# Fourier-Transform Infrared Spectroscopy Study of Molecular Interactions Between o-Chlorophenol with Cyclic/Acyclic Ethers

*Rajendra N. Shelar,*

Department of Physics,
Smt. Pushpatai Hiray Mahila College,
Malegaon Camp Nashik, Maharashtra, India.

**ABSTRACT**

*Fourier-transform infrared spectroscopy (FTIR) is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIRspectrometer simultaneously collects high-spectral-resolution data over a wide spectral range.FTIR relies on the fact that the most molecules absorb light in the infra-red region of the electromagnetic spectrum. This absorption corresponds specifically to the bonds present in the molecule. The frequency range is measured as wave numbers typically over the range 4000 – 400 cm-1.*
*FTIR spectra of binary mixture of o-chlorophenol (OCP) with diethyl ether (DEE), 1, 4 dioxane (DN) and tetra hydrofuran (THF) have been recorded over the entire composition range atroom temperature. The study indicated bonding interaction between the components of liquid mixtures.*

**Keywords:** FTIR, o-Chlorophenol, Ethers, Interactions.

## INTRODUCTION:

As a continuation of our ongoing program of research on thermodynamics, acoustic and transport properties of mixtures of OCP with some cyclic and acyclic ether, We have recently reported viscosities, densities, excess volume and excess viscosity of above binary systems1. The excess thermodynamic functions for the binary mixtures of OCP with DEE, DN and THF have provided evidence for the presence of specific interactions between the components of liquid mixtures. We are not aware of any spectroscopic studies in the literature for the present systems.
Hydrogen bonding is of central importance in the molecular sciences for both; practical and theoretical reasons2-4. It represents the strongest force governing the influence of solvent on molecular structure and reactivity and a quantitative accounting for hydrogen bondinginteractions is a prerequisite for the proper understanding of chemical activity in solution. Hydrogen bonding has held particular interest in recent years due to the central role, it plays with regard to molecular recognition in both; biological and artificial systems5,6. There has been increasing interest in C-H--O hydrogen bonds recently, both theoretically and experimentally7. Because carbon is not particularly electronegative, the ability of the C-H group to serve as a proton donor in hydrogen bonding depends on the carbon hybridization [C (sp)-H > C (sp2)-H > C (sp3)-H] and on the electron-withdrawing strength of adjacent substituents. Although the C-H---O interaction energy varies and is muchweaker than conventiona! hydrogen bonds, it can play important role in molecular conformation, crystal packing and protein folding. Close C-H--O contacts have been observed widely in high resolution protein structures. IR spectroscopy is the leading method for identification of hydrogen bond8. For instance, the formation of an O-H--O hydrogen bond elongates and weakens the O---H bond. The resulting red shift of the O--H bond stretching frequency can be easily detected in the IR spectra and itsmagnitude indicates the strength of the hydrogen bond. Solvent structure determines the nature of molecular interactions. Spectral changes are caused by hydrogen bonding, vander Waals interactions, dipole-dipole interactions, induced-dipole interactions etc. Information about hydrogen bonding is derived from the band width, position and intensity of the first overtone bands of the -OH band (intensity of the first overtone band decreases) 9.

## EXPERIMENTAL:

All chemicals were used of A.R. grade (SRL) with purity > 90% and used as such.Binary mixtures of OCP with

DEE, DN and THF were prepared by mixing a known mass of each liquid in airtight stoppered glass bottle with precision 0.01 mg and care was taken to avoid evaporation and contamination during the mixing process. The uncertainty in the mole fraction is ± 0.0001. The measurements were recorded on a digital balance (SHIMAZ AUX 220) to an accuracy of ± 1 × 10–4 g. Different compositions of mixtures (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9) were obtained by adding the second component to the standard sample and weighing the added amount. FTIR spectra were recorded on a FTIR spectrometer (Model: SHIMADZU 8400S PC) by using KBr pellet in the region 400-4000 cm-1 with 4.0 cm-1 resolution. The transmission values were read in steps of 5%. The spectrometer possesses out to aligned energy optimization and dynamically aligned interferometer. It is fitted with KBr beam splitter, a DLATGS detector. A base line correction was made for the spectra recorded.

## RESULTS AND DISCUSSION:

The FTIR frequencies of the binary mixtures of OCP with ethers over the entirerange of compositions at room temperature are listed in Tables 1-5.

