



THERMODYNAMICS AND SPECTROSCOPIC INVESTIGATIONS OF BINARY MIXTURES OF O-CHLOROPHENOL WITH ETHERS

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Abstract

Density and viscosity of o-chlorophenol with tetrahydrofuran, diphenyl ether and tertbutylmethyl ether at the different temperatures and at atmospheric pressure and spectroscopic study at atmospheric temperature and pressure have been measured experimentally. The excess molar volumes and deviation in viscosities have calculated across the mole composition and interpreted for the intra and intermolecular association among like and unlike molecules. The influence of structure of components on the existing interaction has also been revealed by the behaviour of the excess parameters. The sign and magnitude of excess parameters clearly indicate the presence of specific interactions among the components. These parameters have been studied on the basis of dipole-dipole interaction and hydrogen bonding. The molecular structure and vibrational spectra have been investigated by Density Functional Theory (DFT) using standard B3LYP functional and 6-31G (d, p) basis set. Computed values at DFT (B3LYP)/6-31G (d, p) have analyzed and their characterization was made with help of Gauss view visualization program utilizing the data obtained from the Gaussian 03 calculation

Keywords- Thermodynamics, o-Chlorophenol, ethers, Density Functional Theory (DFT). Spectroscopic.

I. INTRODUCTION

Thermodynamic studies of molecular interaction have got significance importance in industry and engineering applications [1, 2]. The measurement of density and viscosity adequately employed in understanding the nature of molecular interactions in pure liquids and liquid mixtures. These measurements are highly sensitive to molecular interaction and can be used to provide qualitative information about the physical nature and strength of molecular interaction in the liquid mixture [3-5]. The relaxation studies of polar molecule in polar solvent have been widely used to study the molecular structure including the molecular interaction in the liquid mixture [6, 7]. Volumetric, viscometric and spectroscopic studies of liquid mixtures have gained much significance in assessing the nature of molecular interactions and investigating the physico-chemical aspects of binary [8,9] liquid mixtures. The sign and magnitude of excess parameters give an insight into the specific interactions between the component molecules [10, 11]. Hydrogen bonded systems are very interesting because hydrogen bond plays a vital role in chemical, physical and biological processes. The choice of o-chlorophenol (OCP) has been based on its limited association through hydrogen bond in pure state. The *cis* isomer in OCP presents an intra-molecular hydrogen bonding of the type O—H---Cl. This fact determines the inability of formation of hydrogen bonding with another molecule of the same kind. The IR spectra of OCP show O—H---Cl bonding between the *cis* and *trans* isomers. Thus, the addition of other components causes the rupture of inter-molecular and intra-molecular hydrogen bonding in OCP which may be followed by association of unlike molecules through new type of specific interaction.

The most frequently spectroscopic methods for organic chemists are Ultra-Violet, Infra-Red, Nuclear Magnetic Resonance and Mass-Spectrometry. I.R. measurement through liquid mixtures

provide an excellent tool to investigate inter and intramolecular interactions between like and unlike molecules.

Recently, a spectroscopic study of a o-Chlorophenol (OCP) with diphenyl ether (DPE), tetrahydrofuran (THF) and t-butyl methyl ether (TBME) has been made and its various vibrational modes have been assigned using simplified picture of the molecule. Due to existence of many vibrations, it would be difficult to assign the observed frequencies to a particular mode. The density functional theory [12] (DFT) methods have become a powerful tool for the investigation of molecular structure and vibrational spectra. Supplemented by a visualization program, the assignments can accurately be made. The present work has been performed with view point of getting the vibrational frequencies on an optimized geometry of the titled compound. These frequencies are analyzed and compared with the experimental data [13]. Attempts have been made to find out an optimum method using a basis set to get a close agreement between the computed and the experimental data. Literature survey shows that no computational studies have been done so far on the titled compound.

2. Experimental Details:

The densities (ρ) of the pure liquid and the mixtures were measured with a pycnometer [14]. The pycnometer bottle was calibrated with triple distilled water. The estimated uncertainty of density measurement of pure liquid and binary mixtures was $\pm 1 \times 10^{-4}$ g.

The dynamic viscosities were measured using ubbelohde suspended level viscometer [14], calibrated with conduction water. An electronic digital stopwatch with accuracy to ± 0.01 s was used for flow time measurement. At least three repetitions of each data reproducible to ± 0.05 s and result were averaged. The uncertainties in dynamic viscosities are of the order of ± 0.003 mPa s.

All the theoretical calculations on OCP and their mixtures with ethers were performed by the use of G03W series of programs. Geometries of optimizations for all of the investigated molecules in this work were carried out using the DFT/B3LYP method with a medium size 6-31G (d, p) basis set.

All of the chemicals used were of A. R. grade. The Sisco chemicals purity was $>99\%$ directly used. The purity of solvent was ascertained by comparing experimental values of densities (ρ) and viscosities (η) with those reported in the literature (Table1). Our experimental values of ρ and η match very well those reported in the literature. Binary mixtures were prepared by mixing of known mass of each liquid in an airtight, stoppered glass bottle. The masses were recorded on digital balance (SHIMAZ, AUX 220) to an accuracy of $\pm 1 \times 10^{-4}$ g. The estimated error in mole fraction was $< 1 \times 10^{-4}$.

