

CHAPTER - VII

CHEMICAL SHIFT AND RELAXATION STUDIES
IN CARBOXYLIC ACIDS
IN DIOXAN

SOLUTIONS OF ORTHO AND PARA HYDROXY BENZOIC ACID IN DIOXAN

INTRODUCTION

Earlier ultrasonic velocity studies (1,2) 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. The compound OHBA is chelated, whereas the compound PHBA is non-chelated. These studies were carried out at various solute concentrations ranging from 0.01 to 0.10 mole fractions (mf) at different temperatures. The variation of ultrasonic velocity showed two velocity maxima, one at lower solute concentration and another at higher solute concentration. The observed maximum at the lower concentration was explained as due to the formation of hydrogen bonds (O-H...O) between the hydroxyl group (O-H) of OHBA/PHBA with the oxygen of dioxan molecule. The second maxima at the higher concentration was attributed to the formation of hydrogen bonds (O-H...O) between the carboxyl group (COOH) and the oxygen of the dioxan molecule. To obtain further information on the nature of molecular interactions in these solutions, the proton magnetic resonance spectra and spin-lattice relaxation times were studied in these solutions at several solute concentrations and the results are reported in this chapter.

EXPERIMENTAL SET UP

The chemicals used in the present study were of AR/BDH quality and they were used without further purification. High resolution proton magnetic resonance spectra in solutions of OHBA/PHBA in dioxan at a temperature of 32 C were recorded using a Varian EM 390 NMR spectrometer at 90 MHz. In both the systems of OHBA and PHBA in dioxan, the NMR chemical shift of the COOH group and the phenolic O-H group were studied taking dioxan as the standard. The proton spin-lattice relaxation times (T_1) in these solutions at a temperature of 32 C were also measured using a Bruker PC 120 NMR process analyser. The spin-lattice relaxation time (T_1) was measured using 180- τ -90 pulse sequences. The errors in the measured values of (T_1) are around 0.5%.

RESULTS AND DISCUSSION

The chemical shift of the O-H group and COOH group could be distinguished for solutions of OHBA in dioxan. Chemical shift observed around 11.00 ppm can be identified as due to O-H protons (3) whereas chemical shift in the range of 8.3 to 10.00 ppm can be identified as due to COOH protons (4). The recorded NMR spectra in the above solutions are shown in figures 7.1-7.10. The variations of the chemical shift O-H protons and COOH protons in solutions of OHBA in dioxan with solute concentration are shown in figure 7.11. From the figure, it can be seen that the chemical shift of the O-H

FIG. 7.1

90 MHZ SPECTRUM

SOLVENT: DIOXAN (D)

SOLUTE: ORTHO HYDROXY BENZOIC ACID

CONCENTRATION: .01 (S₁) } MOLE FRACTION
.02 (S₂) }

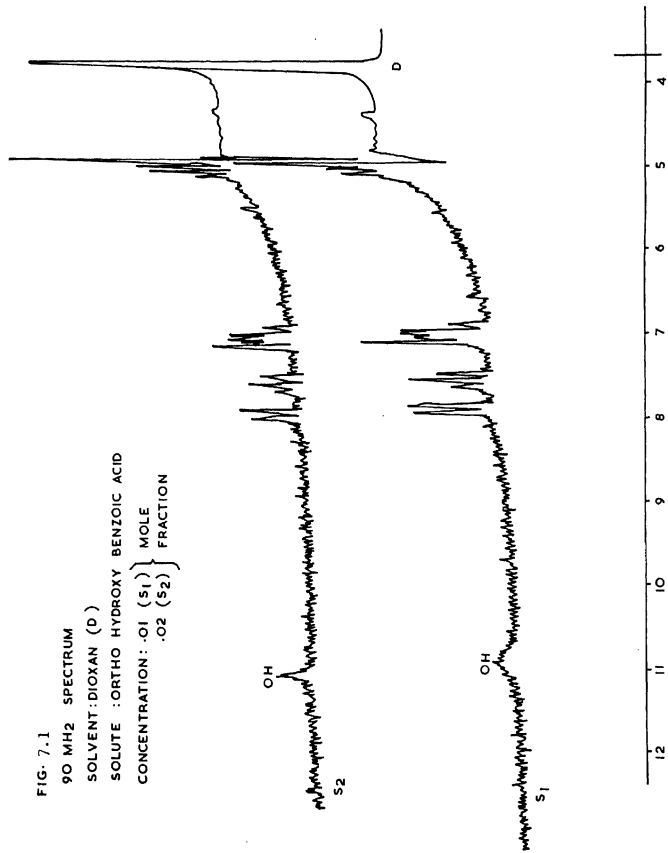


FIG. 7.2

90 MHZ SPECTRUM

SOLVENT : DIOXAN (D)

SOLUTE : ORTHO HYDROXY BENZOIC ACID

CONCENTRATION: .03 (S₃) } MOLE
.04 (S₄) } FRACTION

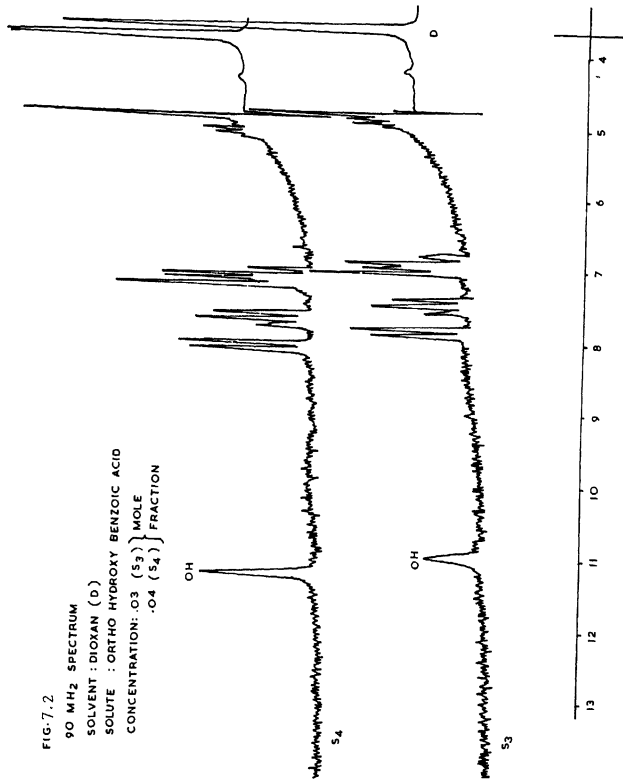


FIG.7:3

90 MH₂ SPECTRUM

SOLVENT : DIOXAN (D)

SOLUTE : ORTHO HYDROXY BENZOIC ACID

CONCENTRATION : .05 (S5) MOLE

.06 (S6) FRACTION

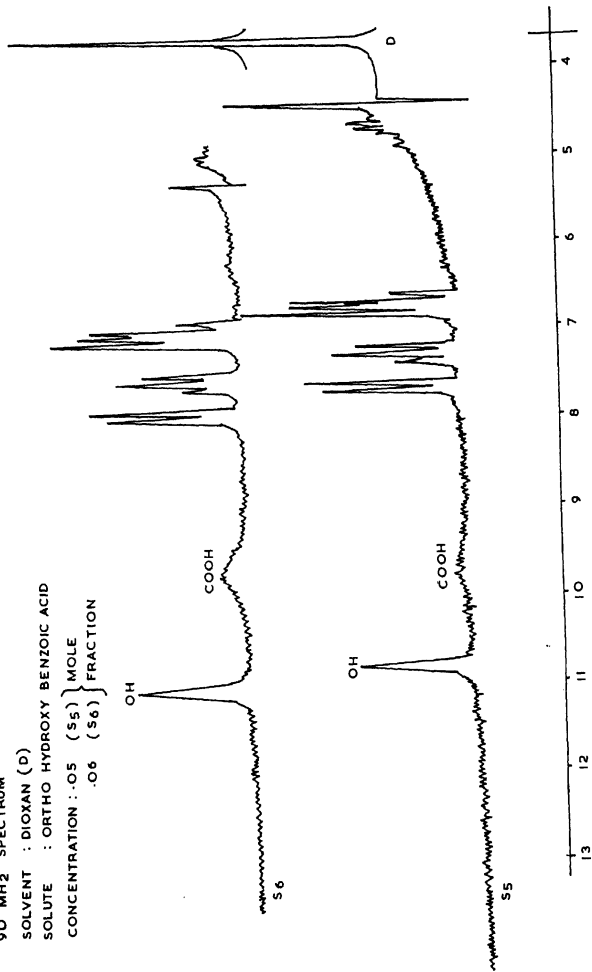


FIG. 7.4

90 MH₂ SPECTRUM

SOLVENT : DIOXAN (D)