### OCP + Ether systems:

### O-H stretching vibrations:

The non-hydrogen-bonded hydroxyl group of phenols absorbs strongly in the 3584-3700 cm-1 region. The sharp free hydroxyl bands are observed in the vapour phase, in verydilute solution in non-polar solvent10. Intermolecular hydrogen bonding increases as theconcentration of solution increases and additional bands appears at lower frequencies at3200-3550 cm-1. In our investigation, magnitude of IR frequencies is more for the binarymixtures OCP + DEE at all compositions as compared to the other binary systems. Itremains same for OCP + THF from mole fraction x1 ≈ 0.2 to 0.7 and maximum at 0.9. It is observed from Table 1 that there are variations inmagnitude for the system OCP + DN.

**Table 1: IR stretching frequencies of -OH (cm-1) in (x1) OCP and (1-x1) ethers systems.**

| 1 | OCP+DEE | OCP+DN | OCP+THF |
|---|---|---|---|
| 0 | -- | -- | -- |
| 0.1 | 3620.51 | 3278.76 | 3230.87 |
| 0.2 | 3539.49 | 3280.69 | 3246.31 |
| 0.3 | 3549.49 | 3278.76 | 3221.23 |
| 0.4 | 3537.57 | 3419.56 | 3259.81 |
| 0.5 | 3539.49 | 3284.55 | 3219.30 |
| 0.6 | 3539.49 | 3298.05 | 3221.23 |
| 0.7 | 3537.57 | 3315.41 | 3225.09 |
| 0.8 | 3541.42 | 3521.78 | 3427.62 |
| 0.9 | 3537.57 | 3521.78 | 3446.90 |
| 1.0 | 3621 | 3621 | 3621 |

### C-H stretching vibrations:

From Table 2, it is observed that the IR absorption frequencies are same for OCP +DN and OCP+THF systems within compositions x1≈ 0.1-0.9. An irregular trend is observed within mole fractions 0.1-0.8 for the systemOCP + DEE. The overall magnitude of C-H stretching vibrations is OCP + DEE > OCP +THF > OCP + DN.

**Table 2: IR stretching frequencies of C-H (cm-1) in (x1) OCP and (1-x1) ethers systems.**

| $X_1$ | OCP+DEE | OCP+DN | OCP+THF |
|---|---|---|---|
| 0 | 2979<br>2868 | 2963<br>2866 | 2975<br>2865 |
| 0.1 | 3020.63 | 2854.45 | 2972.40 |
| 0.2 | 2978.19 | 2854.45 | 2978.19 |
| 0.3 | 2978.19 | 2854.45 | 2976.26 |
| 0.4 | 3018.70 | 2864.09 | 2974.33 |
| 0.5 | 2980.12 | 2858.31 | 2978.19 |
| 0.6 | 2980.12 | 2858.31 | 2978.19 |

| $X_1$ | OCP+DEE | OCP+DN | OCP+THF |
|---|---|---|---|
| 0.7 | 2982.05 | 2860.24 | 2978.19 |
| 0.8 | 3020.63 | 2860.24 | 2978.19 |
| 0.9 | 3018.70 | 2862.17 | 2980.12 |
| 1.0 | 3078 | 3078 | 3078 |

**C=C stretching vibrations:**
Regular trends are observed for all the studied systems. The magnitude offrequencies is same for all systems. Generally strong bands are seen in all systems(Table 3).

**Table 3 IR stretching frequencies of C=C (cm-1) in (x1) OCP and (1-x1) ethers systems.**

| $X_1$ | OCP+DEE | OCP+DN | OCP+THF |
|---|---|---|---|
| 0 | -- | -- | -- |
| 0.1 | 1483.31 | 1483.16 | 1483.31 |
| 0.2 | 1481.38 | 1481.23 | 1481.38 |
| 0.3 | 1481.38 | 1481.23 | 1481.38 |
| 0.4 | 1481.38 | 1481.23 | 1481.38 |
| 0.5 | 1479.45 | 1481.23 | 1481.38 |
| 0.6 | 1481.38 | 1481.23 | 1481.38 |
| 0.7 | 1481.38 | 1481.23 | 1481.38 |
| 0.8 | 1479.45 | 1481.23 | 1481.38 |
| 0.9 | 1481.38 | 1479.30 | 1479.45 |
| 1.0 | 1480 | 1480 | 1480 |

**C-O stretching vibrations:**
No particular trend is observed for the OCP + DEE system. It is seen from the Table 4
that the IR absorption frequencies are constant for system OCP + DN and OCP + THF for all the compositions, IR absorption frequencies increased in the sequence :OCP+DEE > OCP+DN > OCP+THF. The same trend was observed in case of the variations of excess volume withmole fractions1.