3. Computational Details:

Geometry optimization and vibrational frequencies of titled compounds were at the DFT levels with B3LYP (Becke-Lee-Yang-Parr three parameters) hybrid functional with correlation function such as one proposed by Lee, Yang and Parr [15]. B3LYP is most promising in providing reasonable acceptable vibrational wave numbers for organic molecules. Standard 6-311G (d, p) basis set and Gaussian 03 software have been utilized to accomplish all the calculations.

4. Theory:

The measured physical properties of the pure liquid together with literature values are included in Table1. The experimental values of ρ , V^E , η and $\Delta\eta$ at (298-313) K are listed in Tables (2-4) The V^E can be computed from experimental density data using the relationship

$$V^E = (x_1M_1 + x_2M_2) / \rho_m - x_1M_1 / \rho_1 - x_2M_2 / \rho_2 \quad (1)$$

where x_i , M_i , and ρ_i designate the mole fraction, the molecular weight and the density of the component i. ρ_m is the density of mixture. From ρ and flow time (t), the η were obtained using the relation.

$$\eta = \rho (At - B/t) \quad (2)$$

where A and B are viscosity constant. $\Delta\eta$ were obtained as follows

$$\Delta\eta = \eta_{\text{mix}} - (x_1\eta_1 - x_2\eta_2) \quad (3)$$

where η_1 and η_2 are the viscosities of pure component 1 and 2, respectively and η_{mix} is the viscosity of the mixture.

The density functional theory (DFT) methods have become a powerful tool for the investigation of molecular structure and vibrational spectra. Supplemented by a visualization program, the assignments can accurately be made. The present work has been performed with view point of getting an optimized geometry of the titled compound. This program reports energy, dipole moment, charges, vibrational frequencies, bond angle and bond distance. It is also useful tool for calculations on larger and runs calculations very quickly.

5. Results and discussion

Experimental density (ρ), viscosity (η), excess volume (V^E) and deviation in viscosity ($\Delta\eta$) at the experimental temperatures are listed in Tables (2-4).

Fig 1 shows the variation of V^E with mole fraction (x_1) of OCP. The systems OCP+THF, OCP+DPE and OCP+TBME at a given temperatures are under investigation. For system OCP+DPE, V^E is positive over entire compositions range and V^E decreases as the temperature increases. The positive V^E suggests that the dispersion force prevail between OCP with DPE. A peak observed at the mole fraction ≈ 0.4 and 0.6 for all systems at all the temperatures evinces that the self-association of OCP molecules first breaks and then the interaction between unlike components takes place [16-18]. The positive values may be due repulsive forces caused by electronic charges on the component liquids [19]. Such differing trends are attributed to varying interactions depending upon the nature of the second mixing component of the mixture. The V^E in the mixture OCP+THF and OCP+TBME are negative and also are temperature dependent. The V^E remaining negative over entire composition range suggest that, the mixture prefers to have a compact structure in solution [20]. It is also suggest that the component molecules are more close together in the liquid mixture, indicating that strong attractive interaction between component molecules such as hydrogen bonding, dipole-dipole interactions and other specific interaction between unlike molecules are operative in the system [21]. It is observed from Fig1 that V^E values falls in the sequence OCP+TBME < OCP+THF < OCP+DPE for given temperatures.

Figs 2 represent variations of $\Delta\eta$ with x_1 , for binary mixtures of OCP+THF and OCP+TBME shows sigmoid nature at all temperatures. The sigmoid nature of the graph is attributed to the equilibra of state effect. The observed $\Delta\eta$ data of binary mixtures of OCP with THF and TBME, the negative $\Delta\eta$ values in lower region and positive $\Delta\eta$ values in higher region of OCP. For system OCP+THF and OCP+TBME, with further rise in temperature, magnitude of negative $\Delta\eta$ in the lower mole fraction range increases and magnitude of positive $\Delta\eta$ in the higher mole fraction range decreases. The observed $\Delta\eta$ data of binary mixture of OCP + DPE are negative for the whole composition range. Negative $\Delta\eta$ values occur where dispersion or weak dipole – dipole forces are primarily responsible for the interaction between component molecules [22, 23].

All the theoretical calculations on OCP and their mixtures with ethers were performed by the use of G03W series of programs. Geometries of optimizations for all of the investigated molecules in this work were carried out using the DFT/B3LYP method with a medium size 6-31G (d, p) basis set. Optimized geometries are shown in Fig 3 and computed geometrical parameters are listed in Table 5-9

Maximum hydrogen bond distance (O---H) is noted for *Cis* OCP+DPE and minimum distance (i.e. strongest hydrogen bond among complexes) for *Trans* OCP+DPE. Strong intermolecular hydrogen bonds are also observed for, *Cis* /*Trans* OCP + THF, *Trans* OCP + TBME. (Table 5)

Atomic charges (Table 6) unlike the electron density are not a quantum mechanical observable and are not unambiguously predictable. Gaussian jobs perform a Mulliken population analysis, which partitions the total charge among the atoms in the molecule/complex. Mulliken population analysis is an arbitrary scheme for assigning charges. Chlorine atom of *Trans* OCP + DPE showed inversion in sign for *Cis* OCP + DPE. In case of ethers, maximum negative charge is observed for DPE and for complexes; it is maximum for *Cis* OCP + DPE and minimum for *Trans*

