Dielectric and viscosity studies of some Petroleum based lubricating base oils

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ABSTRACT

Dielectric constant (ε_0), dielectric constant at optical frequency (ε_α) of some petroleum based lubricating oils in benzene for different weight fraction of oils (M1, M2,H1 and H2) have been experimentally measured. Values of density (ρ), viscosity (η) and free energy of activation for viscous flow (ΔF_η) of binary mixtures are reported. Further dipole moment (μ) by Onsager method, Kirkwood correlation factor (g) which is a dimensionless parameter has also been calculated. Excess properties like excess molar volume (V^E) and excess viscosity (η^E) were used to explain the nature of molecular interaction. Kinematic viscosity, viscosity index and percentage composition of aromatic, paraffinic and naphthenic carbon values are also measured and their values shows that lubricating oils manufactured from iso-dewaxing and hydro finishing (M1 and M2 samples) technologies is better than the base oils obtained from solvent extraction and hydro finishing technologies (H1 and H2).

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INTRODUCTION

Dielectric studies are of importance and sensitive tool for the study of weakly bonded binary polar mixtures. Weak intermolecular or intra molecular interactions reflect themselves as a considerable change in the dielectric permittivity from the ideal conditions [1]. In this work some petroleum based lubricating oils (M1, M2, H1 and H2) with non-polar solvent benzene were mixed and the various dielectric parameters and excess properties were derived and interpreted. A sustainable effect is being taken to understand the mechanism of molecular interactions associated with the hydrogen bonds. The understanding is not only needed from the point of view of fundamental research, but also it plays an important role in industrial fields [2]. The dielectric properties of oil and water complexes were studied using tetra hertz transmission spectroscopy. In their work they analyzed Poly-glycols and ester oils show excellent lubricant performance as gear oil. Reactions in the presence of water such as hydrolysis or corrosion are possible disadvantages. Although mid-infrared-spectroscopy has been used to study the properties of several oils [3,4] and only very few investigations has been carried out in the far infrared and terahertz region [5]. A dielectric study yields the Kirkwood correlation factor 'g' which is correlated with solute-solvent interactions. The static dielectric constant is a macroscopic property which can play an important role in the solution properties. By using dielectric studies on binary liquid mixtures over a range of molecular interactions, it is possible to obtain valuable information regarding the nature and strength of

interactions in liquid mixtures [6-11]. Treated the dipolar rotation on the basics of a chemical rate process and studied the dielectric dispersion on a number of aliphatic and aromatic polar molecules in dilute solutions of inert solvents. Viscosity is a measure of the internal friction or resistance of an oil to flow. As the temperature of oil is increased, its viscosity decreases and it is therefore able to flow more readily [12, 13]. Some other aspects of viscosity-temperature studies on oils have also been reported in the scientific literature [14-19].

The linear correlation factor is a shape dependant parameter (g) that helps a qualitative interpretation of liquid mixture. If g>1 which indicates the predominance of α-multimers with parallel dipole orientation where as predominance of β-multimers with anti-parallel orientation. The dipole moments of the solutions are calculated by Onsager method. The additional properties like molar volume and viscosity are useful to discuss the nature of hydrogen bonding and the extent of intermolecular interactions in the binary liquid system. Viscosity data of base oils are very important to know the efficiency of the base oils. Here the paper reports the dielectric and viscosity properties of some petroleum based lubricating oils (M1, M2, H1 and H2) and their results were suitably interpreted with their lubricating performance.

MATERIALS AND METHODS

Group II base oils manufactured from reputed refineries using two different technologies used for this study. The samples M1 and M2 are manufactured in iso-dewaxing and hydro finishing technology and the samples H1 and H2 are manufactured using solvent extraction and hydro finishing technology. The solutions (M1, M2, H1 and H2) were prepared by volume mixing Methodology. The dielectric constants of the solutions were measured at 303K using a commercial instrument "Dipole meter DM 01" operated at 220 V using the heterodyne beat method. The operating frequency of the dipole meter is 2 MHz the refractive index of the solutions has been measured by Abbe's refractometer. The viscosities of the solutions were measured by Ostwald's viscometer.