**Table 4: IR stretching frequencies of C-O (cm-1) in (x1) OCP and (1-x1) ethers systems.**

| $X_1$ | OCP+DEE | OCP+DN | OCP+THF |
|---|---|---|---|
| 0 | 1126<br>1077 | 1254<br>1124 | 1184<br>1070 |
| 0.1 | 1219.05 | 1120.56 | 1062.81 |
| 0.2 | 1111.03 | 1122.49 | 1055.10 |
| 0.3 | 1219.05 | 1120.56 | 1057.03 |
| 0.4 | 1217.12 | 1118.64 | 1055.10 |
| 0.5 | 1195.91 | 1122.49 | 1055.10 |
| 0.6 | 1294.28 | 1120.56 | 1053.17 |
| 0.7 | 1294.28 | 1120.56 | 1055.10 |
| 0.8 | 1292.35 | 1120.56 | 1055.10 |
| 0.9 | 1220.98 | 1191.93 | 1055.10 |
| 1.0 | 1190<br>1029 | 1190<br>1029 | 1190<br>1029 |

**C-Cl stretching vibrations:**
All frequencies are of equal magnitude atall mole fractions for the system OCP + DN and OCP + THF. In case of OCP + THF system, it remains the same for x1≈ 0.2-0.8 and a slight variation is observed for OCP +DEE system. Strong absorption bands are recorded atall mole fractions for the system OCP + DEE, (Table 5).

**Table 5: IR stretching frequencies of C-Cl (cm-1) in (x1) OCP and (1-x1) ethers systems.**

| $X_1$ | OCP+DEE | OCP+DN | OCP+THF |
|---|---|---|---|
| 0 | -- | -- | -- |
| 0.1 | 785.05 | 754.12 | 752.26 |
| 0.2 | 839.06 | 754.12 | 750.33 |
| 0.3 | 785.05 | 754.12 | 750.33 |
| 0.4 | 777.34 | 748.33 | 750.33 |
| 0.5 | 731.05 | 752.19 | 750.33 |
| 0.6 | 833.28 | 750.26 | 750.33 |
| 0.7 | 835.21 | 750.26 | 750.33 |
| 0.8 | 790.84 | 750.26 | 750.33 |
| 0.9 | 785.05 | 748.33 | 748.41 |
| 1.0 | 748 | 748 | 748 |

Figs. (1 to 3) shows IR stretching frequencies of -OH (cm-1) for OCP + DEE, OCP+ DN and OCP + THF systems.Spectrum of some ether shows two absorption bands. The sharp band is due to free -OH while weak band is due to hydrogen bonded -OH.The OCP results in O-H stretching and C-O stretching. These vibrations are sensitiveto hydrogen bonding. The C-O stretching and O-H bending modes are not independentvibrational modes because they couple with the vibrations of adjacent groups11. The O-Hstretching frequency of OCP is 3621 cm-1, which decreases with ethers because ofintermolecular hydrogen bonding between them. The decrease in -OH stretching frequencyis not same in all concentrations of OCP + ether systems. The binaries OCP + DN andOCP + THF shows large decrease in the -OH stretching frequencies, because phenolic –OHof OCP form strong intermolecular hydrogen bonding and -O-H is more stretched and hence,frequency decreases but in other binary systems OCP + DEE the decrease is less ascompared to others, due to weak intermolecular H-bonding because of bulkier alkyl group inethers.

