obtain information on the molecular dynamics.

2. Theoretical aspects

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

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

where ρ is the density of the medium, C is the sound velocity in the medium, γ the ratio of two specific heats, C_v the specific heat at constant volume, k the coefficient of thermal conductivity and η_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 in the following way (Narayana *et al* 1975). The $(\alpha/f^2)_{\text{ex}}$ has been equated to

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

where τ is the relaxation time, β_r , the relaxing part of the compressibility, C the velocity of sound and ρ the density of the liquid.

The structural relaxation time τ was related to the molar volume (V) and the free energy difference (ΔF) as follows

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

where η_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 η_s is the shear viscosity.

The relaxing part of the compressibility (β_r) is related to η_v and τ by an expression developed by Litovitz and Davis (1965) as

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

where β_0 is the static compressibility. For viscoelastic liquids the relaxation time may be related to the static compressibility (β_0) and the two viscosities η_v and η_s as follows

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

3. Materials and methods

Ultrasonic absorption in oxalic acid dihydrate, benzoic acid and succinic acid in dioxan was measured at a frequency 10 MHz using a pulse echo interferometer (Systems Dimensions, Bangalore) at a temperature of $30 \pm 0.1^\circ\text{C}$. A cylindrical liquid cell fabricated in this laboratory was used for this purpose. It is a hollow cylinder of brass (length 1 cm, diameter 1.5 cm). At one end of the cell, a quartz crystal of 10 MHz fundamental frequency is rigidly fixed by a suitable adhesive. At the other end, a metal reflector with adjustable screws is provided to make it parallel to the transducer. An

annular rubber washer is also used along with the reflector to prevent leakage of the liquid from the cell.

The RF pulses of 10 MHz and 20 μ_s duration are transmitted and received by the single crystal method (Blitz 1963). The received echoes are displayed on the dual beam oscilloscope and their heights measured. The echo heights are fitted into an exponential curve of the type, $A \exp(-\alpha x)$ and the absorption coefficient α are calculated. The absorptions are represented as $(\alpha/f^2)_{\text{obs}}$ in Nepers $\text{cm}^{-1} \text{sec}^2$. The viscosities of the solutions are determined using Ostwalds viscometer in a constant temperature bath at $30 \pm 0.1^\circ\text{C}$. All the measured and calculated parameters are shown in tables 1-3. The variation of the parameters with concentration is shown in figures 1-2.

4. Results

Figure 1a shows that the measured ultrasonic absorption for the oxalic acid dihydrate, benzoic acid and succinic acid increases with increase in the concentration of the solute, reaches a maximum (the concentration at which the absorption maximum occurs is

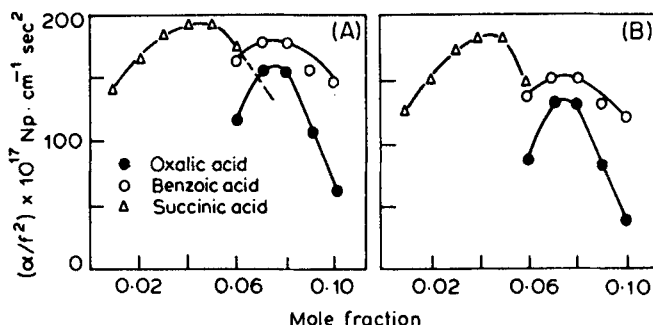


Figure 1. Absorption vs concentration of carboxylic acids in dioxan. A. Ultrasonic. B. Excess.

