to inductive effect. Therefore, though the concentration of aggregates formed between unlike molecules in these two systems may be equal to the corresponding units in THF + phenol system, the strength of hydrogen bridges in the latter system would be greater than those in mixtures of the two cresols with THF. Such differences in the strength of hydrogen bonds would be expected to produce smaller contraction in volume in the mixtures of cresols with THF. The observed values of V^E support the above reasoning.

The excess volumes of the five binary mixtures of phenols with cyclohexanone (Table 1) show that V^E values are negative over the whole range of composition. These excess volumes indicate that the breakup of hydrogen bonds in phenol polymers is accompanied by hydrogen bond association between cyclohexanone and phenols, and that hydrogen bond association between the unlike molecules are stronger than those in phenol polymers. This conclusion lends support to the postulates employed to interpret the V^E data of mixing of phenols with THF. The IR data reported by Singurel et al.[8] support the postulate that hydrogen bonds are formed between molecules of phenols and cyclohexanone.

The values of V^E in equimolar mixtures (Table 2) fall in the order: o-chlorophenol > phenol > o-cresol > p-cresol > p-chlorophenol. The order is similar to that observed in mixtures of THF with the five phenols. This shows that the individual phenols behave identically in solvents containing donor oxygen atoms. However, the negative V^E of the mixtures of phenols with cyclohexanone are smaller than those observed in the mixtures of phenols with THF (Table 2). This difference shows that cyclohexanone is a weaker donor than THF. This conclusion is supported by the IR data reported by Singurel et al.[8] and Sellier et al.[9]. According to the first group of workers the shift νOH of phenol in cyclohexanone is 238 cm^{-1} while the second group of workers reported a value of 285 cm^{-1} for the νOH of phenol in THF. The smaller value in the former case shows that cyclohexanone is a weaker electron donor than THF.

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Compressibility & Hydrogen Bonding in Solutions of p- & o-Hydroxybenzoic Acids in Dioxan

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The velocities of ultrasonic waves in the solutions of p- and o-hydroxybenzoic acids in dioxan and in those of benzoic acid in benzene for several concentrations are measured and their adiabatic compressibilities calculated. The compressibilities for the solutions of p-, o-hydroxybenzoic acids in dioxan show initially a decrease with increase of concentration, attain a minimum value and then show an increase whereas for the solution of benzoic acid in benzene, the compressibility shows an increase with increase in [benzoic acid]. These results indicate that there is a formation of intermolecular hydrogen bonds between the p-, and o-hydroxybenzoic acid and dioxan molecules whereas for the solution of benzoic acid in benzene there is no formation of such hydrogen bonds. In addition, the compressibility is lowered to a greater extent in the solutions of p-hydroxybenzoic acid in dioxan, than for the solutions of o-hydroxybenzoic acid in dioxan, thereby indicating that the intermolecular hydrogen bonds formed are stronger in the former than in the latter. This is due to the fact that o-hydroxybenzoic acid is a chelated hydrogen bonded compound whereas p-hydroxybenzoic acid is non-chelated. These studies suggest the possibility that the velocity of ultrasonic waves may be used as a means to distinguish between the chelated hydrogen bonded compounds and the nonchelated ones.

IT was reported[1] that electric polarization of the solution of benzoic acid in dioxan increases with concentration in the range 0·06 to 0·09 mole fractions and that the increase is due to some kind of association phenomenon involving the formation of hydrogen bonds between benzoic acid and dioxan molecules. Our recent studies[2] on the velocity of ultrasonic waves in the solution of benzoic acid in dioxan showed that the increase in polarization in the above concentration range was due to the formation of hydrogen bonds between oxygen atom of the dioxan molecules and the carboxylic group of the benzoic acid whose dimer form is broken by the dioxan molecules. In would be interesting to see whether such an effect exists in the solution of o-hydroxybenzoic acid in dioxan as o-hydroxybenzoic acid is a chelated compound involving the formation of intramolecular hydrogen bonds. Such a chelation does not occur in p-hydroxybenzoic acid, which is a position isomer of o-hydroxybenzoic acid and the intermolecular hydrogen bond formation in the solutions of o-hydroxybenzoic acid and p-hydroxybenzoic acid in dioxan are likely to be different. In this note, the velocities of ultrasonic waves were measured in solutions of various concentrations of o-hydroxybenzoic acid in dioxan and p-hydroxybenzoic acid in dioxan with a view to studying the
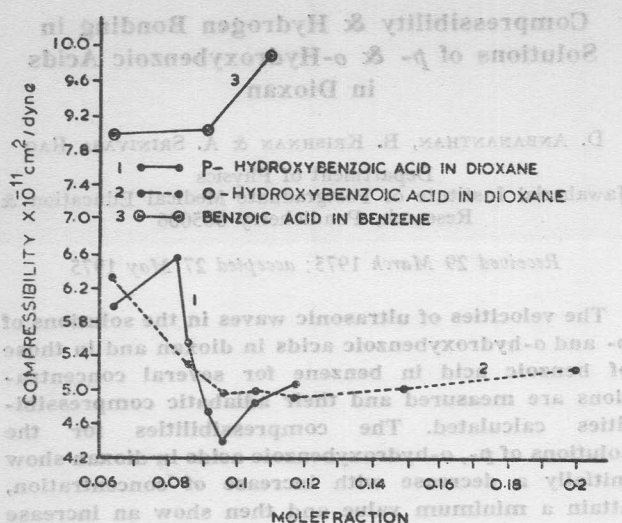
Fig. 1 — Plot of compressibility versus concentration in mole fraction