SOLUTE : ORTHO HYDROXY BENZOIC ACID

CONCENTRATION : .07 (S7) } MOLE
.08 (S8) } FRACTION

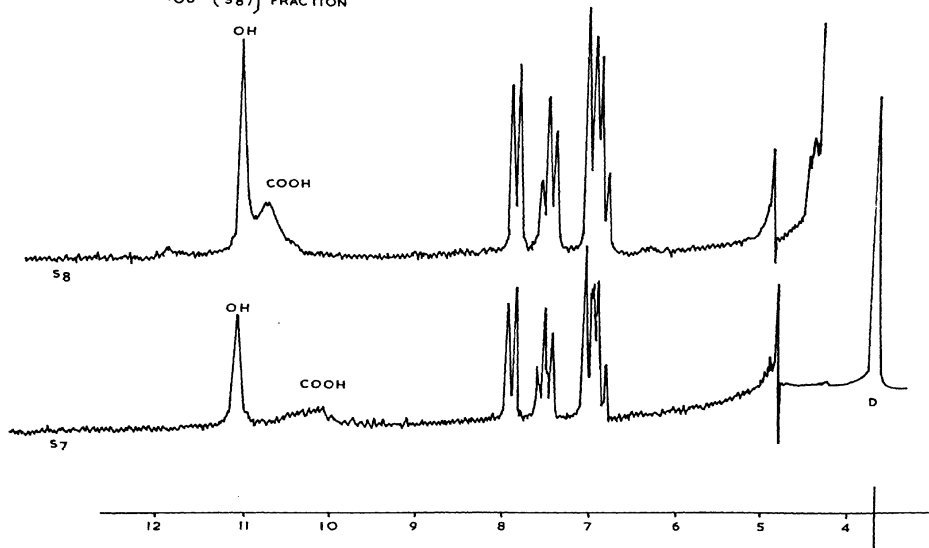


FIG. 7.5

90 MHZ SPECTRUM

SOLVENT : DIOXAN (D)

SOLUTE : ORTHO HYDROXY BENZOIC ACID

CONCENTRATION : 0.9 (S₉) MOLE
0.1 (S₁₀) FRACTION

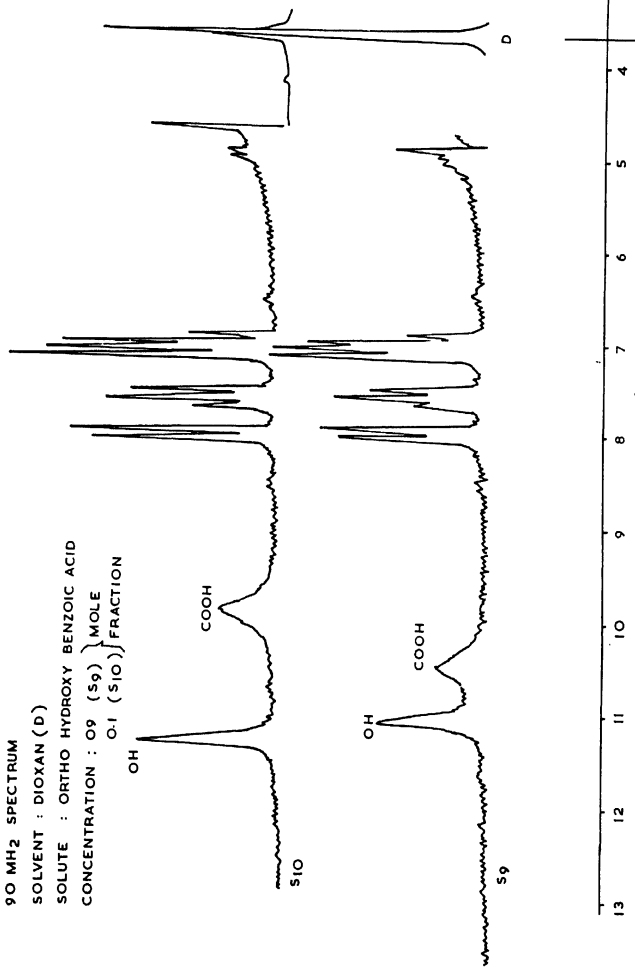


FIG. 7.6
90 MHz SPECTRUM
SOLVENT : DIOXAN (D)
SOLUTE : PARA HYDROXY BENZOIC ACID
CONCENTRATION : .01(S₁) } MOLE
.02(S₂) } FRACTION

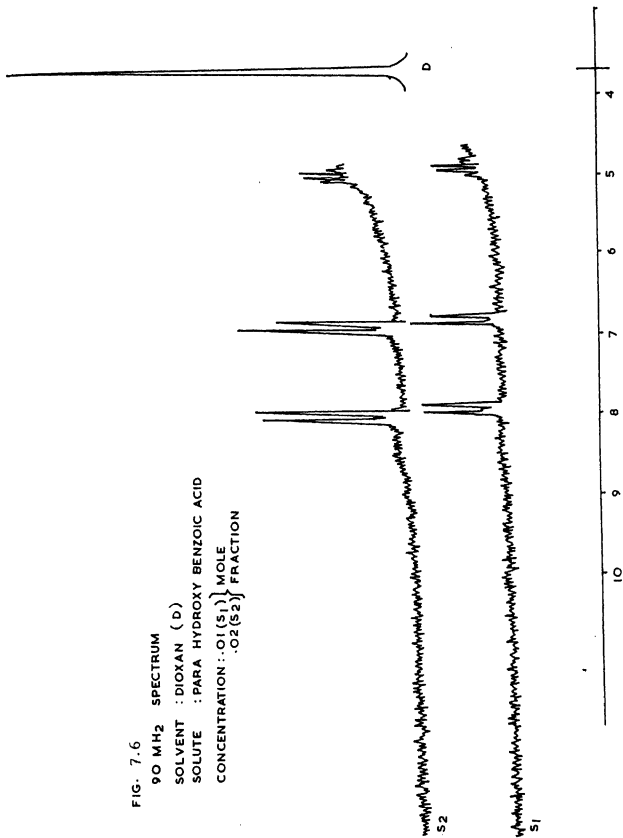


FIG. 7.7

90 MH₂ SPECTRUM

SOLVENT : DIOXAN (D)

SOLUTE : PARA HYDROXY BENZOIC ACID

CONCENTRATION : .03 (S₃) } MOLE
.04 (S₄) } FRACTION

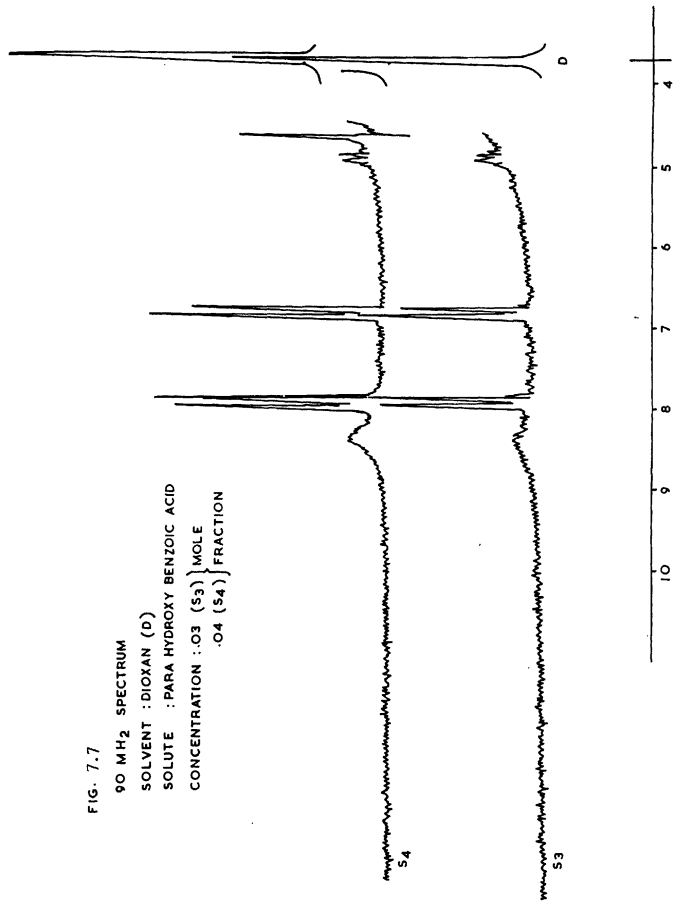


FIG. 7.8

90 MHZ SPECTRUM

SOLVENT : DIOXAN (D)