OCP+DPE. *Cis* and *Trans* OCP complexes are also having the nearly same magnitude of charge on oxygen. *Cis* OCP+THF showed slight increase and *Trans* OCP + DPE showed decrease in the charge on oxygen of OH. Positive charge on hydrogen atom of –OH maximum in *Cis* OCP + TBME and minimum in *Trans* OCP + DPE.

| System | Temp. (K) | $\rho \times 10^{-3} \text{ (kg m}^{-3}\text{)}$ | | $\eta \times 10^{-3} \text{ (kg m}^{-1} \text{ s}^{-1}\text{)}$ | |
|--------|-----------|--|----------------------|---|---------------------|
| | | Expt. | Lit. | Expt. | Lit. |
| THF | 298 | 0.8782 | 0.8789 ^a | 0.468 | 0.468 ^d |
| | | | 0.87918 ^b | | 0.460 ^c |
| | | | 0.8772 ^c | | |
| | 303 | 0.8760 | 0.87636 ^d | 0.442 | 0.442 ^d |
| | 308 | 0.8682 | 0.86882 ^a | 0.422 | --- |
| 313 | 0.8640 | 0.864 ^b | 0.401 | --- | |
| | | 0.8638 ^b | | | |
| DPE | 298 | 1.0711 | --- | 3.785 | --- |
| | 303 | 1.0661 | 1.0661 ^e | 3.342 | --- |
| | 308 | 1.0623 | 1.0611 ^c | 2.899 | --- |
| | 313 | 1.0579 | --- | 2.456 | 2.4594 ^c |
| TBME | 298 | 0.7357 | 0.73543 ^f | 0.350 | 0.3576 ⁱ |
| | | | 0.7353 ^g | | |
| | | | 0.7356 ^h | | |
| | 303 | 0.7306 | 0.73018 ^f | 0.345 | --- |
| | 308 | 0.7251 | 0.72488 ^f | 0.340 | 0.340 ^j |
| 313 | 0.7203 | 0.71944 ^f | 0.335 | 0.3353 ^k | |
| OCP | 298 | 1.2589 | --- | 2.955 | --- |
| | 303 | 1.2529 | -- | 2.716 | --- |
| | 308 | 1.2472 | --- | 2.483 | --- |
| | 313 | 1.2414 | 1.2410 ^e | 2.250 | 2.250 ^e |

Negative value indicates the stability. For individual molecules, it follows: *Trans* OCP > *Cis* OCP > DPE > TBME > THF. (Table 7). The most stable complexes of OCP + ethers which are in the order: *Cis* OCP + DPE > *Trans* OCP + DPE > *Trans* OCP + TBME > *Cis* OCP + TBME > *Trans* OCP + THF > *Cis* OCP + THF.

Gaussian also predicts dipole moments and higher multipole moments. This term indicates the nature i.e. polar or nonpolar. The dipole moment is the first derivative of the energy with respect to an applied electric field. It is a measure of the asymmetry in the molecular charge distribution and is given a vector in three dimensions. Complexes having maximum dipole moment follow: *Trans* OCP + THF > *Trans* OCP + TBME > *Trans* OCP + DPE > *Trans* OCP + THF > *Trans* OCP + TBME > *Cis* OCP + DPE.

VI. CONCLUSIONS

The strong attractive interactions such as hydrogen bonding, dipole-dipole interactions, dipole-induced dipole interactions and other specific interaction between molecules of the given systems.

| | | | | | |
|-----|--------|--------|-------|---------|---------|
| 308 | | | | | |
| | 0.0000 | 0.8682 | 0.422 | 0.0000 | 0.000 |
| | 0.0981 | 0.9267 | 0.275 | -1.2342 | -34.980 |
| | 0.1999 | 0.9767 | 0.444 | -1.8706 | -38.998 |
| | 0.2943 | 1.0233 | 0.869 | -2.2426 | -15.985 |
| | 0.3970 | 1.0669 | 1.421 | -2.4125 | 18.014 |
| | 0.4992 | 1.1051 | 1.981 | -2.3011 | 53.005 |
| | 0.5908 | 1.1361 | 2.410 | -2.0627 | 77.020 |
| | 0.6916 | 1.1676 | 2.789 | -1.7107 | 94.191 |
| | 0.8025 | 1.1984 | 2.976 | -1.1521 | 90.016 |
| | 0.9011 | 1.2249 | 2.915 | -0.7018 | 64.013 |
| | 1.0000 | 1.2472 | 2.483 | 0.0000 | 0.000 |
| 313 | | | | | |
| | 0.0000 | 0.8640 | 0.401 | 0.0000 | 0.000 |
| | 0.0981 | 0.9242 | 0.207 | -1.4143 | -39.980 |
| | 0.1999 | 0.9770 | 0.341 | -2.1205 | -47.998 |
| | 0.2943 | 1.0213 | 0.719 | -2.5025 | -29.984 |
| | 0.3970 | 1.0639 | 1.285 | -2.6026 | 5.014 |
| | 0.4992 | 1.1025 | 1.809 | -2.5305 | 36.005 |
| | 0.5908 | 1.1343 | 2.224 | -2.3625 | 58.196 |
| | 0.6916 | 1.1652 | 2.564 | -1.9709 | 71.006 |
| | 0.8025 | 1.1967 | 2.767 | -1.4825 | 68.017 |
| | 0.9011 | 1.2204 | 2.794 | -0.8025 | 50.014 |
| | 1.0000 | 1.2414 | 2.501 | 0.0000 | 0.000 |