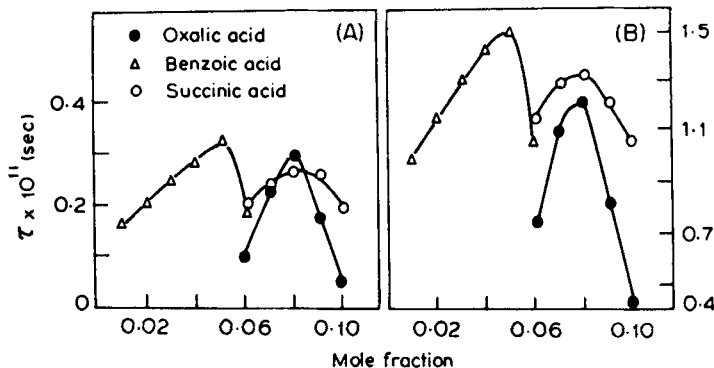


Figure 2. Volume viscosity and relaxation time vs concentration of carboxylic acids in dioxan. A. Volume viscosity. B. Relaxation time.

Table 1. Ultrasonic absorption and related parameters for the solutions of oxalic acid in dioxan.

M.F. X	m s ⁻¹ C	g cm ⁻³ ρ	dyne.cm ² β _s	× 10 ¹⁷ Np.cm ⁻¹ .sec ²		poise η _s	sec τ × 10 ¹¹	k _{cal} /M ΔF	cm ² .dyne ⁻¹ β _r	× 10 ¹⁷ Np.cm ⁻¹ .sec ² (α/f ²) _{ex} cal
				(α/f ²) _{obs}	(α/f ²) _{cl}					
0-06	1269	1-136	5-466	119-08	28-46	88-62	0-1016	1-327	4-138	86-38
0-07	1428	1-168	4-198	156-00	21-62	134-38	0-2262	1-139	3-607	131-22
0-08	1534	1-189	3-570	156-00	19-91	136-09	0-2987	1-189	3-115	137-14
0-09	1508	1-194	3-682	108-00	23-22	84-78	0-03576	1-151	2-891	83-84
0-10	1408	1-205	4-187	59-70	29-18	30-62	0-03728	1-950	2-144	30-59

Table 2. Ultrasonic absorption and related parameters for the solutions of benzoic acid in dioxan.

M.F. X	m s ⁻¹ C	g cm ⁻³ ρ	dyne ⁻¹ .cm ² β _s	× 10 ¹⁷ Np.cm ⁻¹ .sec ²		poise η _s	sec τ × 10 ¹¹	k _{cal} /M ΔF	cm ² .dyne β _r × 10 ¹¹	× 10 ¹⁷ Np.cm ⁻¹ .sec ² (α/f ²) _{ex} cal
				(α/f ²) _{obs}	(α/f ²) _{cl}					
0-06	1380	1-041	5-044	164-04	25-00	139-04	0-1982	1-147	4-154	135-00
0-07	1440	1-044	4-619	177-40	23-22	154-17	0-2435	1-294	4-013	154-00
0-08	1506	1-046	4-215	175-20	21-79	153-41	0-2775	1-337	3-692	153-37
0-09	1540	1-050	4-016	155-90	20-41	135-43	0-03002	1-215	3-466	134-41
0-10	1420	1-055	4-700	148-70	20-89	123-81	0-03125	1-069	3-582	113-23

Table 3. Ultrasonic absorption and related parameters for the solutions of succinic acid in dioxan.

M.F. X	m s ⁻¹ C	g cm ⁻³ ρ	dyne.cm ² β _s × 10 ¹¹	× 10 ¹⁷ Np.cm ⁻¹ .sec ²		poise η _s	sec τ × 10 ¹¹	k _{cal} /M ΔF	cm ² .dyne ⁻¹ β _r × 10 ¹¹	× 10 ¹⁷ Np.cm ⁻¹ .sec ² (α/f ²) _{ex} cal
				(α/f ²) _{obs}	(α/f ²) _{cl}					
0-01	1344	1-047	5-287	142-20	15-67	126-52	0-01514	0-841	4-704	126-48
0-02	1360	1-048	5-158	166-86	15-57	151-29	0-01560	0-729	4-677	151-28
0-03	1396	1-054	4-868	184-61	19-17	165-44	0-02089	0-853	4-363	165-47
0-04	1436	1-055	4-596	195-00	18-06	176-94	0-02144	0-810	4-171	176-87
0-05	1528	1-069	4-006	195-00	19-15	175-85	0-02776	0-954	3-614	175-84
0-06	1424	1-075	4-587	172-90	23-10	149-80	0-02725	1-192	3-865	123-65