SOLVENT : PARA HYDROXY BENZOIC ACID

CONCENTRATION : $\left. \begin{array}{l} -0.5 (S_5) \\ -0.6 (S_6) \end{array} \right\} \text{MOLE FRACTION}$

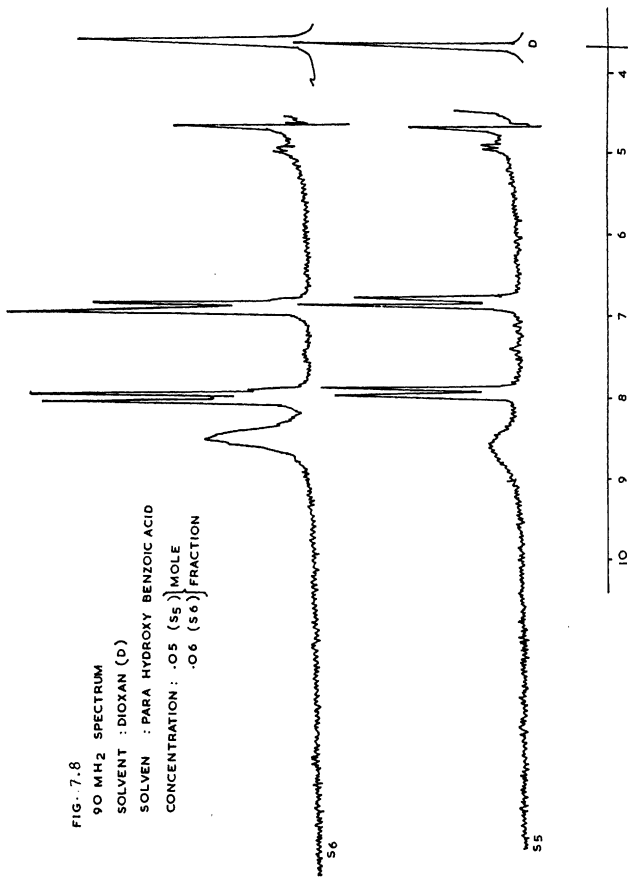


FIG.. 7.9

90 MH2 SPECTRUM

SOLVENT : DIOXAN (D)

SOLUTE : PARA HYDROXY BENZOIC ACID

CONCENTRATION : .07 (S7) } MOLE
.08 (S8) } FRACTION

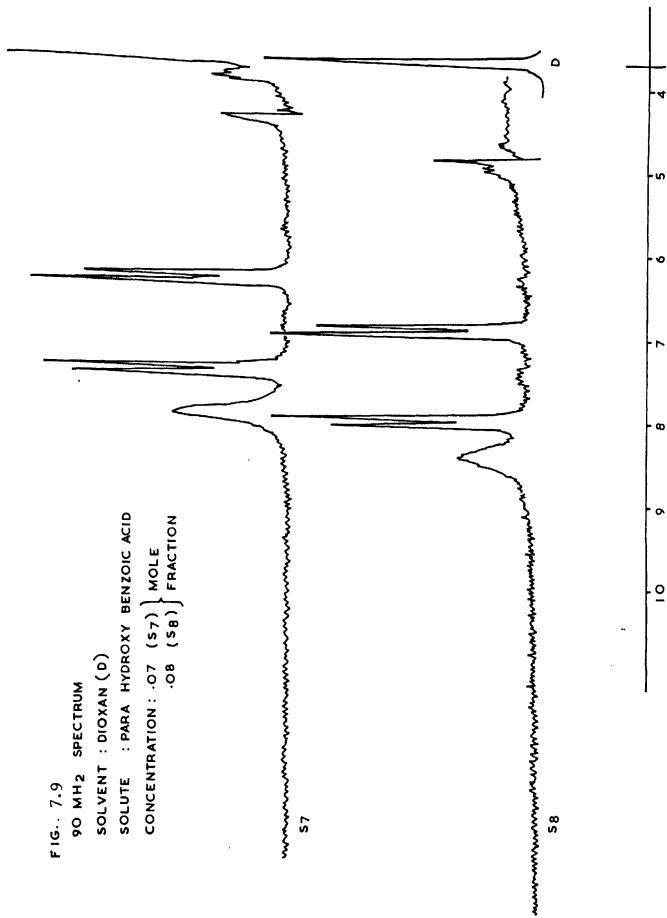


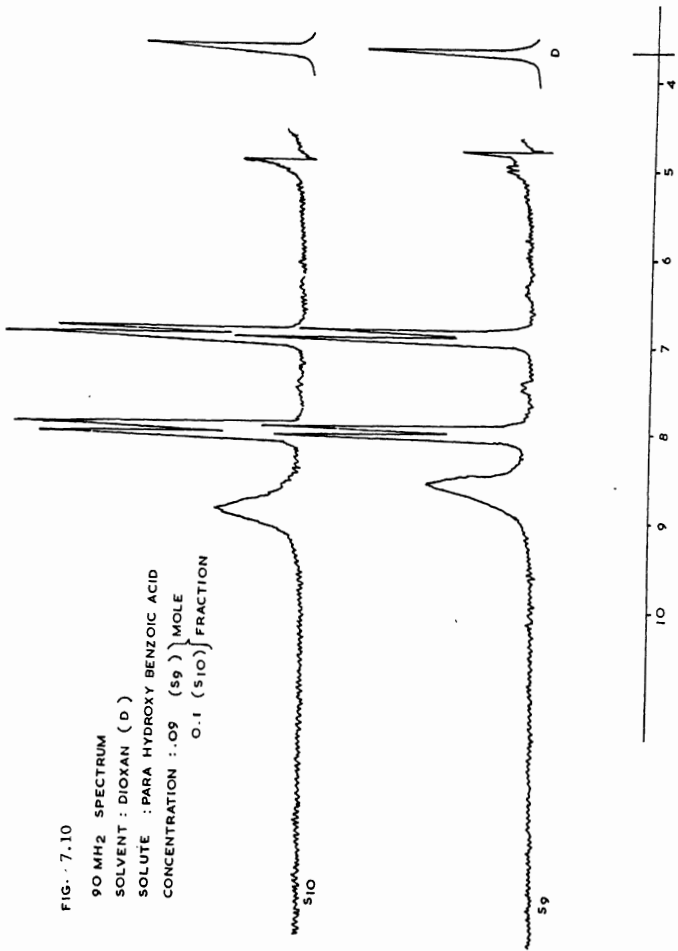
FIG. 7.10

90 MHZ SPECTRUM

SOLVENT : DIOXAN (D)

SOLUTE : PARA HYDROXY BENZOIC ACID

CONCENTRATION : .09 (S₉) MOLE
0.1 (S₁₀) FRACTION

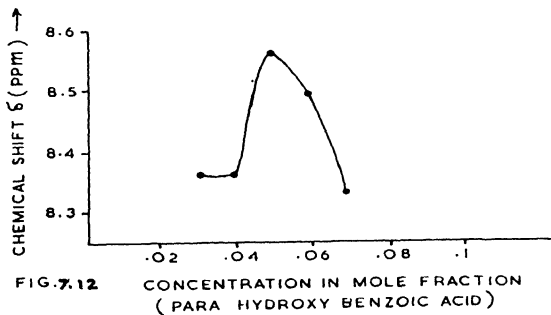
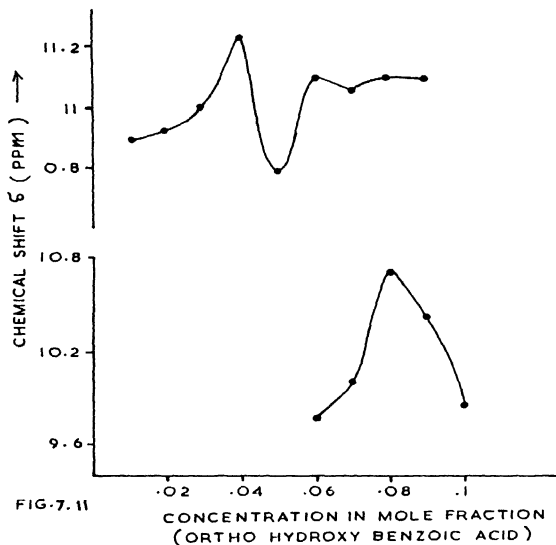


proton increases with increase of solute (OHBA) concentration and attains a maximum at a solute concentration of 0.4 mf. Further, increase of solute concentration slightly increases the chemical shift and it remains approximately the same in the solute concentration range of 0.5 mf. The chemical shift of COOH proton increases with increase in solute concentration of 0.08 mf and then decreases with further increase of solute concentration.