Table 3 Densities (ρ), Viscosities (η), Excess Molar Volumes (V^E) and Deviation in Viscosities ($\Delta\eta$) for the OCP + DPE system.

| Temp K | x_1 | $\rho \times 10^{-3}$ (kg m^{-3}) | $\eta \times 10^3$ ($\text{kg m}^{-1}\text{s}^{-1}$) | $V^E \times 10^6$ ($\text{m}^3\text{mol}^{-1}$) | $\Delta\eta \times 10^3$ ($\text{kg m}^{-1}\text{s}^{-1}$) |
|-----------|--------|---|---|--|---|
| 298 | 0.0000 | 1.0711 | 3.785 | 0.0000 | 0.000 |
| | 0.1040 | 1.0830 | 3.641 | 0.1644 | -5.787 |
| | 0.2018 | 1.0947 | 3.522 | 0.3507 | -9.638 |
| | 0.3099 | 1.1088 | 3.407 | 0.5572 | -12.085 |
| | 0.3949 | 1.1205 | 3.326 | 0.7432 | -13.128 |
| | 0.5001 | 1.1369 | 3.234 | 0.8825 | -13.546 |
| | 0.5970 | 1.1535 | 3.165 | 0.9900 | -12.438 |
| | 0.6983 | 1.1742 | 3.102 | 0.9365 | -10.287 |
| | 0.8069 | 1.1993 | 3.037 | 0.8106 | -7.798 |
| | 0.8987 | 1.2254 | 2.993 | 0.4776 | -4.608 |
| | 1.0000 | 1.2589 | 2.954 | 0.0000 | 0.000 |

| | | | | | |
|-----|--------|--------|-------|--------|---------|
| 303 | 0.0000 | 1.0661 | 3.342 | 0.0000 | 0.000 |
| | 0.1040 | 1.0782 | 3.234 | 0.1266 | -4.323 |
| | 0.2018 | 0.0903 | 3.135 | 0.2624 | -8.132 |
| | 0.3099 | 1.1043 | 3.042 | 0.4680 | -10.633 |
| | 0.3949 | 1.1164 | 2.981 | 0.5947 | -11.394 |
| | 0.5001 | 1.1331 | 2.910 | 0.7044 | -11.903 |
| | 0.5970 | 1.1500 | 2.860 | 0.7834 | -10.932 |
| | 0.6983 | 1.1704 | 2.816 | 0.7578 | -8.831 |
| | 0.8069 | 1.1960 | 2.777 | 0.5903 | -5.993 |
| | 0.8987 | 1.2206 | 2.744 | 0.3894 | -3.492 |
| | 1.0000 | 1.2529 | 2.715 | 0.0000 | 0.000 |
| 308 | 0.0000 | 1.0623 | 2.899 | 0.0000 | 0.000 |
| | 0.1040 | 1.0745 | 2.819 | 0.0923 | -3.719 |
| | 0.2018 | 1.0865 | 2.751 | 0.2322 | -6.427 |
| | 0.3099 | 1.1006 | 2.682 | 0.4038 | -8.829 |
| | 0.3949 | 1.1128 | 2.638 | 0.5188 | -9.718 |
| | 0.5001 | 1.1293 | 2.590 | 0.6335 | -10.109 |
| | 0.5970 | 1.1461 | 2.558 | 0.7087 | -9.228 |
| | 0.6983 | 1.1664 | 2.533 | 0.6704 | -7.579 |
| | 0.8069 | 1.1913 | 2.515 | 0.5519 | -4.827 |
| | 0.8987 | 1.2162 | 2.497 | 0.3048 | -2.779 |
| | 1.0000 | 1.2472 | 2.483 | 0.0000 | 0.000 |
| 313 | 0.0000 | 1.0578 | 2.456 | 0.0000 | 0.000 |
| | 0.1040 | 1.0702 | 2.399 | 0.0645 | -3.555 |
| | 0.2018 | 1.0822 | 2.355 | 0.1766 | -5.974 |
| | 0.3099 | 1.0965 | 2.315 | 0.3190 | -7.686 |
| | 0.3949 | 1.1087 | 2.294 | 0.4323 | -8.075 |
| | 0.5001 | 1.1253 | 2.273 | 0.5159 | -8.024 |
| | 0.5970 | 1.1421 | 2.262 | 0.5866 | -7.065 |
| | 0.6983 | 1.1626 | 2.257 | 0.5270 | -5.504 |
| | 0.8069 | 1.1871 | 2.257 | 0.4379 | -3.295 |
| | 0.8987 | 1.2113 | 2.263 | 0.2465 | -1.601 |
| | 1.0000 | 1.2414 | 2.250 | 0.0000 | 0.000 |

Table 4 Densities (ρ), Viscosities (η), Excess Molar Volumes (V^E) and Deviation in Viscosities ($\Delta\eta$) for the OCP + TBME system.