labelled, hereafter referred to as C_m) and then decreases further with increase in concentration. The maximum in the ultrasonic absorption is found to be at 0.075 mole fraction for oxalic acid, benzoic acid and at 0.045 mole fraction for succinic acid. In figure 1b the excess absorption is found to vary similarly. The variation of volume viscosity and relaxation time is similar and show a maximum at the same concentration as mentioned above. The free energy difference between the two states was also estimated using (3) and found to be 1.45 kcal/mol and 1.33 kcal/mol for succinic acid and benzoic acid respectively at the critical concentration.

5. Discussion

Tables 1, 2, 3 reveal that the $(\alpha/f^2)_{\text{obs}}$ is about 4–5 times greater than the $(\alpha/f^2)_{\text{cl}}$. This is a characteristic feature of the mixtures where there is a strong association due to molecular interaction (Blandermer 1973). The variation of $(\alpha/f^2)_{\text{cl}}$ is comparatively much smaller than the variation of $(\alpha/f^2)_{\text{obs}}$. This suggests that the excess absorption may be mainly due to intermolecular association.

The carboxylic acid molecules dissociate in dioxan and form hydrogen bonds with the dioxan. Therefore the two states may be assumed for the mixture as (1) dimeric state of carboxylic acid (D states), (2) the hydrogen bonded state of the monomeric carboxylic acid with dioxan molecule (M states). A compression during wave propagation will produce a change in the number of molecules in both the states, caused by the breaking of intermolecular bonds. Therefore it is not unreasonable to apply Hall's two-state model to explain the excess absorption. The excess absorption calculated from (2) and (1) agrees very well within 7% of the experimental value. This shows that the application of two-state model for this system is reasonable.

The value of η_v estimated using (4) also increases with increase in the concentrations of oxalic acid, benzoic acid and succinic acid upto C_m and decreases with further increase in the concentration of the carboxylic acids. It is reasonable to assume that as the solute concentration is increased, M states increase upto the critical concentration and then D states may be preferred over M states.

It is possible that a dynamic equilibrium may exist between the M and D states which may increase the cohesive forces in these dioxan rich mixtures. This may explain the observed maximum in the η_v at C_m .

The values of ΔF for the system at C_m is comparable to similar values observed in methanol and ethanol (Narayana and Swamy 1975). The dimer acid hydrogen bond strength of succinic acid is 6.5 kcal/mol and for benzoic acid is 4.2 kcal/mol. This indicates that the hydrogen bonds of succinic acid with dioxan are stronger compared to benzoic acid in dioxan, and hence the higher ΔF in succinic acid. This property is also reflected in the absorption (figure 1a), where the solution containing succinic acid has higher absorption compared to the benzoic acid in dioxan. The higher absorption maximum observed in the solution of succinic acid in dioxan at C_m indicates that the solution is highly structured as compared to benzoic acid. This may be due to the fact that the hydrogen bond energy is larger for succinic acid than benzoic acid.

It can be seen from figure 2b that the relaxation times also increase with increase in the concentration of carboxylic acids in dioxan and show a maximum at C_m . The relaxation time is longer for succinic acid than for other. This may be due to the higher ΔF in the case of succinic acid as explained earlier.

The present study reveals that the excess absorption observed in the systems can be explained on the basis of Hall's two-state model because of the associative nature of the system.

Finally it may be mentioned that the value of C_m found for oxalic acid and benzoic acid is 0.075 mole fraction and for succinic acid is 0.045 in the present study. These values are nearly the same as those found by the velocity method (Nambinarayanan 1981) which are 0.08 mole fraction for oxalic acid, 0.09 for benzoic acid and at 0.05 for succinic acid. The small difference obtained for benzoic acid may be attributed to the different methods of measurement.

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