Kirkwood correlation factor 'g' is given by:

$$g = \frac{9KT\left(2\varepsilon_{12} + \varepsilon_{12_\infty}\right)^2}{4\pi N_A \mu_2^2 X_2 \left(\varepsilon_{12_\infty} + 2\right)^2 \left(2\varepsilon_{12} + 1\right)}$$
$$\left[\phi_{12}\left(\frac{\varepsilon_{12} - 1}{\varepsilon_{12}}\right) - \frac{3X_1\phi_1(\varepsilon_1 - 1)}{(2\varepsilon_{12} + \varepsilon_1)} - \frac{3X_2\phi_2(\varepsilon_{2\alpha} - 1)}{(2\varepsilon_{12} + \varepsilon_{2\alpha})}\right] \qquad (1)$$

The free energy of activation for viscous flow (ΔF_η) has been calculated by using Eyring's equations,

$$\Delta F\eta = \frac{N_A h}{V}\exp\left[\frac{\Delta F\eta}{RT}\right] \qquad (2)$$

Kinematic viscosity measurement was carried out using the equipment CAV 2000 automatic viscometer. The bath temperature was controlled to an accuracy of ± 0.01°C at 40°C or 100°C. Kinematic viscosity is expressed in centistokes and it is normally determined at 40°C and 100°C.

RESULTS AND DISCUSSION

The variation of statics dielectric constant (ε_0), refractive index (n_D), and activation energy (ΔF_η) were calculated and presented in Table 1. The dipole moment (μ) and Kirkwood correlation factor (g) were also calculated and reported in Table 2.Excess properties such as excess molar volume (V^E) and excess viscosity (η^E) were also calculated and reported in Table 2. Depending upon the values of (V^E) and (η^E) the nature of molecular interactions were discussed. As the concentration of the oil samples increases the density values remain constant and the viscosity gets increased in M1 & M2 samples but the similar trend

was not observed in the case of H1 & H2 samples (Table-2). The formation of molecular clusters in organic solution of vegetable oils had earlier been reported [20]. M1 & M2 showed increasing viscosity with increase in concentrations due to the favorable environment for the formation of molecular clusters but in H1 sample, the viscosity remains almost constant due to the non favorable environment to form the molecular clusters. However, H2 shows slight increasing trend of viscosity due to the probable formation of clusters [21].

The activation energy of M1 & M2 showed steep increases with increase of concentration. But in H1 & H2 samples slight increase in activation energy with increase of concentrations were observed. The increasing trend of activation energy is well accounted for the formation of solute-solvent hydrogen bond interactions.

Dielectric constant values of M1 & M2 in a particular concentration are greater than H1 & H2 samples. The concentration of the solute (M1, M2, H1 and H2) oil sample increases the dielectric constant (ε_0) values non–linearly increases for shown in fig (1). The Kirkwood linear correlation factor (g) shown in fig (2).

Table 1: Variation of Density (p), Viscosity (η), Dielectric constant (C) , Refractive index (n_D) and Activation Energy ($\Delta F\eta$) with weight fraction of respective oil samples

System	Weight fraction of oils (w_2)	Density (p)	Viscosity (η)	Dielectric Constant (ε_0)	Refractive Index (n_D)	Activation Energy ($\Delta F\eta$)
M1+ Benzene	0.0212	0.8721	0.6976	2.2858	1.4934	12.786
	0.0500	0.8678	0.7264	2.2759	1.4924	12.976
	0.0822	0.8673	0.7657	2.2621	1.4909	13.197
	0.0995	0.8664	0.8069	2.5212	1.4894	13.379
M2 + Benzene	0.0887	0.8705	0.8157	2.4337	1.4914	13.376
	0.154	0.8663	0.9665	2.5653	1.4879	13.987
	0.2117	0.8659	1.1207	2.7204	1.4840	14.428
	0.2168	0.8649	1.3195	3.0795	1.4810	15.141
H1 + Benzene	0.0289	0.8766	0.7328	2.3836	1.4939	12.922
	0.0487	0.8758	0.7614	2.6568	1.4929	13.073
	0.0781	0.8034	0.7227	2.3167	1.4904	13.218
	0.1147	0.8029	0.7376	2.5802	1.4889	13.39
H2 + Benzene	0.0886	0.8713	0.7418	2.6692	1.4944	12.981
	0.1521	0.8703	0.7932	2.5046	1.4934	12.872
	0.2119	0.8689	0.8163	2.5129	1.4924	13.685
	0.2342	0.8672	0.912	2.6518	1.4800	13.837

Table 2 : Variation of μ, g, V^E and η^E with weight fraction of respective oil samples in Benzene

