

ON THE RAMAN SPECTRA OF DILUTE SOLUTIONS OF
PARA- AND METACHLOROTOLUENE

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(Plate 3)

ABSTRACT. The Raman spectra of 5% and 20% solutions of para- and meta-chlorotoluene in carbon tetrachloride have been studied using a spectrograph of high resolving power and a suitable filter to suppress the continuous background in the spectra and these have been compared with the spectrum of the pure liquid. It has been observed that the Raman frequency 1092 cm^{-1} of *p*-chlorotoluene increases to 1098 cm^{-1} in the case of the 5% solution and the Raman lines 683 cm^{-1} and 996 cm^{-1} of *m*-chlorotoluene shift to 688 cm^{-1} and 1000 cm^{-1} respectively when the strength of the solution is reduced to 5%. It has been concluded that in the 5% solution in both the cases the molecules are monomeric while in the pure liquid they are dimers formed through hydrogen bond.

I N T R O D U C T I O N

Numerous workers studied previously the influence of solvents on the Raman spectra of organic molecules (Gray and Hidalgo, 1952; Feneant, 1952; Puranik, 1952; Bollamy 1959; Rea, 1960 and others). The changes in the spectra observed by most of the previous workers are due to association or formation of hydrogen bond. The strengths of the solution used in some of these investigations are generally not below 20%, because it is difficult to record the Raman spectra of very dilute solutions owing to the presence of strong continuous background in the overexposed spectrum of the light scattered by the solvent. In the investigation on the infra-red spectra of such compounds, however, the strengths of the solutions used range generally from 3 to 5%, but unless a careful comparison of such a spectrum is made with that of the pure liquid slight shifts of the bands which may take place owing to the influence of the solvent may sometimes be overlooked.

Recently, Mukherjee *et al.* (1965) observed by recording the infrared spectra of each of a few substituted toluenes in the vapour and liquid phases on the same chart that the molecules of the meta- and para compounds in the liquid state are dimeric and even in the vapour state certain percentages of these molecules are dimers and the rest are monomers. The shift of certain bands with the formation of the dimers observed by them are small, being of the order of about 4 cm^{-1} — 10 cm^{-1} . In the case of dilute solution in carbon tetrachloride they observed the

dimers to be broken up into monomers. In order to verify these results by studying the Raman spectra of these compounds it would be necessary to record the spectra due to very dilute solutions. It was therefore thought worthwhile to study the Raman spectra of such dilute solution of meta- and para chlorotoluene of different strengths in carbon tetrachloride in order to find out whether the shifts of some of the bands observed by Mukherjee *et al.* are also observed in the Raman spectra and whether the conclusions drawn by them are corroborated by such results.

EXPERIMENTAL

The liquids used were taken from the same packing from which Mukherjee *et al.* had taken their samples. Carbon tetrachloride used as solvent was of chemically pure quality and it was redistilled before use. The Raman spectra were photographed using a Hilger two-prism spectrograph provided with medium dispersion camera, the inverse dispersion in the 4358A region being 18A/mm. Agfa 'Isopan' films were used to photograph the spectra. The resolving power of this spectrograph being fairly large shifts of the order of 4 cm^{-1} could be easily detected. A very dilute aqueous solution of NaNO_2 was used to cut off radiations of wavelength shorter than 4046A in the incident light in order to suppress the continuous background in the spectrum.

RESULTS AND DISCUSSION

The spectrograms are reproduced in Figs. 1 and 2, Plate 3. The changes observed in the positions of some of the Raman lines are shown in Table I.

TABLE I
Changes in Raman frequencies

Substance	Raman frequencies in cm^{-1}			Assignment (corresponding modes of C_6H_6)
	State			
	Pure	20% Soln. in CCl_4	5% Soln. in CCl_4	
<i>p</i> -Chlorotoluene	1091 (5) p	1092 (s)	1098 (s)	19 A
<i>m</i> -Chlorotoluene	683 (7) p	683 (b)	688 (w)	9 B
	996 (10) p	996 (b)	1000 (s)	1

p-polarised s-sharp w-weak b-broad

It can be seen from Fig. 1 that the line 1092 cm^{-1} of pure para chlorotoluene appears unaltered in position and width in the spectrum due to the 20% solution

