

Volumetric, viscometric and spectroscopic investigations of binary mixtures of o-chlorophenol with ethers

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Density and viscosity of o-chlorophenol with tetrahydrofuran, diphenyl ether and tertbutylmethyl ether at 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 been 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 been revealed by the behavior of the excess parameters. The sign and magnitude of excess parameters clearly indicates 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 been analyzed and their characterization has been made with the help of Gauss view visualization program utilizing the data obtained from the Gaussian 03 calculation.

Keywords: Volumetric, Viscometric, o-chlorophenol, Ethers, Density Functional Theory, Spectroscopic

1 Introduction

Thermodynamic studies of molecular interaction have significant importance in industry and engineering applications^{1,2}. The measurement of density and viscosity is 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 mixture³⁻⁶. 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^{7,8}. 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 liquid mixtures⁹⁻¹¹. The sign and magnitude of excess parameters give an insight in to the specific interactions between the component molecules^{12, 13}. Hydrogen bonded system is very interesting because hydrogen bond plays a vital role in chemical, physical

and biological processes. The choice 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 shows O—H---Cl bonding between the *cis* and *trans* isomers. Thus, the addition of other components causes the rupture of inter- 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 used spectroscopic methods for organic chemists are UV-IR, NMR, and mass-spectrometry. IR measurement through liquid mixtures provides an excellent tool to investigate inter- and intra-molecular 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

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would be difficult to assign the observed frequencies to a particular mode. The density functional theory^{14,15} (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 a view point of getting the vibrational frequencies on an optimized geometry of the titled compound. These frequencies are analyzed and compared with the experimental data¹⁶. 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 Procedure

The densities (ρ) of the pure liquid and the mixtures were measured with a pycnometer¹⁷. The pycnometer bottle was calibrated with triple distilled water. The dynamic viscosities were measured using ubbelohde suspended level viscometer¹⁷, 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 purity of Sisco chemicals was $>99\%$ and these were directly used. The purity of solvent was ascertained by comparing experimental values of densities (ρ) and viscosities (η) with those reported in the literature (Table 1). 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 Study

Geometry optimization and vibrational frequencies of titled compounds were at the DFT levels with B3LYP (Becke-Lee-Yang-Parr three parameters)

Table 1—Comparison of experimental data of density (ρ) and viscosity (η) with literature

System	Temperature (K)	$\rho \times 10^{-3}$ (kg m ⁻³)		$\eta \times 10^{-3}$ (kg m ⁻¹ s ⁻¹)		
		Experimental	Literature	Experimental	Literature	
THF	298	0.8782	0.8789 ¹⁹	0.468	0.468 ²²	
			0.87918 ²⁰		0.460 ²¹	
			0.8772 ²¹			
			0.87636 ²²		0.442 ²²	
	303	0.8760	0.87636 ²²	0.442	0.442 ²²	
	308	0.8682	0.86882 ¹⁹	0.422	—	
	313	0.8640	0.864 ²⁰	0.401	—	
			0.8638 ²⁰			
DPE	298	1.0711	—	3.785	—	
			1.0661 ²³		3.342	—
			1.0611 ²¹		2.899	—
			—		2.456	2.4594 ²¹
	303	1.0661	1.0661 ²³	3.342	—	
	308	1.0623	1.0611 ²¹	2.899	—	
	313	1.0579	—	2.456	2.4594 ²¹	
TBME	298	0.7357	0.73543 ²⁴	0.350	0.3576 ²⁷	
			0.7353 ²⁵		—	
			0.7356 ²⁶		0.340 ²⁸	
			0.73018 ²⁴		0.3353 ²⁹	
	303	0.7306	0.7353 ²⁵	0.345	—	
	308	0.7251	0.7356 ²⁶	0.340	0.340 ²⁸	
	313	0.7203	0.73018 ²⁴	0.335	0.3353 ²⁹	
			0.72488 ²⁴			
			0.71944 ²⁴			
OCP	298	1.2589	—	2.955	—	
			1.2529		—	
			1.2472		—	
			1.2410 ²³		2.250 ²³	
	303	1.2529	—	2.716	—	
	308	1.2472	—	2.483	—	
	313	1.2414	1.2410 ²³	2.250	2.250 ²³	

hybrid functional with correlation function such as one proposed by Lee, Yang and Parr¹⁸. B3LYP is the 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 Table 1. 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:

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

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:

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

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

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

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 the 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 a useful tool for calculations on larger and runs calculations very quickly.

5 Results and Discussion

Table 1 shows literature values of density (ρ), viscosity (η)¹⁹⁻²⁹ and 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.