System	Weight fraction of oils (w_2)	Dipole Moment μ(D)	Correlation Factor (g)	Excess Molar volume $V^E \times 10^{-6} M^3$ vol^{-1}	Refractive Index (n_D) $\eta^E \times 10^{-3}$Nm -2 S
M1+ Benzene	0.0212	0.0073	0.974	-0.228	-0.070
	0.0500	0.0048	0.977	0.309	-0.041
	0.0822	0.0025	0.981	0.466	-0.002
	0.0995	0.0011	0.984	0.629	0.038

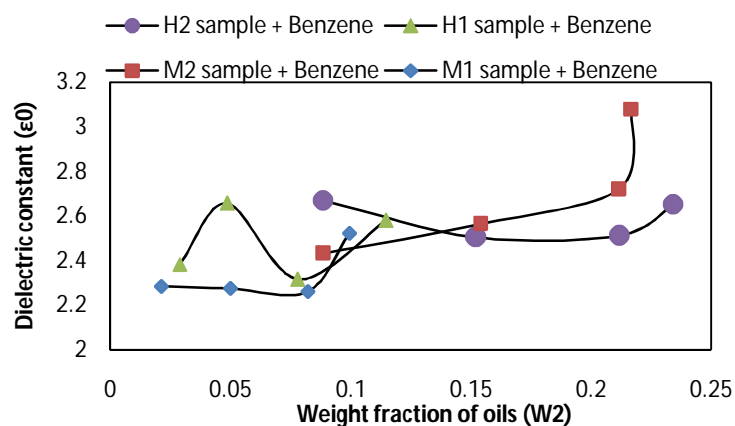| M2 + Benzene | 0.0887 | 0.0136 | 0.907 | -0.307 | 0.034 |
	0.154	0.0141	0.850	0.059	0.175
	0.2117	0.0166	0.792	0.626	0.326
	0.2168	0.0176	0.682	-0.012	0.505
H1 + Benzene	0.0289	0.0168	0.932	-0.376	-0.037
	0.0487	0.024	0.855	-0.345	0.009
	0.0781	0.0143	0.956	0.256	-0.049
	0.1147	0.0178	0.999	0.679	-0.037
H2 + Benzene	0.0886	0.0183	0.822	-0.222	-0.031
	0.1521	0.0199	0.889	-0.143	0.016
	0.2119	0.0173	0.877	-0.001	0.144
	0.2342	0.0164	0.811	0.175	0.121

Fig 1: Dielectric constant (ε_0) values of oil samples with benzene Vs weight fraction of the solute (W_2)
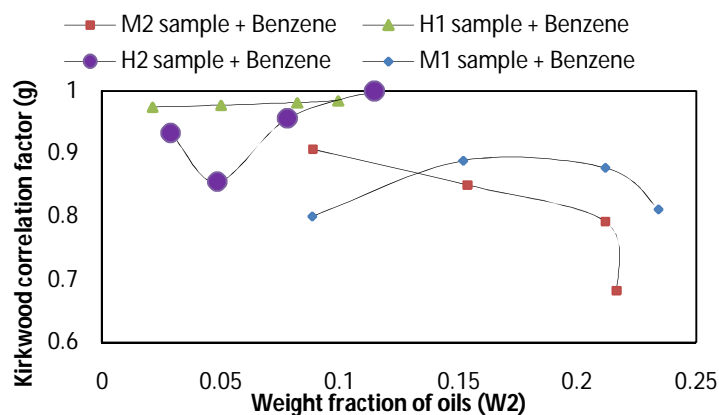

Fig 2: Kirkwood correlation factor (g) values of oil samples with benzene Vs weight fraction of the solute (W_2)

The dipole moment (μ) values of M1 & M2 in a particular concentration are lesser than that of H1 & H2 samples. These observations supported the presence of aromatic hydrocarbons in H1 & H2 samples. The concentration of the solute increases the (g) factor values gets increased for (M1 + Benzene). The remaining system shows non linear variations. The (g) factor values exhibits less than unity for all the

studied systems. It indicates that the anti–parallel orientation of the dipoles in the systems. In our studied systems (H2 sample + Benzene) the (g) factor values are decreases and then increased. It indicates that the anti–parallel to parallel alignment of dipoles in the system. The (g) factor values are decreases for (M1, M2 and H1) oil samples except H2 oil sample. It indicates that the anti–parallel alignments of the dipoles were existed for these systems.