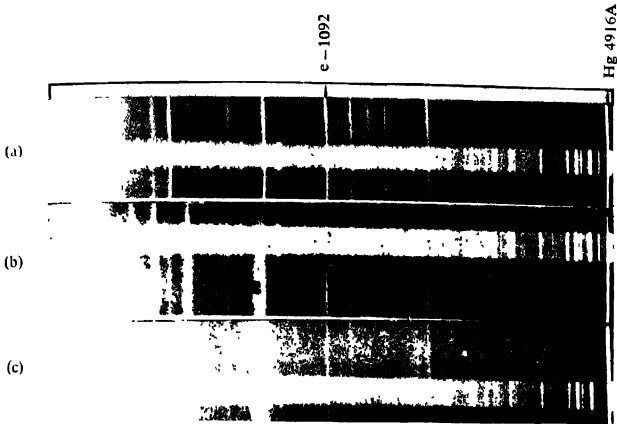


Fig. 1. Raman spectra of *p*-chlorotoluene
(a) Pure liquid (b) 20% Solution in CCl₄ (c) 5% Solution in CCl₄

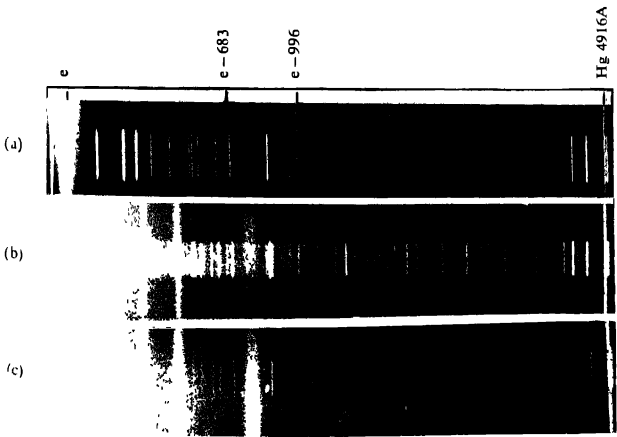


Fig. 2. Raman spectra of *m*-chlorotoluene
(a) Pure liquid (b) 20% Solution in CCl₄ (c) 5% Solution in CCl₄

in carbon tetrachloride so that it coincides with a line 4576.2A in the iron arc spectrum as in the spectrum due to the pure liquid, but in the case of the 5% solution the line shifts slightly towards red so that the Raman shift increases to 1098 cm^{-1} . This can also be seen by measuring the distance of the line from the iron line 4556.13A. In the infrared spectrum of the compound in the vapour phase Mukherjee *et al.* (1965) observed two bands at 1088 and 1096 cm^{-1} but the liquid was found to give only one band at 1088 cm^{-1} . Hence the conclusion drawn by them that in the vapour phase some of the molecules are in monomeric state giving the band 1096 cm^{-1} and the rest are dimers is corroborated by the results mentioned above, because in the 5% solution in carbon tetrachloride all the dimeric molecules are expected to be split up into monomeric ones giving the line 1098 cm^{-1} . The fact that no change is observed in the case of the 20% solution shows that only at very low concentration the molecules are truly dissolved in the solvent and exist as monomers. Owing to the presence of the strong Raman lines of carbon tetrachloride in the spectrum due to the solution changes in some other Raman lines could not be observed, but the spectra show that the line 3062 cm^{-1} does not undergo any change probably because in the formation of the hydrogen bond only one of the four hydrogen atoms is involved.

Fig. 2 shows more significant differences between the spectrum due to *m*-chlorotoluene in the liquid and that of the solution. The sharp line 683 cm^{-1} of the liquid broadens towards red in the spectrum due to the 20% solution and it again becomes sharp but appears at 688 cm^{-1} in the spectrum due to the 5% solution. Similarly, the line 996 cm^{-1} becomes broad in the spectrum due to the 20% solution and it appears as a sharp line at 1000 cm^{-1} in the spectrum due to the 5% solution. Assuming the line 1000 cm^{-1} to be due to the monomeric molecule, it is concluded that the 20% solution contains a mixture of both monomeric and dimeric molecules. These results further corroborate the conclusions drawn by Mukherjee *et al.*, that the compound in the vapour phase consists of a mixture of monomeric and dimeric molecules.

The results discussed above lead to the conclusion that in both the liquids only dimeric molecules formed through hydrogen bond are present and they persist in the solution unless the strength is reduced to about 5%.

It may be pointed out here that the influence of the solvent observed in the present case is different from that observed by Gray and Hidalgo (1952) in the case of dilute solutions of acetophenone in carbon tetrachloride and cyclohexane. They observed that the 1684 cm^{-1} line of the $\text{C}=\text{O}$ group of acetophenone shifts to 1690 cm^{-1} in the case of a solution containing 5 Mols in 100 Mols of carbon tetrachloride, but in the case of similar solution in cyclohexane the line was found to shift to 1695 cm^{-1} . They attributed the shift to the breaking up of the anti-parallel alignment of the two $\text{C}=\text{O}$ groups of the two neighbouring molecules,

but in the present case the breaking up of the hydrogen bond between two molecules is postulated.

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