Figure 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 temperature

Table 2—Densities (ρ), viscosities (η), excess molar volumes (V^E) and deviation in viscosities ($\Delta\eta$) for the OCP + THF system

Temperature (K)	x_1	$\rho \times 10^{-3}$ (kg m ⁻³)	$\eta \times 10^3$ (kg m ⁻¹ s ⁻¹)	$V^E \times 10^6$ (m ³ mol ⁻¹)	$\Delta\eta \times 10^3$ (kg m ⁻¹ s ⁻¹)
298	0.0000	0.8782	0.468	0.0000	0.000
	0.0981	0.9345	0.482	-0.9838	-22.976
	0.1999	0.9869	0.755	-1.6102	-20.998
	0.2943	1.0308	1.160	-1.9223	-3.981
	0.3970	1.0742	1.916	-1.9622	46.097
	0.4992	1.1121	2.629	-1.9204	91.974
	0.5908	1.1436	3.250	-1.7128	131.359
	0.6916	1.1746	3.725	-1.3206	153.767
	0.8025	1.2313	3.863	-0.9019	140.020
	0.9011	1.2461	3.642	-0.3732	93.378
1.0000	1.2589	2.954	0.0000	0.000	
303	0.0000	0.8760	0.442	0.0000	0.000
	0.0981	0.9334	0.345	-1.2339	-31.978
	0.1999	0.9854	0.557	-1.7401	-33.998
	0.2943	1.0297	0.982	-2.1277	-12.983
	0.3970	1.0726	1.645	-2.2476	30.016
	0.4992	1.1101	2.237	-2.1004	66.006
	0.5908	1.1414	2.756	-1.9127	97.815
	0.6916	1.1719	3.183	-1.5008	116.815
	0.8025	1.2038	3.357	-1.0618	109.018
	0.9011	1.2229	3.261	-0.5519	77.015
1.0000	1.2529	2.716	0.0000	0.000	
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

Temperature (K)	x_1	$\rho \times 10^{-3}$ (kg m ⁻³)	$\eta \times 10^3$ (kg m ⁻¹ s ⁻¹)	$V^E \times 10^6$ (m ³ mol ⁻¹)	$\Delta\eta \times 10^3$ (kg m ⁻¹ 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	1.0903	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

Temperature (K)	x_1	$\rho \times 10^{-3}$ (kg m ⁻³)	$\eta \times 10^3$ (kg m ⁻¹ s ⁻¹)	$V^E \times 10^6$ (m ³ mol ⁻¹)	$\Delta\eta \times 10^3$ (kg m ⁻¹ 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	0.417	-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	0.381	-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	0.432	-2.1706	-38.103
	0.2004	0.8385	0.522	-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

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 place³⁰⁻³². The positive values may be due to repulsive forces caused by electronic charges on the component liquids³³. 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 suggests that, the mixture prefers to have a compact structure in solution³⁴. It 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 system³⁵. It is observed from Fig. 1 that V^E values falls in the sequence OCP+TBME < OCP+THF < OCP+DPE for given temperatures.

Figure 2 represents 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 negative $\Delta\eta$ values in lower region and positive $\Delta\eta$ values in higher region of OCP are observed in the binary of OCP with THF

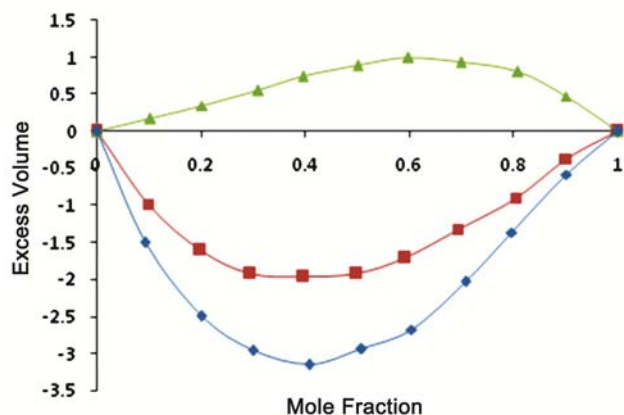


Fig. 1—Variation of excess molar volumes (V^E) with mole fraction (x_1) in binary mixture of OCP + THF (■), OCP+DPE (▲), OCP+TBME (◆) at temperature 298 K

and TBME. 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^{36,37}.