The 'g' factor values exhibit less than unity. It shows long chain lubricating oil molecules existing anti-parallel orientation in benzene solvent. The sign of V^E of a system depends upon the relative magnitude of expansion and contraction on mixing of two liquids. When the factors causing expansion outweigh the factors causing contraction, V^E becomes positive. But if the contractive factors dominant over the expansion factor V^E becomes negative. The factors that are responsible for volume expansion are:

1. Break down of one or both components in solution system. A suitable example of this is rupture of H-bonding of one component by other is breaking up of associates held together by weaker physical forces, such as dipole-dipole or dipole induced dipole interactions or by vanderWaals forces.

2. The geometry of molecular structure which does not favor fitting of molecules with each other.

3. Steric hindrance which opposes the proximity of the constituent molecules.

4. Chemical interaction between constituent molecules. Association through weaker physical forces on any other forces.

5. Accommodation of molecules of one component into the structural network of mixtures of the other component.

The (V^E) values for all the studied systems are shown in fig (3). The (V^E) values are shows negative values at lower concentration of oil samples and positive values at higher concentration. It indicates that at lower concentration the expansion factor dominants where as at higher concentration of oil samples the contractive factor dominates.
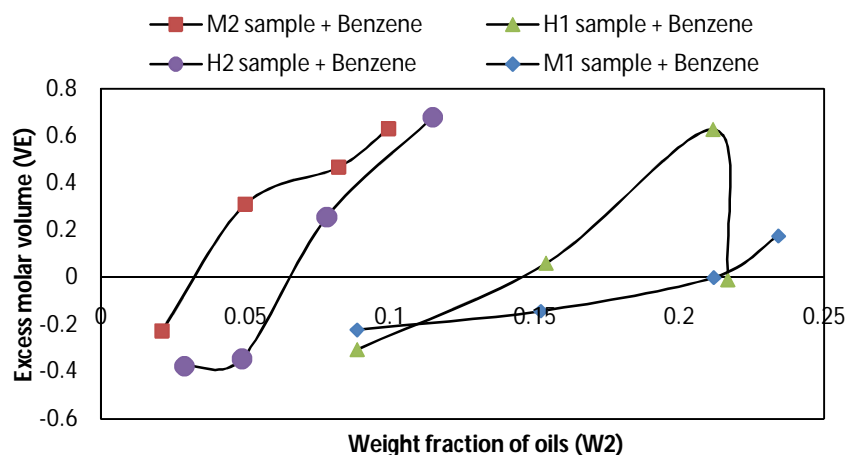

Fig 3: Excess molar volume (V^E) values of oil samples with benzene Vs weight fraction of the solute (W_2)

In our study V^E values are showing both negative and positive values. A negative value shows strong specific interaction existing between oil and solvent molecules where as positive V^E shows less interaction. Kinematic viscosity and density values of oil samples without solvent are measured and given in Table 3.

Table 3 : Viscosity and Density values of M1, M2 and H1, H2 Base oils.

	M1	H1	M2	H2
Density g/ml	0.8401	0.8521	0.8525	0.8644
KV @ 40°C	31.00	32.56	90.20	88.01
KV @ 100°C	5.48	5.40	10.80	10.76

| VI | 119 | 105 | 108 | 106 |
| KV @ 100°C | 5.56 | 5.49 | 10.93 | 10.98 |

KV - Kinematic Viscosity, VI – Viscosity Index, a – sample heating at 200°C for 2 hours

The dielectric constant of H1 is higher than that of M1, the similar trend is also observed between H2 and M2 samples. The lesser contribution of dielectric constant value and the larger contribution of activation energy values of M1 & M2 samples explained its better stability characters. The viscosity Index of M1 & M2 is greater than that of the H1 & H2 samples. Generally high viscosity index (VI) values show better lubricant properties due to the enhancing trend of stability characteristics [16]. Hence M1 & M2 samples are more suitable for engine lubricant purpose than H1 & H2 samples. Further the kinematic viscosity values are drastically reduced at high temperatures. At high temperature the average chain length values are reduced due to the rupturing of bonds hence the presence of less ordered molecules which leads to low viscosity values.

