FTIR STUDY OF MOLECULAR INTERACTIONS BETWEEN o-CHLOROPHENOL WITH DIISOPROPYL ETHER, DIPHENYL ETHER AND TERT-BUTYLMETHYL ETHER

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ABSTRACT

FTIR spectra of binary mixture of o-chlorophenol (OCP) with diisopropyl ether (DIPE), diphenyl ether (DPE) and t-butyl methyl ether (TBME) have been recorded over the entire composition range at room temperature. The study indicated bonding interaction between the components of liquid mixtures.

Key words: 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 systems[1]. The excess thermodynamic functions for the binary mixtures of OCP with DIPE, DPE and TBME 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 reasons[2-4]. It represents the strongest force governing the influence of solvent on molecular structure and reactivity and a quantitative accounting for hydrogen-bonding interactions is a prerequisite for the proper understanding of chemical activity

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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 systems[5,6].

There has been increasing interest in C-H--O hydrogen bonds recently, both theoretically and experimentally[7]. 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 (sp^2)-H > C (sp^3)-H] and on the electron-withdrawing strength of adjacent substituents. Although the C-H---O interaction energy varies and is much weaker than conventional 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 bond[8]. 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 its magnitude indicates the strength of the hydrogen bond. Solvent structure determines the nature of molecular interactions. Spectral changes are caused by hydrogen bonding, van der 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 DIPE, DPE and TBME 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 entire range 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 very dilute solution in non-polar solvent[10]. Intermolecular hydrogen bonding increases as the concentration of solution increases and additional bands appears at lower frequencies at 3200-3550 cm^{-1}. In our investigation, magnitude of IR frequencies is more for the binary mixtures OCP + DPE at all compositions as compared to the other binary systems. It remains same for OCP + DIPE from mole fraction $x_1 \approx 0.2$ to 0.7 and maximum at 0.9, while minimum at 0.1. It is observed from Table 1 that there are not much variations in magnitude for the system OCP + DPE.

Table 1: IR stretching frequencies of -OH (cm^{-1}) in (x_1) OCP and (1-x_1) ether systems

x_1	OCP + DIPE	OCP + DPE	OCP + TBME
0	-	-	-
0.1	3207.73	3525.63	3440.8
0.2	3217.37	3525.63	3421.5
0.3	3217.37	3523.70	3438.8
0.4	3217.37	3523.70	3425.3
0.5	3217.37	3523.70	3219.0
0.6	3217.37	3523.70	3224.8
0.7	3217.37	3521.78	3222.8
0.8	3225.91	3519.85	3438.8
0.9	3525.91	3519.85	3446.6
1.0	3621	3621	3621

C-H stretching vibrations

From Table 2, it is observed that the IR absorption frequencies are same for OCP +

TBME system within compositions $x_1 \approx$ 0.2-0.9 and at composition $x_1 \approx$ 0.2-0.6 for system OCP + DIPE. An irregular trend is observed within mole fractions 0.1-0.9 for the system OCP + DPE. The overall magnitude of C-H stretching vibrations is OCP + DIPE $\approx$ OCP + TBME > OCP + DPE.

Table 2: IR stretching frequencies of C-H (cm^{-1}) in (x_1) OCP and (1-x_1) ether systems

x_1	OCP + DIPE	OCP + DPE	OCP + TBME
0	2973	3040	2977
0.1	2978.19	2925.81	2925.8
0.2	2976.26	2925.81	2976.0
0.3	2976.26	2925.81	2976.0
0.4	2976.26	2927.74	2976.0
0.5	2976.26	2925.81	2976.0
0.6	2976.26	2929.67	2976.0
0.7	2974.33	2869.88	2976.0
0.8	2974.33	2869.88	2976.0
0.9	2976.26	2956.67	2976.0
1.0	3078	3078	3078

C=C stretching vibrations

Irregular trends are observed for all the studied systems. The magnitude of frequencies is more for OCP + DPE system. Generally strong bands are seen in all systems (Table 3).