| Temp K | x_1 | $\rho \times 10^{-3}$ (kg m^{-3}) | $\eta \times 10^3$ ($\text{kg m}^{-1}\text{s}^{-1}$) | $V^E \times 10^6$ ($\text{m}^3\text{mol}^{-1}$) | $\Delta\eta \times 10^3$ ($\text{kg m}^{-1}\text{s}^{-1}$) |
|-----------|--------|---|---|--|---|
| 298 | 0.0000 | 0.7357 | 0.034 | 0.0000 | 0.000 |
| | 0.0930 | 0.7878 | 0.282 | -1.4956 | -30.903 |
| | 0.2004 | 0.8469 | 0.528 | -2.4917 | -34.803 |
| | 0.2996 | 0.8988 | 1.070 | -2.9629 | -6.003 |
| | 0.4070 | 0.9556 | 1.809 | -3.1558 | 39.996 |
| | 0.5073 | 1.0070 | 2.456 | -2.9431 | 78.496 |
| | 0.6045 | 1.0576 | 3.109 | -2.6764 | 118.496 |
| | 0.7073 | 1.1089 | 3.560 | -2.0337 | 136.885 |
| | 0.7949 | 1.1522 | 3.716 | -1.3656 | 129.575 |
| | 0.9009 | 1.2058 | 3.578 | -0.5849 | 88.225 |
| | 1.0000 | 1.2589 | 2.954 | 0.0000 | 0.000 |

| | | | | | |
|-----|--------|---------|-------|---------|---------|
| 303 | 0.0000 | 0.7306 | 0.344 | 0.0000 | 0.000 |
| | 0.0930 | 0.7836 | 0.217 | -1.7004 | -34.804 |
| | 0.2004 | 0.8443 | 0.447 | -2.9215 | -37.704 |
| | 0.2996 | 0.8967 | 0.926 | -3.4424 | -12.904 |
| | 0.4070 | 0.9535 | 1.577 | -3.6130 | 26.797 |
| | 0.5073 | 1.0054 | 2.183 | -3.4431 | 63.597 |
| | 0.6045 | 1.0553 | 2.687 | -3.0734 | 90.916 |
| | 0.7073 | 1.1065 | 3.163 | -2.4037 | 114.200 |
| | 0.7949 | 1.15031 | 3.282 | -1.7548 | 105.300 |
| | 0.9009 | 1.2036 | 3.126 | -0.9140 | 64.597 |
| | 1.0000 | 1.2529 | 2.715 | 0.0000 | 0.000 |
| 308 | 0.0000 | 0.7251 | 0.340 | 0.0000 | 0.000 |
| | 0.0930 | 0.7801 | 0.181 | -2.0303 | -35.804 |
| | 0.2004 | 0.8416 | 0.396 | -3.3721 | -37.703 |
| | 0.2996 | 1.8939 | 0.744 | -3.8720 | -23.803 |
| | 0.4070 | 0.9522 | 1.351 | -4.2034 | 13.897 |
| | 0.5073 | 1.0041 | 1.894 | -3.9833 | 46.696 |
| | 0.6045 | 1.0530 | 2.390 | -3.4841 | 75.495 |
| | 0.7073 | 1.1048 | 2.779 | -2.8341 | 92.398 |
| | 0.7949 | 1.1486 | 2.897 | -2.1645 | 85.397 |
| | 0.9009 | 1.1990 | 2.856 | -1.0347 | 58.397 |
| | 1.0000 | 1.2472 | 2.483 | 0.0000 | 0.000 |
| 313 | 0.0000 | 0.7203 | 0.335 | 0.0000 | 0.000 |
| | 0.0930 | 0.7759 | 0.132 | -2.1706 | -38.103 |
| | 0.2004 | 0.8385 | 0.322 | -3.6817 | -40.003 |
| | 0.2996 | 0.8913 | 0.637 | -4.2629 | -27.203 |
| | 0.4070 | 0.9502 | 1.144 | -4.6430 | 2.967 |
| | 0.5073 | 1.0027 | 1.619 | 4.4834 | 31.310 |
| | 0.6045 | 1.0516 | 2.092 | -3.9535 | 59.997 |
| | 0.7073 | 1.1040 | 2.444 | -3.3347 | 75.498 |
| | 0.7949 | 1.1471 | 2.571 | -2.5751 | 71.396 |
| | 0.9009 | 1.1948 | 2.542 | -1.1850 | 48.197 |
| | 1.0000 | 1.2414 | 2.250 | 0.0000 | 0.000 |

Table 5 Optimized bond distance (Å) of systems at B3LYP level using 6-31G (d,p) basis set.

| Sr. No | System | O-H (Å) | C-Cl (Å) | H---Cl (Å) | O---H (Å) | O---Cl (Å) |
|--------|-----------------------|---------|----------|------------|-----------|------------|
| 1 | <i>Cis</i> OCP | 0.97881 | 1.83519 | -- | -- | -- |
| 2 | <i>Trans</i> OCP | 0.97634 | 1.81533 | -- | -- | -- |
| 3 | <i>Cis</i> OCP+DPE | 0.98998 | 1.83191 | 3.03111 | 1.82224 | 3.51041 |
| 4 | <i>Cis</i> OCP+THF | 1.00450 | 1.83187 | 3.36626 | 1.66987 | 3.42959 |
| 5 | <i>Cis</i> OCP+TBME | 1.00484 | 1.83176 | 2.71961 | 1.68131 | 3.40766 |
| 6 | <i>Trans</i> OCP+DPE | 1.04941 | 1.81194 | -- | 1.52013 | 5.52896 |
| 7 | <i>Trans</i> OCP+THF | 1.00243 | 1.82142 | -- | 1.64257 | 5.61509 |
| 8 | <i>Trans</i> OCP+TBME | 1.00251 | 1.82088 | 4.98830 | 1.64924 | 5.63344 |