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

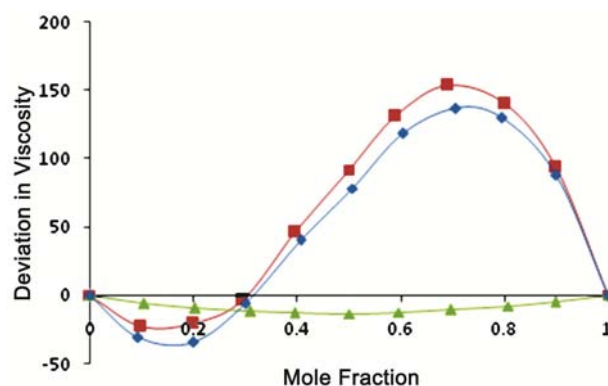
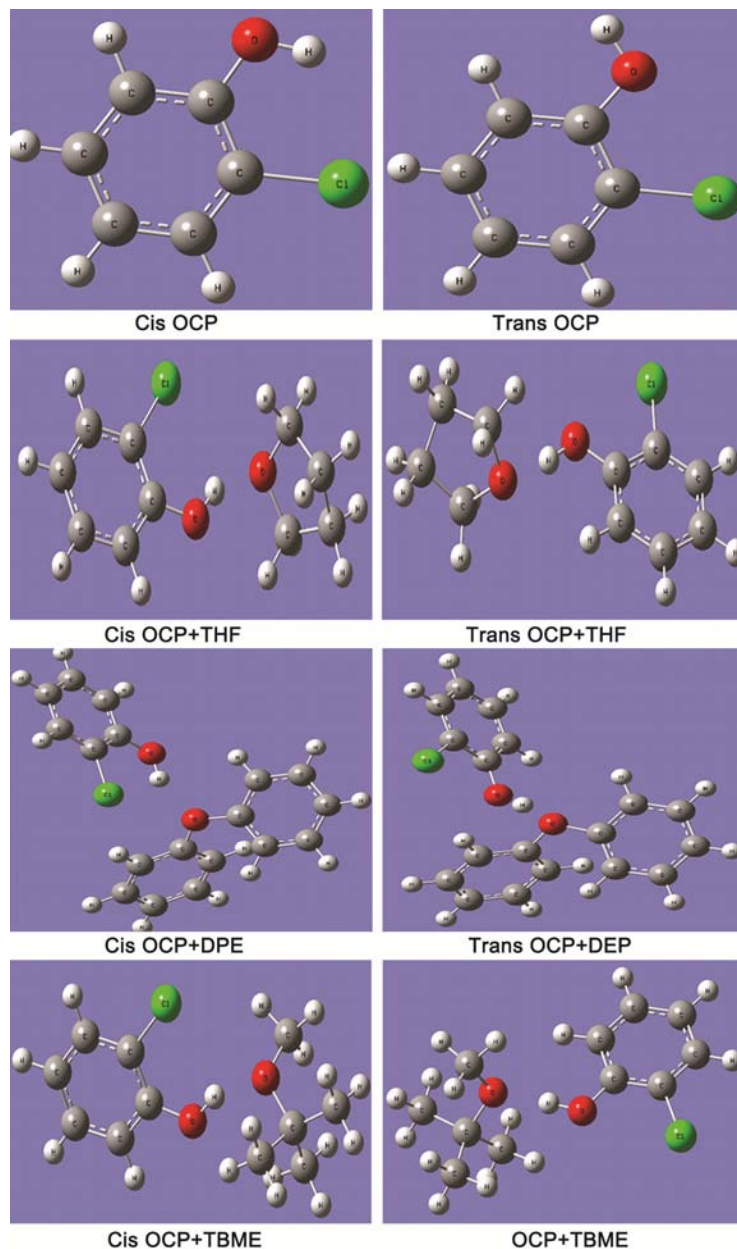


Fig. 2—Variation of deviation in viscosity ($\Delta\eta$) with mole fraction (x_1) in binary mixture of OCP+THF(■), OCP+DPE(▲), OCP+TBME(◆) at temperature 298 K

Fig. 3—Optimized geometries of molecules by DFT method at B3LYP/6-31G(*d, p*) levelTable 5—Optimized bond distance of systems at B3LYP level using 6-31G (*d, p*) basis set

S. 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

S. 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

S. 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

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.

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

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

S. No.	System	Theoretical –OH stretching frequency (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 is 3621.00 cm⁻¹

Table 9—Optimized bond angle 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

∠C-O-H_(OCP); ∠C-O-C_(ether); Intermolecular hydrogen bond ∠C-Cl_(OCP)---H_(OCP)

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.

6 Conclusions

The present report shows that the nature of molecular interaction of OCP with ethers may be dipole-dipole, dipole-induced dipole and other specific interaction between molecules of the given systems. The trends of deviation/excess properties indicate the presence molecular interaction in the binary mixtures under study. It may be qualitatively inferred that the interaction between unlike molecules mainly due to hydrogen bonding through highly polar lone pair oxygen atom of OCP and ethers.

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