difference in the intermolecular hydrogen bond formation between the two position isomers. These velocities were also measured in solutions of benzoic acid in benzene, where there is no possibility of intermolecular hydrogen bond formation between the benzoic acid and benzene molecules.

Chemically pure samples of benzoic acid, o-, and p-hydroxybenzoic acids, dioxan and benzene were used in the present study. Solutions of benzoic acid in benzene, p-hydroxybenzoic acid in dioxan and o-hydroxybenzoic acid in dioxan of different mole fractions in the range 0·06 to 0·20 were prepared. The ultrasonic velocities in the above solutions were determined using optical diffraction method[3]. As these solutions are electrically conductive, there is a possibility of short circuiting the electrodes attached to the crystal through the liquid. This is avoided by constructing a glass trough with two compartments separated by a thin membrane. The experimental liquid is taken in one compartment and the other is filled with water. The electrodes and the crystal were well immersed in the water compartment near the membrane. The frequency of ultrasonic waves used was 4 MHz. Taking water as a standard, the velocities (V) in the above solutions of different mole fractions were measured to an accuracy of ±3%. The measurement of velocity of the ultrasonic waves were made at a temperature of 30°C. The adiabatic compressibility (β) was calculated using the formula $\beta = (V^2 \rho)^{-1}$ where ρ is the density of the solution which was determined by using a specific gravity bottle.

The results of the experiment are shown in Fig. 1. In the case of benzoic acid in benzene, the compressibility is increasing with concentration thereby indicating the weakening of the intermolecular forces as there is no possibility of forming hydrogen bonds within the system. It is observed that in the solution of p-hydroxybenzoic acid in dioxan, the compressibility decreases and attains a minimum value at the mole fraction 0·0952. This phenomenon

is analoguous to the behaviour of the solution of benzoic acid in dioxan[2] and it is interesting to note that the minimum value of compressibility is attained at almost the same concentration in both the systems. The sudden decrease in the compressibility may be attributed to the formation of hydrogen bonds between the monomer p-hydroxybenzoic acid and the dioxan molecules. The increase in compressibility above the mole fraction 0·0952 has already been explained for the case of benzoic acid in dioxan[2] and the same explanation appears to be valid for the case of p-hydroxybenzoic acid in dioxan. In the solution of o-hydroxybenzoic acid in dioxan, there is a gradual decrease in compressibility with a tendency to increase at higher concentrations in contrast to the solution of p-hydroxybenzoic acid in dioxan where there is a sudden decrease in the compressibility followed by a sudden increase (Fig. 1). The results further show that the compressibility is lowered to a greater extent in the case of p-hydroxybenzoic acid in dioxan than in the solution of o-hydroxybenzoic acid in dioxan. This can be understood by recognizing the fact that o-hydroxybenzoic acid is a chelated compound forming strong intramolecular hydrogen bonds and, hence, the intermolecular bonds formed with dioxan are likely to be weaker. As p-hydroxybenzoic acid is not chelated, it forms stronger hydrogen bonds with dioxan and hence the compressibility is lowered to a greater extent in this case. Melting points of p-hydroxybenzoic acid and o-hydroxybenzoic acid are 213°C and 159°C respectively and this clearly indicates that the intermolecular hydrogen bonding involving the formation of dimers is stronger in the case of p-hydroxy benzoic acid than in o-hydroxybenzoic acid. The sudden increase in compressibility in the solution of p-hydroxybenzoic acid in dioxan above the molefraction 0·0952 as compared to the solution of o-hydroxybenzoic acid may be explained by postulating that the dioxan is unable to break the strong dimers of p-hydroxybenzoic acid so that additional monomers are not available to form hydrogen bonds with dioxan molecules as in the case of benzoic acid and dioxan[2]. For o-hydroxybenzoic acid the dimer hydrogen bonds are weak and hence they are easily broken and there is a gradual increase in the compressibility above the mole fraction of 0·0952. These observations lend further support to those reported earlier[2].

These ultrasonic studies suggest that compressibility may be used as a means to distinguish the chelated hydrogen bonded compound from the non-chelated.

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