H_(OH of OCP)---Cl_(OCP); Hydrogen bond : O_(ether)---H_(OCP); O_(ether)---Cl_(OCP)

Table 6 Optimized Mulliken atomic charges of systems at B3LYP level using 6-31G (d,p) basis set.

| Sr. No | System | O _(OH) | H _(OH) | Cl _(OCP) | Cl _(ODB) | O _(ether) |
|--------|-----------------------|-------------------|-------------------|---------------------|---------------------|----------------------|
| 1 | <i>Cis</i> OCP | -0.613 | 0.385 | 0.061 | -- | -- |
| 2 | <i>Trans</i> OCP | -0.600 | 0.377 | 0.103 | -- | -- |
| 3 | DPE | -- | -- | -- | -- | -0.614 |
| 4 | THF | -- | -- | -- | -- | -0.527 |
| 5 | TBME | -- | -- | -- | -- | -0.530 |
| 6 | <i>Cis</i> OCP+DPE | -0.659 | 0.441 | 0.059 | -- | -0.682 |
| 7 | <i>Cis</i> OCP+THF | -0.682 | 0.443 | 0.056 | -- | -0.562 |
| 8 | <i>Cis</i> OCP+TBME | -0.677 | 0.447 | 0.056 | -- | -0.570 |
| 9 | <i>Trans</i> OCP+DPE | -0.247 | 0.223 | -1.140 | -- | -0.169 |
| 10 | <i>Trans</i> OCP+THF | -0.662 | 0.429 | 0.072 | -- | -0.579 |
| 11 | <i>Trans</i> OCP+TBME | -0.660 | 0.434 | 0.075 | -- | -0.581 |

Table 7 Optimized energy and dipole moment of systems at B3LYP level using 6-31G(d,p) basis set.

| Sr No | System | Energy (a.u.) | Dipole Moment (Debye) |
|-------|-----------------------|---------------|-----------------------|
| 1 | <i>Cis</i> OCP | -766.9550 | 1.4210 |
| 2 | <i>Trans</i> OCP | -766.9595 | 3.6860 |
| 3 | DPE | -538.3818 | 1.2731 |
| 4 | THF | -232.3713 | 2.2377 |
| 5 | TBME | -272.9014 | 1.5407 |
| 6 | <i>Cis</i> OCP+DPE | -1305.3583 | 1.4612 |
| 7 | <i>Cis</i> OCP+THF | -999.3643 | 3.0228 |
| 8 | <i>Cis</i> OCP+TBME | -1039.8839 | 2.2686 |
| 9 | <i>Trans</i> OCP+DPE | -1289.9895 | 5.7817 |
| 10 | <i>Trans</i> OCP+THF | -999.3650 | 6.2126 |
| 11 | <i>Trans</i> OCP+TBME | -1079.8842 | 6.0799 |

Table 8 Optimized frequencies (scaling factor 0.96) of systems at B3LYP level using 6-31G(d,p) basis set.

| Sr. No | System | -OH stretching frequency theoretical (cm ⁻¹) |
|--------|-------------------------|--|
| 1 | <i>Cis</i> OCP | 3631.95 |
| 2 | <i>Trans</i> OCP | 3671.67 |
| 3 | <i>Cis</i> (OCP+DPE) | 3413.33 |
| 4 | <i>Trans</i> (OCP+DPE) | 3346.42 |
| 5 | <i>Cis</i> (OCP+THF) | 3142.33 |
| 6 | <i>Trans</i> (OCP+THF) | 3170.53 |
| 7 | <i>Cis</i> (OCP+TBME) | 3132.51 |
| 8 | <i>Trans</i> (OCP+TBME) | 3166.16 |

Experimental stretching frequency of -OH: 3621.00 cm⁻¹

Table 9 Optimized bond angle (degree) of systems at B3LYP level using 6-31G (d,p) basis set.

| Sr. No | System | ∠C-O-H (degree) | ∠C-O-C (degree) | ∠C-Cl-H (degree) |
|--------|------------------|-----------------|-----------------|------------------|
| 1 | <i>Cis</i> OCP | 111.66311 | -- | 69.52293 |
| 2 | <i>Trans</i> OCP | 111.65061 | -- | 47.84810 |

| | | | | |
|----|-----------------------|-----------|-----------|----------|
| 3 | DPE | -- | 121.93416 | -- |
| 4 | THF | -- | 111.51682 | -- |
| 5 | TBME | -- | 118.03619 | -- |
| 6 | <i>Cis</i> OCP+DPE | 117.58449 | 120.99270 | 69.34821 |
| 7 | <i>Cis</i> OCP+THF | 118.86327 | 109.35055 | 69.64116 |
| 8 | <i>Cis</i> OCP+TBME | 119.65852 | 118.45596 | 69.61983 |
| 9 | <i>Trans</i> OCP+DPE | 105.47616 | 115.71489 | 47.98053 |
| 10 | <i>Trans</i> OCP+THF | 113.18141 | 109.71137 | 53.62460 |
| 11 | <i>Trans</i> OCP+TBME | 113.41506 | 105.65937 | 47.92914 |