Table 3: IR stretching frequencies of C=C (cm^{-1}) in (x_1) OCP and (1-x_1) ether systems

x_1	OCP + DIPE	OCP + DPE	OCP + TBME
0	-	1487	-
0.1	1465.95	1485.09	1481.2
0.2	1481.38	1485.09	1479.3
0.3	1465.95	1485.09	1479.3
0.4	1477.52	1483.16	1481.2

x_1	OCP + DIPE	OCP + DPE	OCP + TBME
0.5	1481.38	1483.16	1479.3
0.6	1481.38	1483.16	1481.2
0.7	1481.38	1483.16	1481.2
0.8	1479.45	1481.23	1481.2
0.9	1479.45	1479.30	1481.2
1.0	1480	1480	1480

C-O stretching vibrations

No particular trend is observed for the studied systems. It is seen from the Table 4 that the IR absorption frequencies increased in the sequence : OCP + DPE > OCP + DIPE > OCP + TBME. The same trend was observed in case of the variations of excess volume with mole fractions[1].

Table 4: IR stretching frequencies of C-O (cm^{-1}) in (x_1) OCP and ($1-x_1$) ether systems

x_1	OCP + DIPE	OCP + DPE	OCP + TBME
0	1016	1237	1085
0.1	1120.68	1236.29	1193.9
0.2	1126.47	1236.29	1193.9
0.3	1116.82	1234.36	1193.9
0.4	1126.47	1238.21	1195.8
0.5	1193.98	1238.21	1195.8
0.6	1192.05	1238.21	1195.8
0.7	1192.05	1238.21	1193.8
0.8	1197.83	1240.14	1193.9
0.9	1197.83	1247.86	1195.8
1.0	1199	1199	1199

C-Cl stretching vibrations

All frequencies are of equal magnitude and strong absorption bands are recorded at all mole fractions for the system OCP + TBME and OCP + DPE. In case of OCP + DPE

system, it remains the same for $x_1 \approx$ 0.1-0.7 and a slight variation is observed for OCP + DIPE system (Table 5).

Table 5: IR stretching frequencies of C-Cl (cm^{-1}) in (x_1) OCP and (1-x_1) ether systems

x_1	OCP + DIPE	OCP + DPE	OCP + TBME
0	-	-	-
0.1	748.41	750.26	750.3
0.2	748.41	750.26	750.3
0.3	748.41	750.26	750.3
0.4	748.41	750.26	750.3
0.5	750.33	750.26	750.3
0.6	750.33	750.26	750.3
0.7	750.33	750.26	750.3
0.8	750.33	748.33	750.3
0.9	748.41	748.33	750.3
1.0	748	748	748