It is interesting that in the solutions of OHBA in dioxan the NMR peak of O-H proton appears in the entire solute concentration range of 0.01 to 0.1 mf whereas the peak corresponding to the COOH proton appears only at solute concentrations above 0.5 mf. This may be due to the fact that COOH groups generally occur as rigid dimer structure and these structure are almost solid like, which makes the signal broad due to nuclear dipole-dipole interaction. It is known that at higher solute concentration, the dimers are broken (1,2) and dipole-dipole interaction is considerably reduced. This process enables the detection of NMR signal at higher solute concentrations.

For solutions of PHBA in dioxan only one NMR peak was observed at 8.55 ppm. The spectra observed at 11.00 ppm in solution of PHBA in dioxan is absent in the solutions of PHBA in dioxan and this may be due to rapid exchange of protons between the hydroxyl and carboxyl groups (5). Such

CHEMICAL SHIFT (δ) VS CONCENTRATION



an exchange may not be possible in solutions of OHBA in dioxan as OHBA is a chelated compound. The variation of chemical shift of the observed proton with solute (PHBA) concentration is shown in figure 7.12. From the figure, it can be seen that the chemical shift increases with increase of solute concentration, reaches a maximum around 0.05 mf solute concentration and then decreases with further increase of solute concentration.

The downfield chemical shift observed in the solution of OHBA in dioxan may be due to hydrogen bonding (5). The possible hydrogen bonds in this solution are between the O-H and COOH groups of OHBA molecule with oxygen of dioxan. The chemical shift of the O-H proton in solutions of OHBA in dioxan increases and attains a maximum at a solute concentration of 0.04 mf, this indicates that the hydrogen bonds between the O-H groups and the oxygen of dioxan molecule are extremely strong at this concentration. This is in agreement with the ultrasonic velocity measurements of Sosamma et al (2), where a velocity maximum was observed in these solutions at a solute concentration of 0.04 mf. The variation of the chemical shift of COOH proton in the solution of OHBA in dioxan also shows a maximum at a solute concentration of 0.08 mf. This maximum can be interpreted as due to the strong hydrogen bond between COOH group and oxygen of dioxan molecule. This result is also in conformity with the earlier ultrasonic observations.

In the ultrasonic studies in solutions of PHBA in dioxan (2) two maxima in the ultrasonic velocity were observed. The first maximum occurred at a solute concentration of 0.03 mf and another at 0.08 mf. These maxima were interpreted as due to formation of hydrogen bonds between OH/COOH group of PHBA and oxygen in dioxan. In the present NMR studies, only one peak was observed due to chemical exchange and hence no conclusion could be drawn as to the nature of hydrogen bonding in these solutions. It appears that ultrasonic studies are not sensitive to chemical exchange.

The variation of spin-lattice relaxation time (T_1) with solute concentration at a temperature of 32 C in the solutions of OHBA in dioxan are shown in figure 7.13. The magnetization decay in these solutions is found to be mono exponential and the relaxing protons are probably the ones involved in hydrogen bonds. For solutions of OHBA in dioxan, T_1 generally decrease with increase in solute concentration. A decrease in T_1 generally indicates (6) increase in the hydrogen bond energy in the solution. The plot of dT_1/dc verses concentration (figure 7.14) shows that T_1 decreases significantly at solute concentrations of 0.03 and 0.07 mf. A sharp decrease in the value of T_1 may be interpreted as due to the formation of hydrogen bonds. This study generally supports the present NMR chemical shift

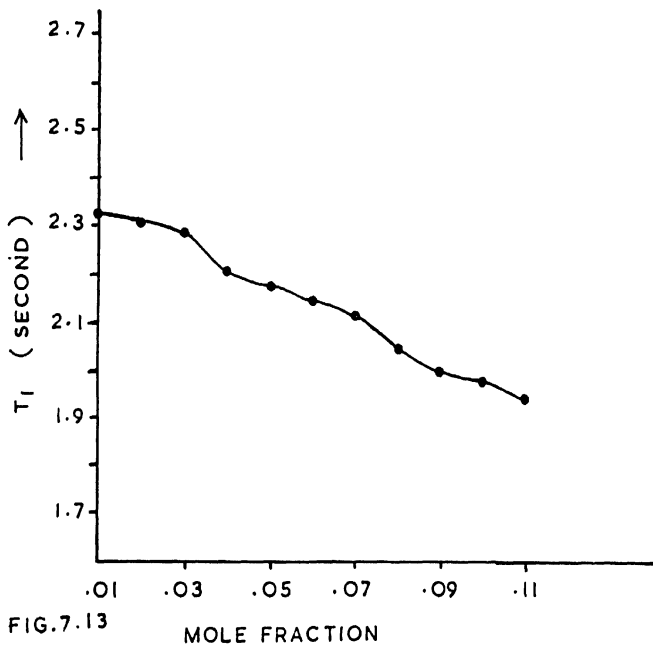


FIG.7.13

ORTHO HYDROXY BENZOIC ACID

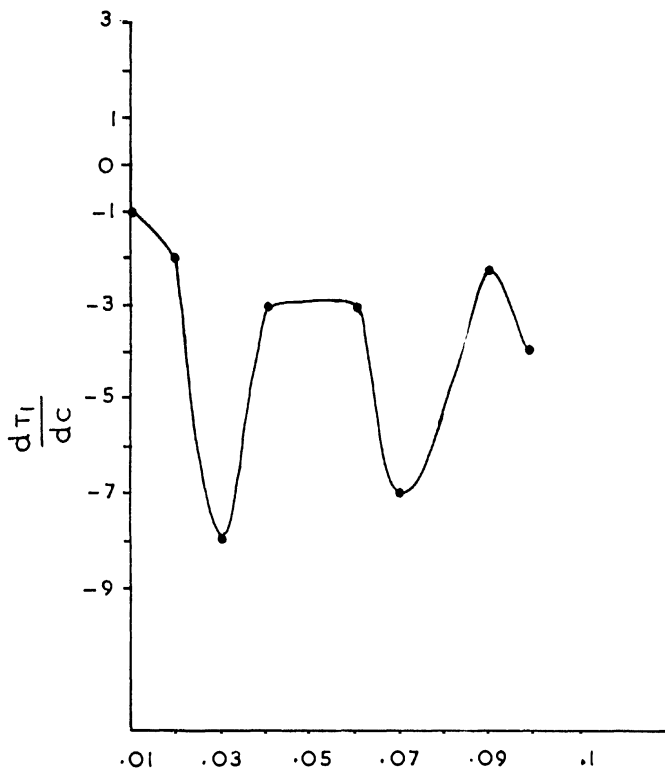


FIG. 7.14

CONCENTRATION

ORTHO HYDROXY BENZOIC ACID

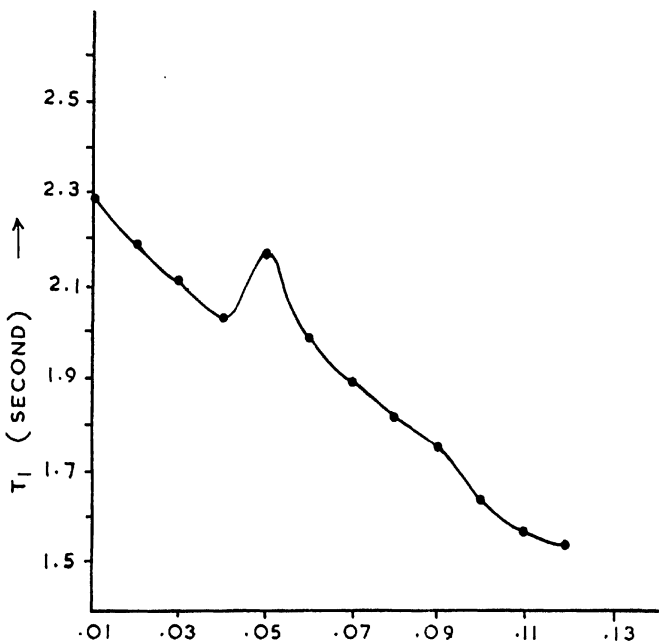


FIG.7.15

MOLE FRACTION
PARA HYDROXY BENZOIC ACID

measurements and the earlier ultrasonic studies. The variation of T_1 against solute concentration in solutions of PHBA in dioxan at a temperature of 32 C shows a minimum value of T_1 at a solute concentration of 0.04 mf (figure 7.15). This observation is similar to the result obtained in NMR chemical shift studies in these solutions.