**Fig 1: IR stretching frequencies of -OH (cm-1) for OCP+DEE system.**

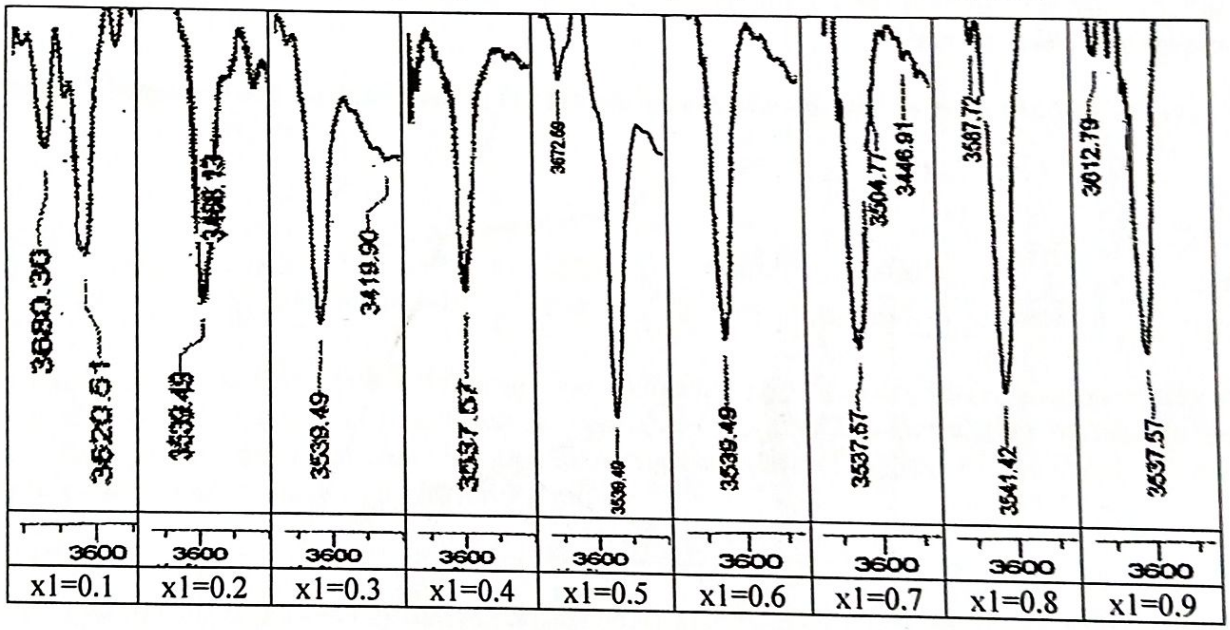


**Fig 2: IR stretching frequencies of -OH (cm-1) for OCP+DN system.**

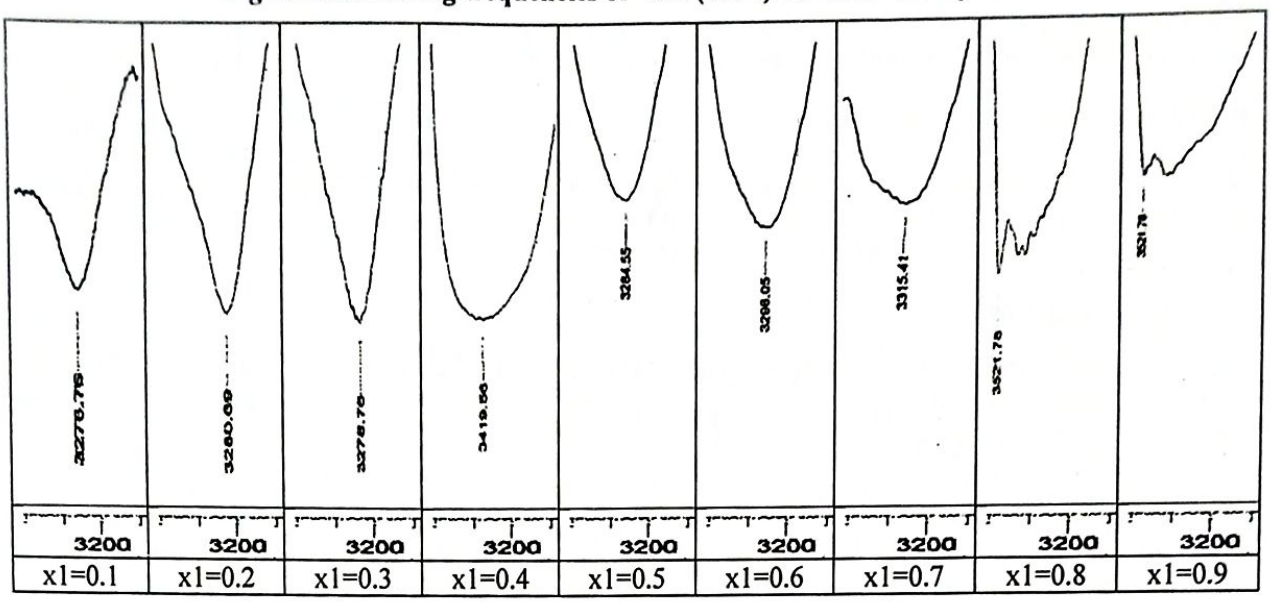
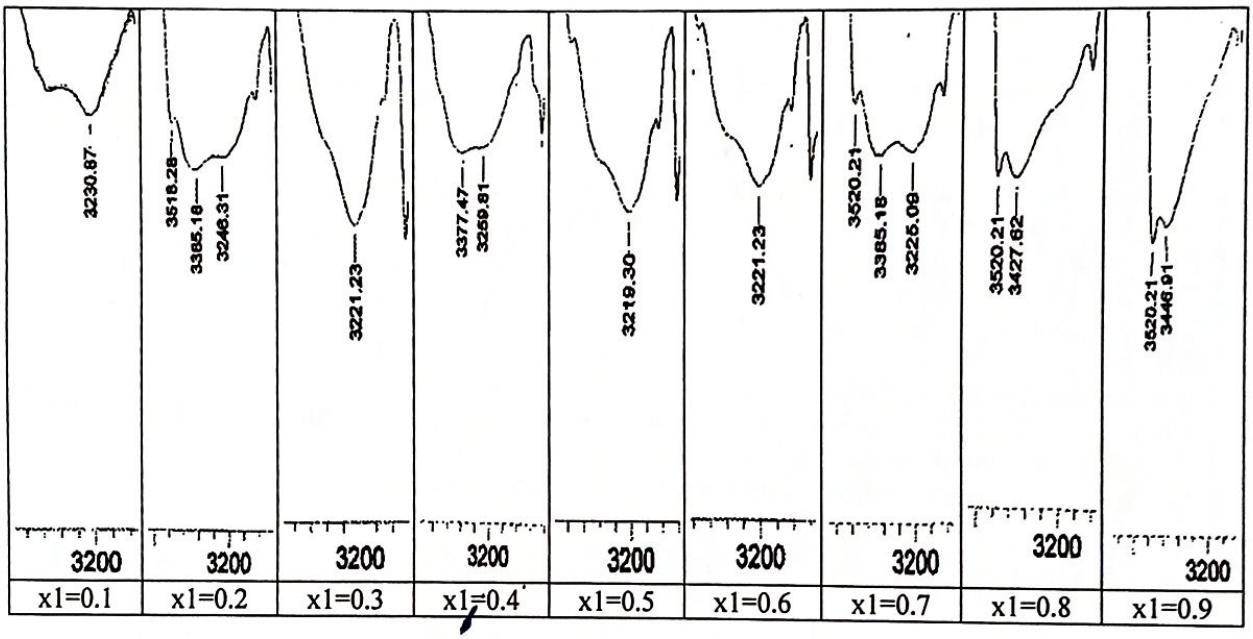