Figs. (1 to 3) shows IR stretching frequencies of -OH (cm^{-1}) for OCP + DIPE, OCP + DPE and OCP + TBME 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 sensitive to hydrogen bonding. The C-O stretching and O-H bending modes are not independent vibrational modes because they couple with the vibrations of adjacent groups[11]. The O-H stretching frequency of OCP is 3621 cm^{-1}, which decreases with ethers because of intermolecular hydrogen bonding between them. The decrease in -OH stretching frequency is not same in all concentrations of OCP + ether systems. The binaries OCP + DIPE and OCP + TBME shows large decrease in the -OH stretching frequencies, because phenolic -OH of OCP form strong intermolecular hydrogen bonding and -O-H is more stretched and hence, frequency decreases but in other binary systems OCP + DPE the decrease is less as compared to others, due to weak intermolecular H-bonding because of bulkier alkyl group in ethers.
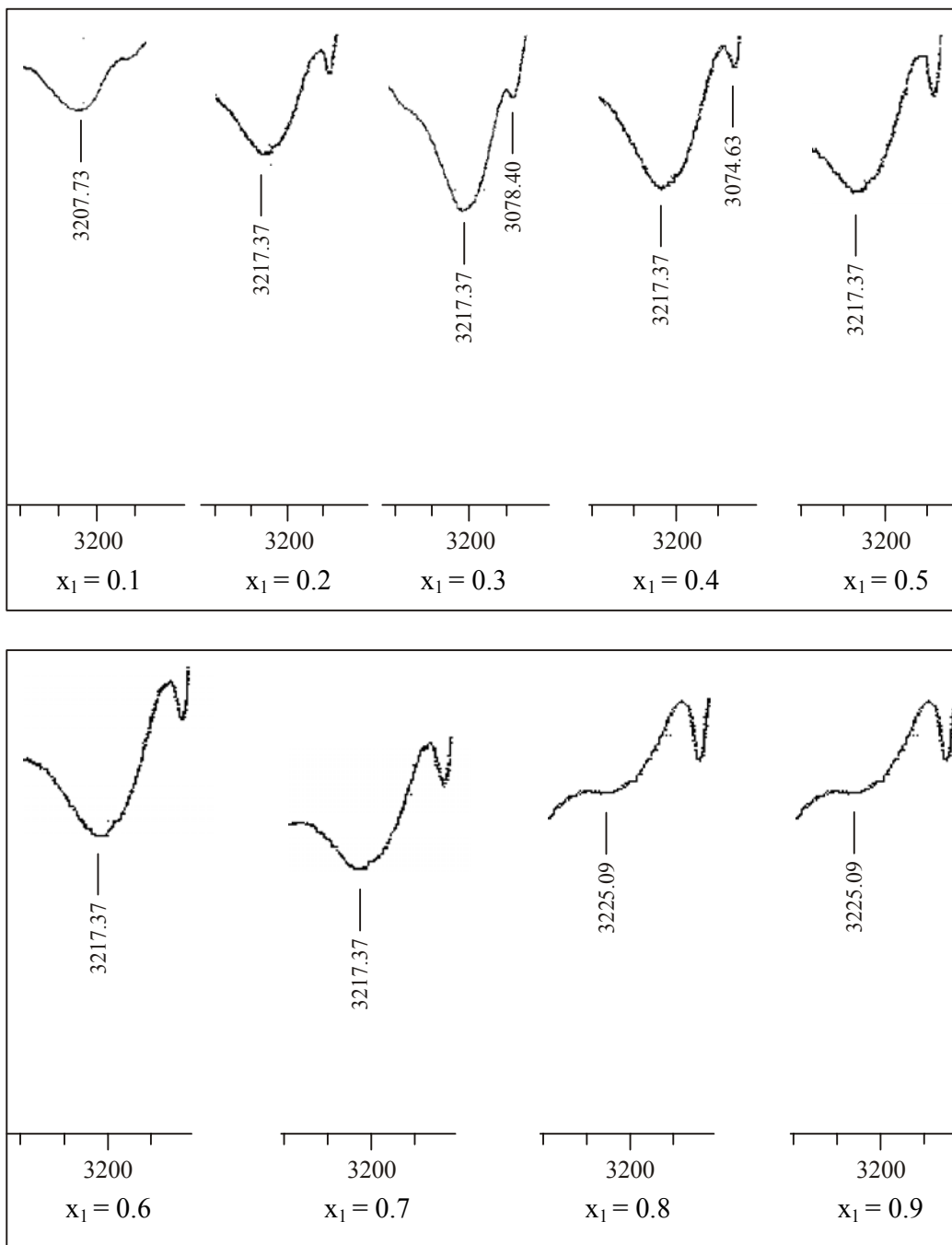
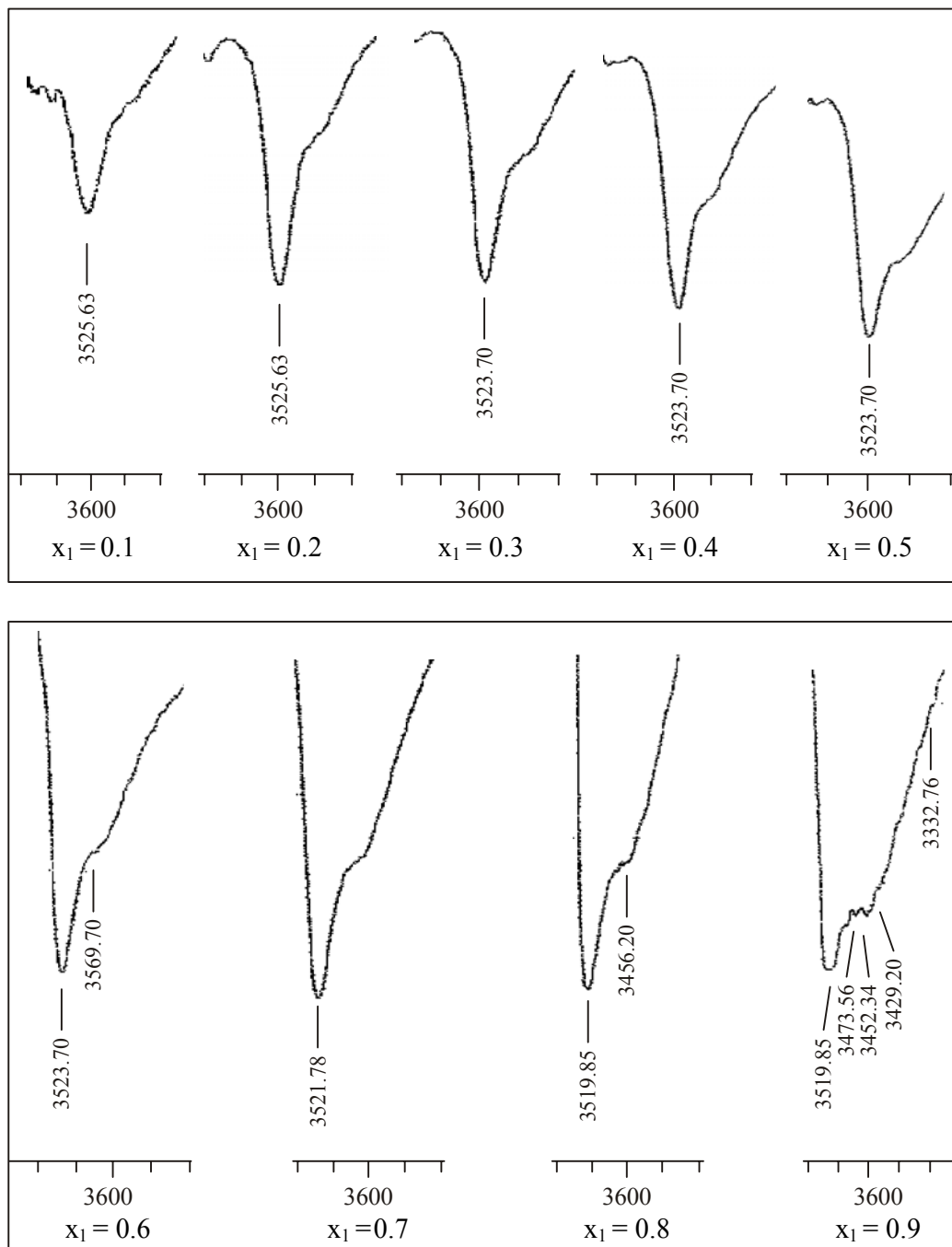**Fig. 1: IR Stretching frequencies of -OH (cm^{-1}) for OCP + DIPE system**