It is possible to estimate the strength of the hydrogen bonds in these solutions from the variation of T_1 with hydrogen bond energy (6). The estimated hydrogen bond energy in the solutions of OHBA in dioxan comes out to be around 2.5 k cal/mole at 0.04 and 0.08 mf solute concentration. This estimate appears to be reasonable and the hydrogen bonds formed in the above solutions are rather weak.

In conclusion, it should be mentioned that the present study throws some light on the nature of molecular interactions in these solutions. It may also be possible to distinguish chelated and non-chelated compounds by NMR studies.

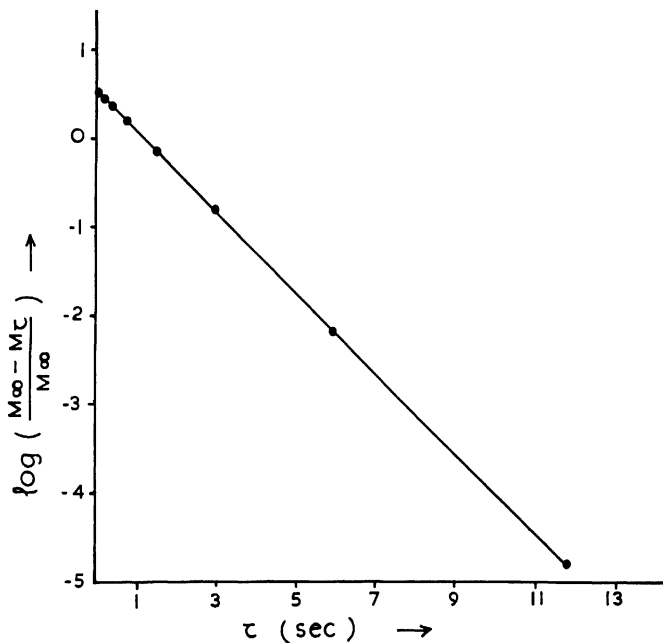
META TOLUIC AND ORTHO TOLUIC ACIDS IN DIOXAN

Earlier ultrasonic velocity studies (7) in solutions of meta toluic acid (M) and ortho toluic acid (O) in dioxan indicated the possibility of hydrogen bonding in these solutions. These studies were carried out at various solute concentrations ranging from 0.01 to 0.10 mole fraction (mf) at different temperatures. The variation of ultrasonic

velocity in both solutions with solute concentration showed a velocity maxima at particular solute concentration. The observed maxima was explained as due to formation of hydrogen bonds (O-H...O) between the carboxyl group (COOH) and the oxygen of dioxan molecule. In order to confirm the observations made by ultrasonic studies, the present high resolution proton NMR chemical shift and relaxation studies were carried out in the solutions of M and O toluic acid in dioxan at several solute concentrations and the results are reported.

EXPERIMENTAL SET UP

high resolution proton magnetic resonance spectra in solutions of O and M toluic acid in dioxan at a temperature of 32 C were recorded using a Varian EM 390 NMR spectrometer at 90 MHz. In both the systems of M/O toluic acid in dioxan, the NMR chemical shift of COOH group was studied taking dioxan as the standard. The relaxation times (T_1) in these solutions were studied using Bruker PC 120 NMR process analyser. Figure 7.16,7.17 shows the decay of magnetisation in these solutions. From the figure it can be seen that the decay is found to be mono exponential and the relaxing protons are probably the ones involved in hydrogen bonding. The recorded NMR spectra in the above solutions are shown in figures 7.18-7.26.



$\log \left(\frac{M_{\infty} - M_t}{M_{\infty}} \right)$ VERSUS τ OF M-TOLUIC ACID

FIG. 7 16

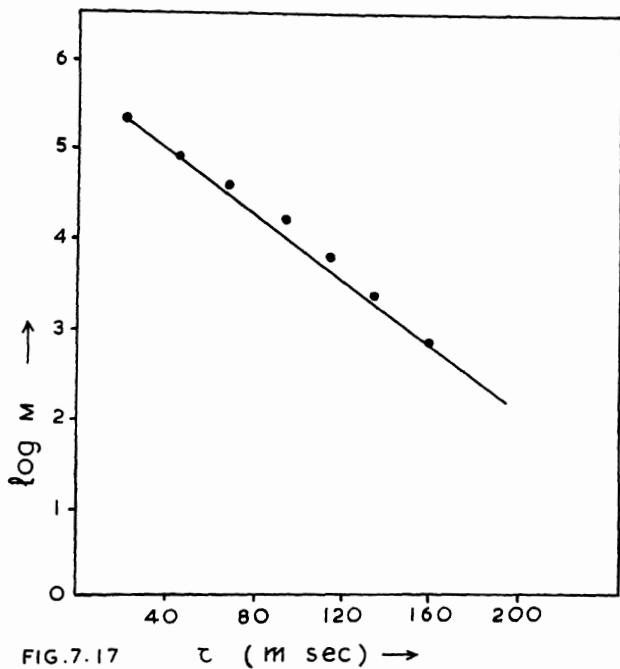


FIG.7.17

$\log M$ VERSUS τ OF M-TOLUIC ACID

FIG. 7-18

90 MHZ SPECTRUM

SOLVENT : DIOXAN (D)

SOLUTE : M-TOLUIC ACID

CONCENTRATION : 0.04 (S₁)
0.05 (S₂) / FRACTION

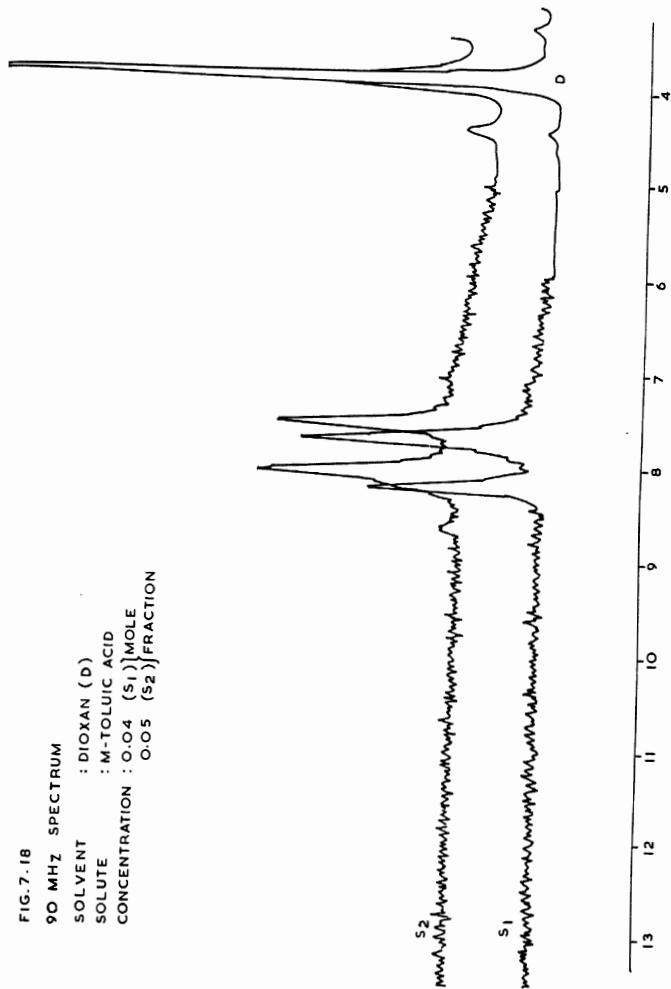


FIG. 7. 19

90 MHZ SPECTRUM

SOLVENT : DIOXAN (D)