$\angle C-O-H_{(OCP)}$; $\angle C-O-C_{(ether)}$; Intermolecular hydrogen bond $\angle C-Cl_{(OCP)}---H_{(OCP)}$

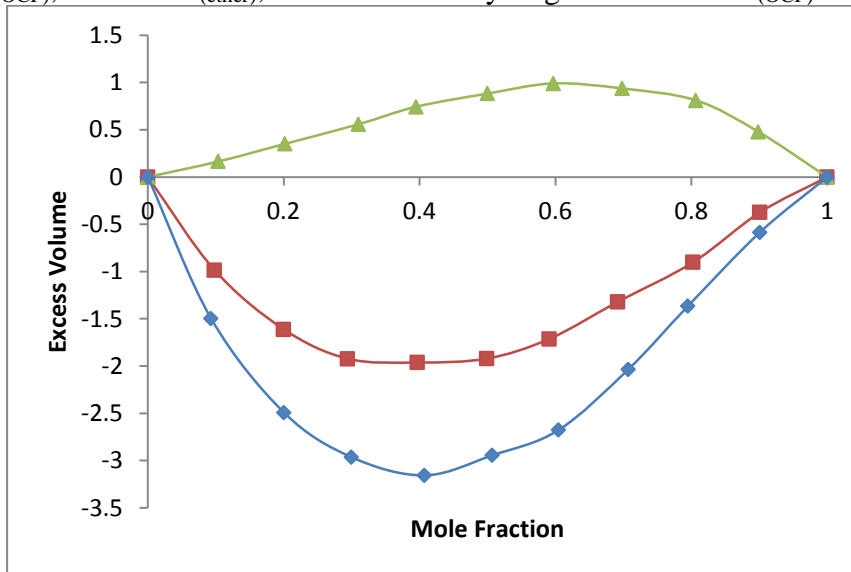


Fig 1.-Variation of excess molar volumes (V^E) with mole fraction (x_1) in binary mixture of OCP + THF (■), OCP+DPE (▲), OCP+TBME (◆) at temperature 298⁰K.

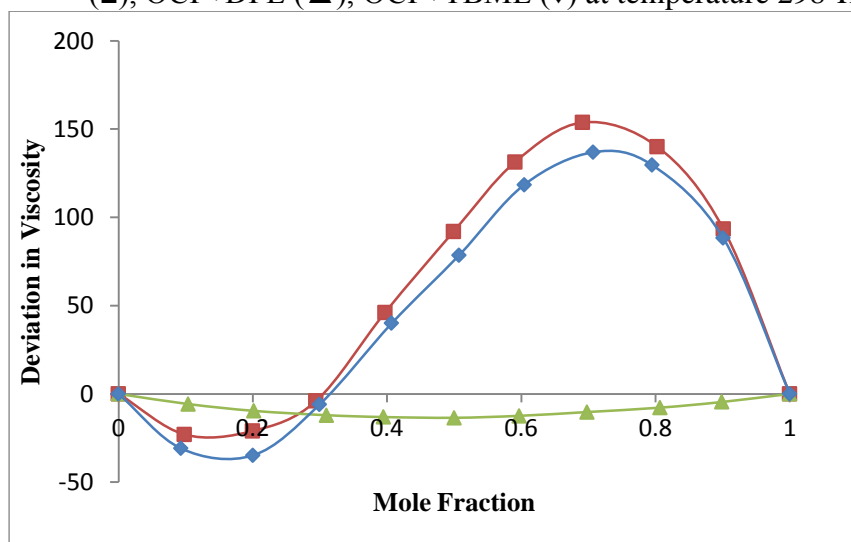


Fig 2.-Variation of deviation in viscosity ($\Delta\eta$) with mole fraction (x_1) in binary mixture of OCP+THF(■), OCP+DPE(▲), OCP+TBME(◆) at temperature 298⁰K.