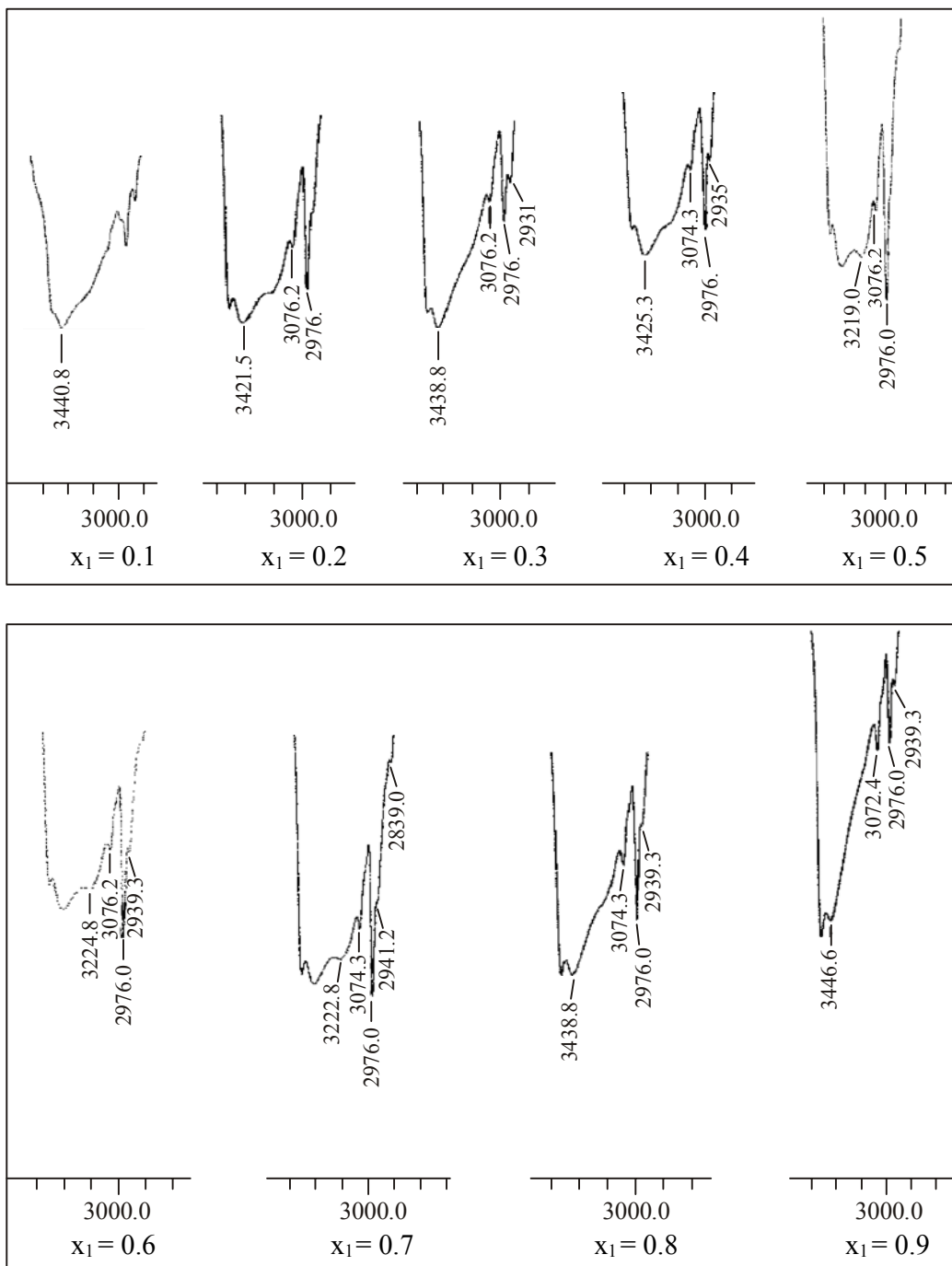**Fig. 2: IR Stretching frequencies of -OH (cm^{-1}) for OCP + DPE system**

Fig. 3: IR Stretching frequencies of -OH (cm⁻¹) for OCP + TBME system

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

CONCLUSION

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

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