The VI value also depends upon the types of carbon present in the samples. The presence of aromatic and naphthenic carbons leads to lesser stability of lubricating oils [22]. In Table 4, the presence of aromatic carbons (C_A) is nil for M1 & M2 samples whereas H1 & H2 samples containing around 4% of aromatic carbons. Hence M1 & M2 samples show better stability than that of H1 & H2. Similarly the higher composition of naphthenic carbons (C_n) in H1 & H2 samples leads to lesser stability. Generally the presence of paraffinic (C_P) and iso-paraffinic carbons (Cip) enhanced the oxidation stability [22]. Hence, M1 & M2 samples have larger composition of C_p values explained their better lubricating properties.

Table 4: Percentage composition of Aromatic, Paraffinic and Naphthenic carbons

Types of Carbon	M1	H1	M2	H2
C_A	-	3.76	-	3.62
C_P	69.18	60.92	70.81	63.39
C_N	30.82	36.29	29.19	32.98

APPLICATIONS

Kinematic viscosity, viscosity index and percentage composition of aromatic, paraffinic and naphthenic carbon values shows that lubricating oils manufactured from iso-dewaxing and hydro finishing (M1 and M2 samples) technologies is better than the base oils obtained from solvent extraction and hydro finishing technologies (H1 and H2).

CONCLUSIONS

The viscosity and dielectric studies of four lubricating oils (M1, M2 and H1, H2), leads to the following conclusions.
1. The M1 and M2 lubricating oils derived from iso-dewaxing and hydro finishing technology samples are more suitable for internal combustion engines.

2. The viscosity index value shows that the M1 and M2 samples consisting with more percentage of paraffinic and less percentage of naphthenic carbons.

3. The decrease in viscosity from low to high temperature is attributed due to the decrease in average chain length values.

4. The dielectric study concluded that strong interactions are existing in M1 & M2 base oil molecules where as similar trend was not observed in H1 & H2 samples.

5. Iso-dewaxing & hydro finishing technology oil samples (M1 & M2) are better than the oil samples obtained from solvent extraction and hydro finishing technology.

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REFERENCES

[1]   M.K. Kroeger, J. *Mol. Liquids,* **1987**, 36, 101.
[2]   Stefan Gorenflo, Ulrike Tauer, *Chemical Physics Letters,* **2006**, 421, 494-498.
[3]   A. Boren, R.J. Poppi, *Vib spectroscopy*, **2005**, 37, 27.
[4]   R.C. Barthus, R.J. Poppi, *Vib spectroscopy*, **2001,** 26, 99.
[5]   M. Naftaly, A.P. Foulds, R.E. Miles, A.G. Davies, *Int. J. Infrared Milli Waves.* **2005**, 26, 55.
[6]   D. Balamurugan, S. Kumar and S. Krishnan, *J. Mol. Liquids.* **2005**, 122, 11-14.
[7]   H. Eyring, *J. Phys. Chem.* **1963**, 7, 547.
[8]   C.G. Seigel, F. Herrera, P.H. Cappella, *J. Mol. Liquids*, **1990**, 44, 175.
[9]   T. Zeegers, Huyskens, *J. Mol. Liquids*, **2006**, 126, 38.
[10]   M. Davies, *Chem. Soc. London,* **1977**, 1-3
[11]   P.L. Kollman, *Bull soc. Chime. Belg,* **1972**, 83, 283.
[12]   J. Peredi, M. Szungyi, Olaj, Szappan, Kozmet, **1976**, 25 (2), 45.
[13]   Ayhan Demirbas, *Fuel,* **2008**, 87 1743-1748.
[14]   I.O. Igwe, I.S. Odeh, *J. Chem. Soc*. **2000**, 25, 96.
[15]   Y.P. Varshi, S.N. Scriwstera, *J. Phys. Chem*. **1958**, 62,706.
[16]   B.K. Sharma, J.M. Adhvaryu, Perez and S.Z. Erhan, *Fuel Processing Technology* **2008**, 89, 984.
[17]   A. Abolle, L. Kouakou and H.Planche, *Biomass and bioenergy*, **2009**, 33, 1116.
[18]   Isaaco, O. Igwe, *Industrial crops and products*, **2004**, 19, 185.
[19]   P.S. Lathi, and Bo Mattiason, *Applied Catalysis,* **2007**, 69, 207.
[20]   S.A. Ibemesi, I.O. Igwe, *J. Am. Oil. Chem, Soc,* **1990**, 68 (3) 147.
[21]   Isaac. O. Igwe, *Industrial crops and products*, **2004**, 19, 185-190.
[22]   A. Adhvaryu, S.Z. Erhan, S.K. Sahoo, I.D. Singh, *Fuel*, **2002**, 81, 785-791.