SOLUTE : M-TOLUIC ACID

CONCENTRATION : 0.06 (S₃) MOLE
0.07 (S₄) } FRACTION

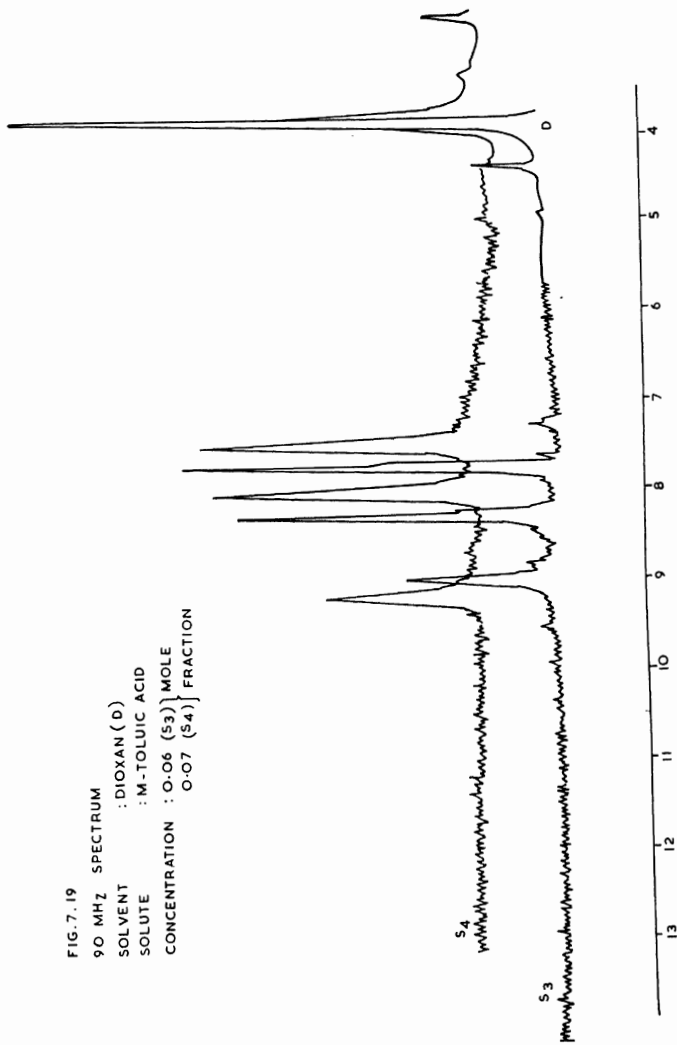


FIG. 7. 20

90 MHZ SPECTRUM
SOLVENT : DIOXAN (D)
SOLUTE : M-TOLUIC ACID
CONCENTRATION : 0.08 (S5)
0.09 (S6)
0.1 (S7)

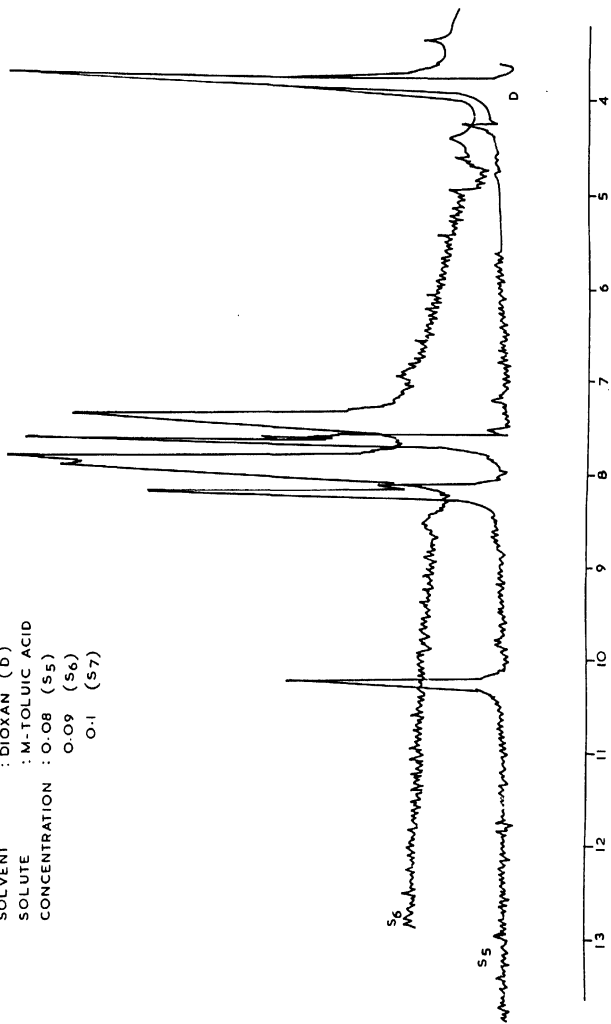


FIG. 7. 21

90 MHZ SPECTRUM
SOLVENT : DIOXAN (D)
SOLUTE : O-TOLUIC ACID
CONCENTRATION : 0.02 (S₁) } MOLE
 0.03 (S₂) } FRACTION

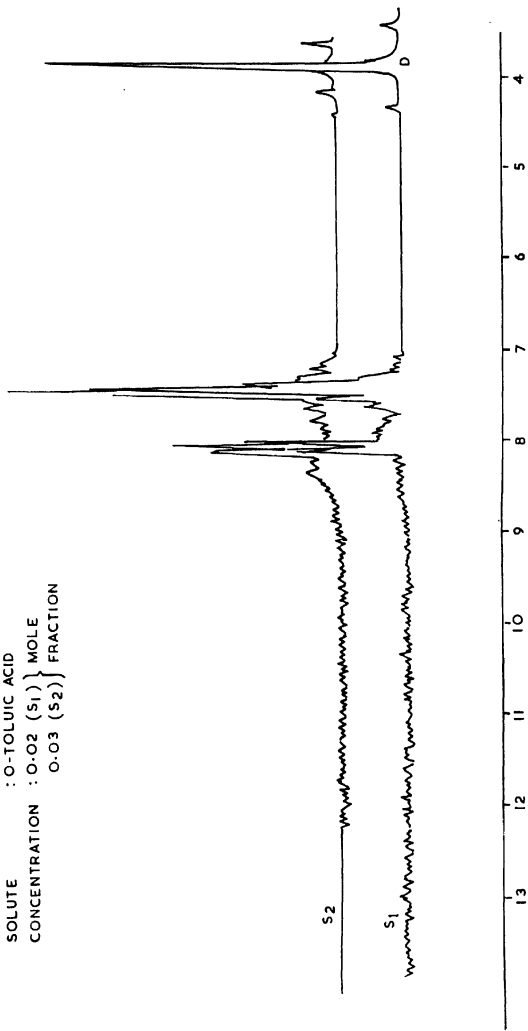


FIG. 7.22

90 MHz SPECTRUM

SOLVENT : DIOXAN

SOLUTE : O-TOLUIC ACID

CONCENTRATION : 0.04 (S₃) MOLE FRACTION
0.05 (S₄)

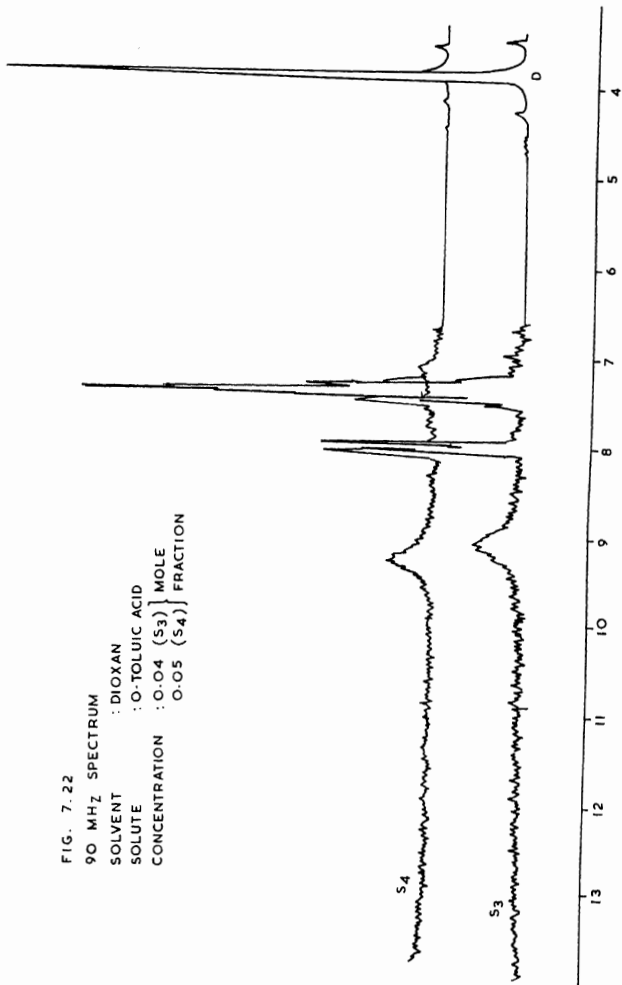


FIG. 7. 23

90 MHZ SPECTRUM

SOLVENT : DIOXAN (D)