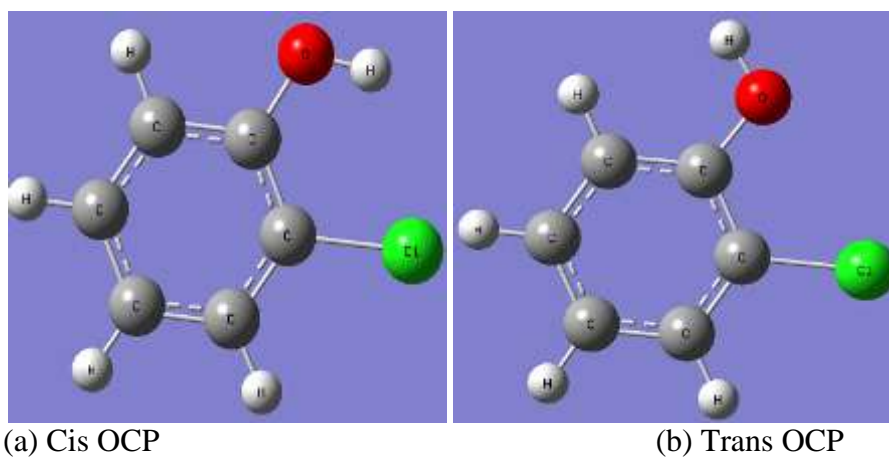
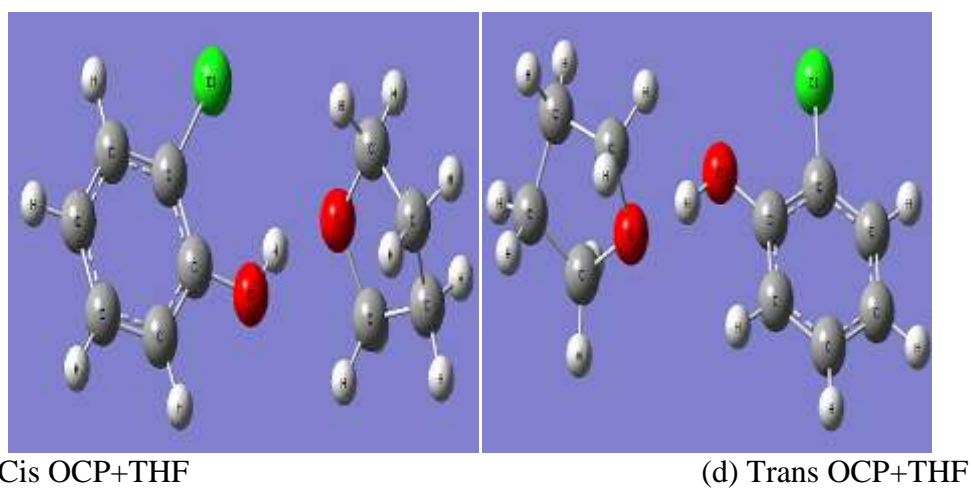
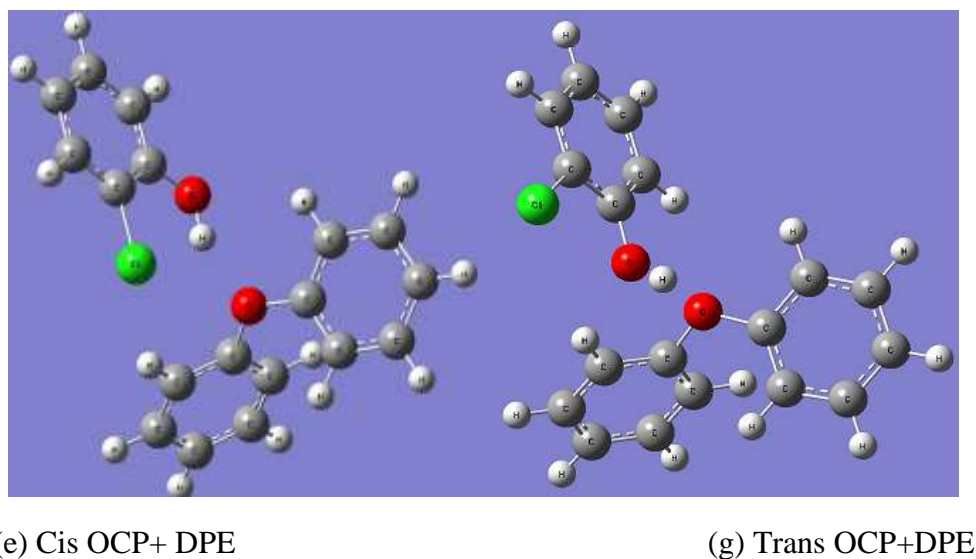
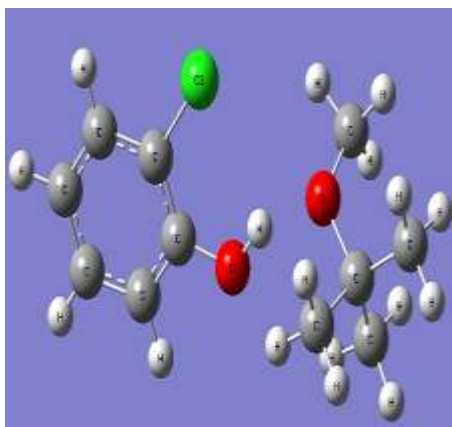


Fig 3 Optimized geometries of molecules by DFT method at B3LYP/6-31G(d,p) level.

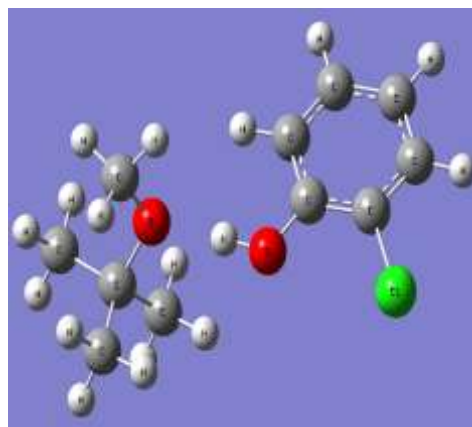


Conti. Fig 3





(h) Cis OCP+TBME



(i) Trans OCP+TBME

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