**Fig 3: IR stretching frequencies of -OH (cm-1) for OCP + THF system.**




Hydrogen bonding alters the force constant of groups involved in hydrogen bondinghence, both; stretching and bending vibration of group changes. Intermolecular hydrogenbonding causes association of two or more molecules of same or different compounds i.e.dimerization/polymerization of molecules. The bands that result from intermolecularhydrogen bonding appear at lower value.

## CONCLUSION:

Present study confirms the presence of hydrogen bonding between -OH of OCP with oxygen of studied ethers.

## REFERENCES:

R. N. Shelar, V. S. Savale, R. Y. Borse, Mehdi Hasan and A. B. Sawant, Indian J.Pure Appl. Phys., 45, 552 (2008).
G. C. Pimemental and A. L. McClellan, The Hydrogen Bond, W. H. Freeman, SanFrancisco (1990).
M. D. Josesten and L. Schaad, Hydrogen Bonding, Marcel Dekker, New York (1974).
S. N. Vinogradav and R. H. Linnell, Hydrogen Bonding, Van Nostand Reinhold, NewYork (1971).
G. C. Pimemental, A. L. McClellan and W. H. Freeman, The Hydrogen Bond, SanFrancisco (1960).

P. S. Kalsi, Spectroscopy of Organic Compounds, New Age International Publishers,New Delhi (2008).
R. D. Green, Hydrogen Bonding by C-H Groups, Willey, New York (1974).
G. A. Jeffery and W. Saenger, Hydrogen Bonding in Biological Structures, Springer-Verlag, Berlin (1991).
U. B. Kadam, Mehdi Hasan and A. B. Sawant, Int. J. Chem. Sci., 4(2), 458 (2006).
R. M. Silverstein and F. X. Webster, Spectrometric Identification of OrganicCompounds, 6th Edn., John Wiley & Sons, Inc., New York (2006).
V. Krishnakumar, R. John Xavier and V. Balachandra, Spectrochim Acts A, 65, 147(2006).

---