SOLUTE : O-TOLUIC ACID

CONCENTRATION : 0.06 (S₅) } MOLE
0.07 (S₆) } FRACTION

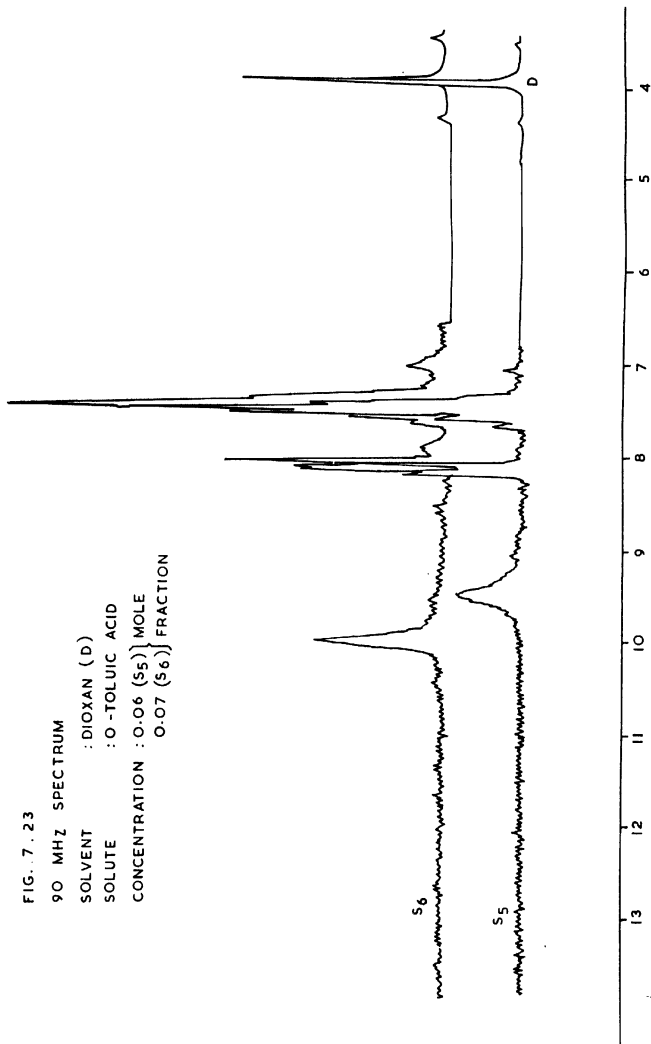


FIG. 7.24

90 MHz SPECTRUM

SOLVENT : DIOXAN (D)

SOLUTE : O-TOLUIC ACID

CONCENTRATION : 0.08 (S7) MOLE
0.09 (S8) } FRACTION

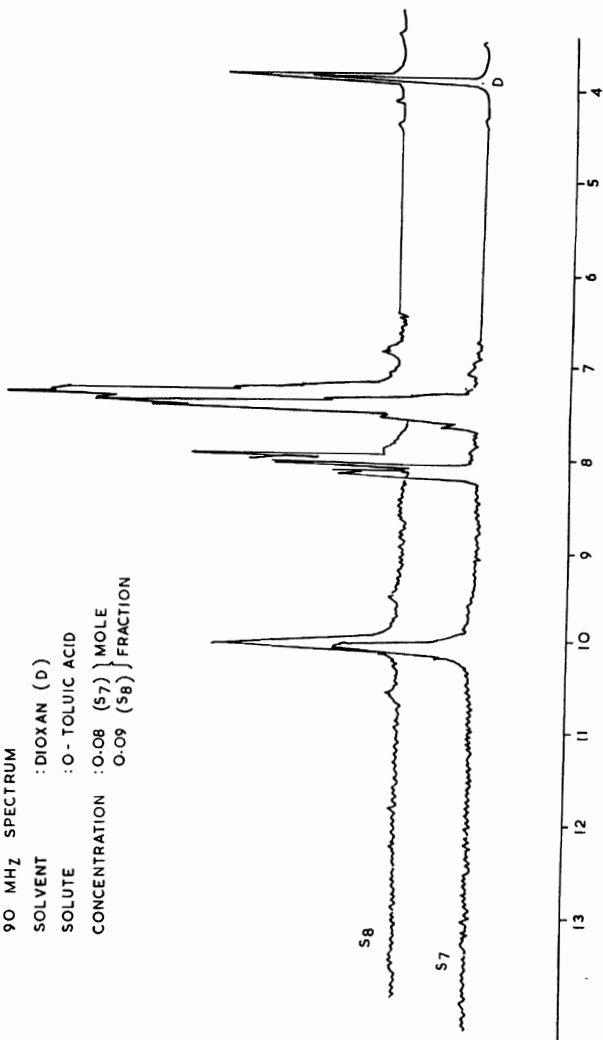


FIG. 7. 25

90 MHZ SPECTRUM

SOLVENT : DIOXAN (D)

SOLUTE : O - TOLUIC ACID

CONCENTRATION : 0.10 (S₉) MOLE
0.11 (S₁₀) } FRACTION

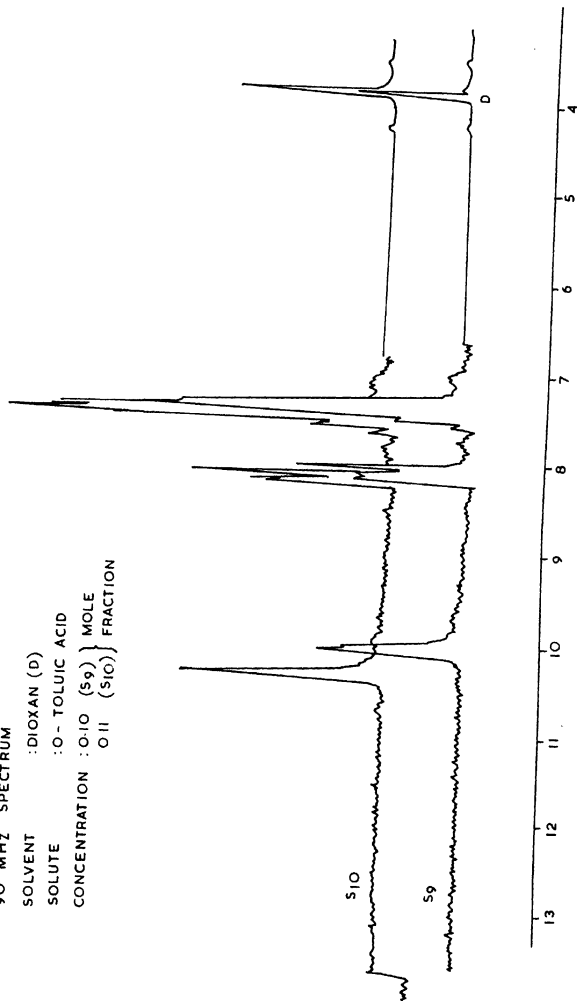


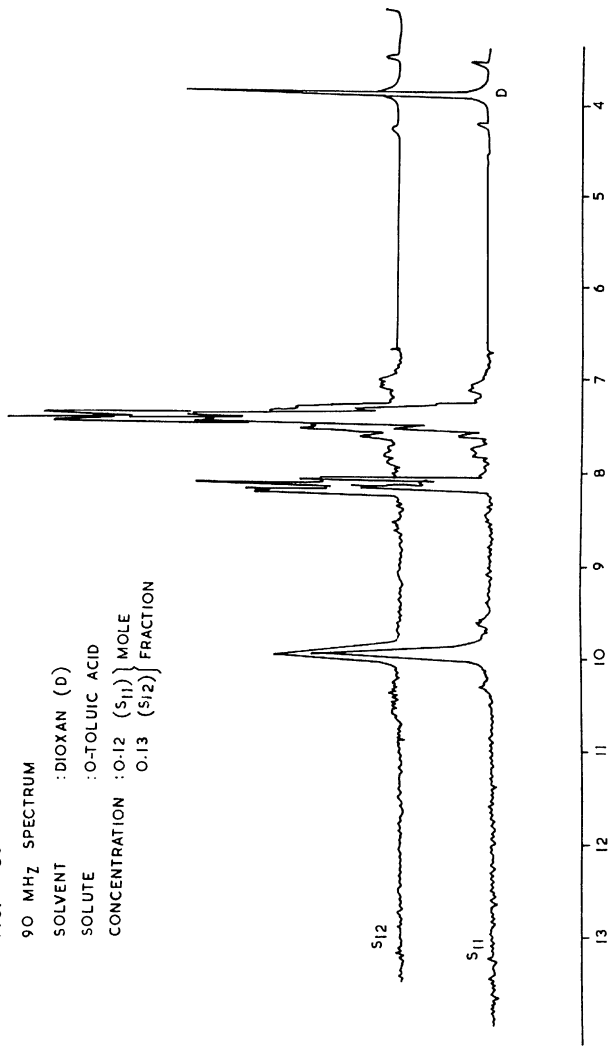
FIG. 7. 26

90 MHz SPECTRUM

SOLVENT : DIOXAN (D)

SOLUTE : O-TOLUIC ACID

CONCENTRATION : 0.12 (S₁₁) } MOLE
0.13 (S₁₂) } FRACTION



RESULTS AND DISCUSSION

The observed chemical shifts in the above solutions are plotted against concentrations of M-toluic acid in dioxan are shown in figure 7.27(a). From the figure, it can be seen that the chemical shift increases with increase of concentration upto 0.07 mf and decreases with further increase of solute concentration. The variation of NMR proton spin lattice relaxation time (T_1) with concentration of M-toluic acid in dioxan is shown in figure 7.27(b). The relaxation time is found to decrease with increase of solute concentration. Figure 7.28(a) shows the variation of chemical shifts with solute concentrations of O-toluic acid in dioxan, from the figure, it can be seen that the chemical shift shows an increase upto 0.11 mf and then decreases with further increase of solute concentration. The relaxation time is found to decrease with increase of solute concentration (figure 7.28(b)).

The chemical shift observed in the range of 8.3 to 10.00 ppm can be identified as due to COOH protons. From figures 7.27,7.28 the peak corresponding to COOH protons appears only at solute concentration above 0.04 mf for M-toluic acid in dioxan, and the solute concentration above 0.02 mf for O-toluic acid. This may be due to the fact that COOH groups generally occur as strong dimer structures and the NMR signal is broad due to nuclear dipole-dipole

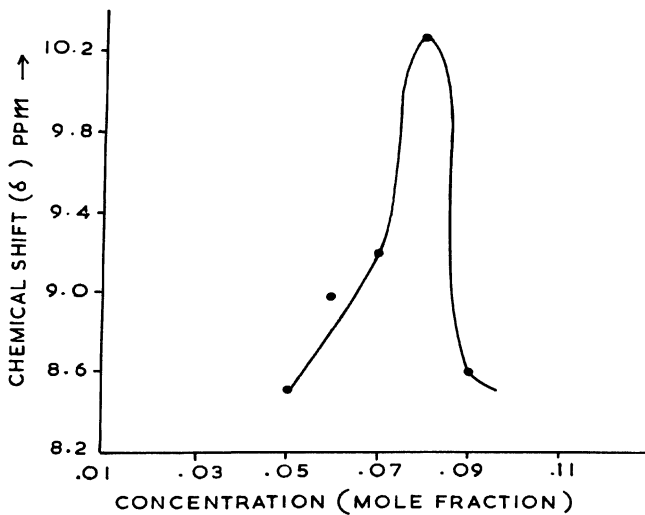
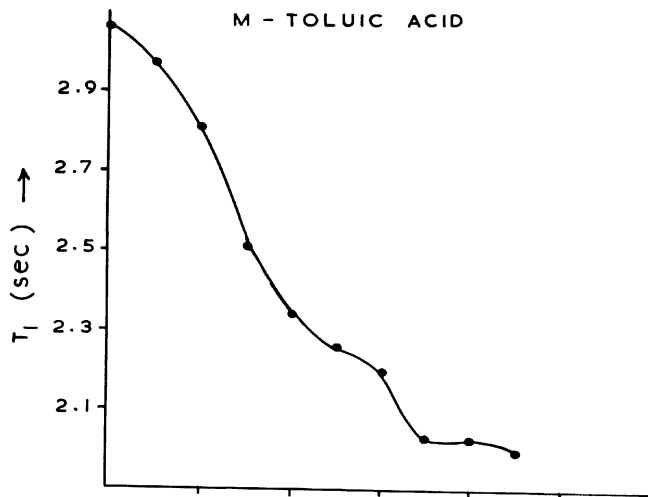


FIG. 7.27

interaction. It is known that at higher solute concentration, the dimers are broken (1,2) and dipole-dipole interaction is considerably reduced. This process enables the detection of NMR signal at higher solute concentration.

From the figure 7.27(a), it can be seen that in the case of M-toluic acid system the chemical shift initially increases with increase of solute concentration, attains a maximum at 0.08 mf and then decreases with increase of solute concentration. The increases chemical shift indicates the formation of hydrogen bonds in these solutions (8). The proton chemical shift depends only on the strength of the hydrogen bonds in the solution. In M-toluic acid in dioxan a decrease in the proton chemical shift is observed after 0.08 mf solute concentration. As the concentration increases, the average proton-proton distance decreases and it is known that such proximity of the protons weakens the hydrogen bonds (Lippincot and Srinivasa Rao) (9). The value of (T_1) generally decreases with increase in solute concentration and attains a minimum value at 0.08 mf solute concentration. A decrease in (T_1) generally indicate (6) increase in the hydrogen bond energy in the solution. The relaxation study also supports the conclusion drawn by chemical shift. The peak observed at 0.08 mf in the variation of chemical shift with solute concentration may be interpreted as due to the formation of hydrogen bonds in the above solutions. The

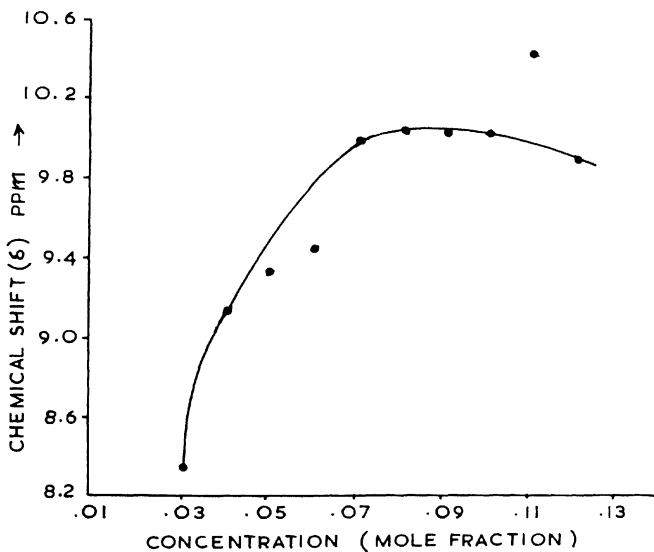
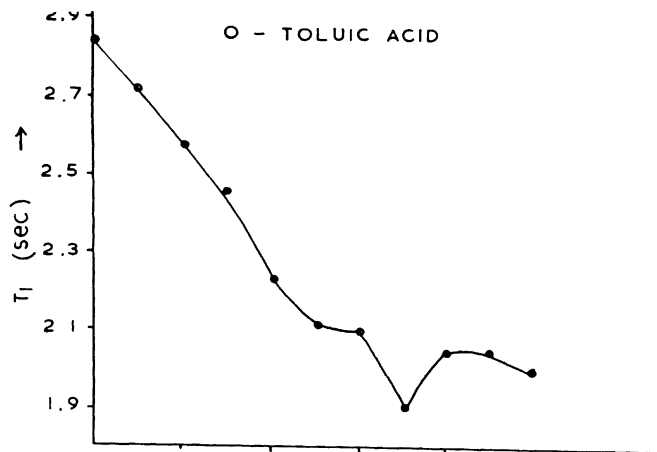


FIG. 7.28

small differences in the variation of (T_1) against solute concentration for the above systems may be attributed to the steric influence of methyl groups in ortho and meta positions of toluic acid (7).

These observations are in general agreement with the results obtained in ultrasonic studies (7). The results obtained in solutions of O-toluic acid in dioxan are similar to the results in M-toluic acid in dioxan. The relaxation times T_1 shows a minimum at 0.08 mf solute concentration indicating the formation of strong hydrogen bonds. In the figure 7.28, it can be seen that the chemical shift also shows a broad maximum around 0.08 mf solute concentration. The peak observed at 0.11 mf cannot be explained and needs further study. This results generally confirm the earlier ultrasonic observations.

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