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Structural Determination Of Ci Engine Fuel Additives Through Dielectric Relaxation Studies

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Abstract— The objective of this paper is to investigate the molecular interaction between corrosion inhibitors and oxygenates molecules through dielectric relaxation studies. It makes one to understand the fuel additives its structure. Fuel additives is a chemical substance, added to fuel ,in concentration typically of less than 1% to impart or enchance needed properties or to overwhelm objectionable properties. They include octane enhancers, antiknock compounds and oxygenates, as well as corrosion inhibitors, detergents, and dyes. It alters the rate at which fuel burns, reduce harmful emissions, prevent premature detonation, stop corrosion, and prevent the formation of deposits in the fuel system and combustion chambers. In view of this, amine and alcohol mixtures most important one. because of amine can be used as a antioxidants,corrosion inhibitors and also be used to control the deposits in engine. Antioxidants are the molecule that inhibits the oxidation of other molecule and used as fuel additives when creating fuel blends. Alcohol can be used as oxygenates. They are used to reduce the carbon monoxide emissions creating when burning fuel.Therefore it is seemed important to examine the molecular interaction studies on those additives. Dielectric relaxation studies are of great help in the assignment of the molecular structure or configurations, particularly those of organic compounds and also helps to detect the formation and composition of complexes in them. The molecular complex formation can be investigated by studying the dielectric relaxation parameter values such as static permittivity (ε_0), Permittivity at optical frequency (ε_∞), dielectric constant at microwave frequency (ε'),dielectric loss (ε'') at microwave frequency, density (ρ) and the coefficient of viscosity (η) for the system,1-butanol in (benzene + tert.butylamine) and 1-propanol in (benzene + tert.butylamine) taken for the investigation at three different temperatures 303K, 313K and 323K are reported. Using these parameters values of most probable relaxation time (τ_0), relaxation time corresponding to group rotation (τ_1) which is otherwise known as intramolecular relaxation time, relaxation time due to overall rotation of the molecule (τ_2) and distribution of relaxation time (α) are obtained using Higasi model and the values are also reported. The hetero interaction through hydrogen bonding between the molecules of corrosion inhibitors and oxygenates have been identified by the dielectric relaxation process.

Index Terms— multifunctional fuel additive, hetero interaction, oxygenates, corrosion inhibitor.

I. INTRODUCTION

Additives are chemical agents added to oils, fuels, and coolants to impart specific beneficial properties to the finished products. It creates new fluid properties, enhance properties already present and reduce the rate at which undesirable changes take place in a fluid during service. Some additives have multi-functional properties. Multifunctional diesel additive packages are frequently more complex and may combine deposit control additive with cetane number improver, Oxygenates, antifoam additive, corrosion inhibitor, antioxidants, metal deactivators and demulsifier [1].Oxygenates – are fuels infused with oxygen. They are used to reduce the carbon monoxide emissions creating when burning fuel. Oxygenates can be based on either alcohol or ethers [2]. Literature survey shows that Butanol is a feasible alternative to ethanol due to its higher energy density, being less prone to water contamination, less corrosive, better blending stability and higher cetane number with respect to ethanol [3]. Tert-butylamine are generally considered to better than secondary or primary amines as fuel antioxidants [4] as well as deposit control additives and corrosion inhibitor [2].The present work was aimed to get better understanding of the nature of molecular interaction pr based on the study of the temperature dependent dielectric relaxation in multifunctional additive mixtures of 1) 1-butanol in (benzene +tert-butylamine) and 2) 1-Propanol in (benzene +tert-butylamine) at microwave frequencies.

II. MATERIALS AND METHODS

Compounds used in the present study were of AR grade and were all procured from SRL, India. The static permittivity ε_o at 1 KHz was measured using a digital VLCR-7 meter supplied by M/S Vasavi electronics, India, after calibrating it for standard liquids like carbon tetrachloride, benzene, toluene and chlorobenzene. The permittivity at optical frequency ε_∞ was obtained by squaring the refractive Index for sodium D-line, which was measured with the help of an Abbe's refractometer. The uncertainties in static permittivity, refractive index and density were ±0.0005, ±0.0002 and ±0.0001 g/cc respectively. All measurements were made at 303±1K, 313±1K, and 323±1K using a water circulating thermostat arrangement. For density measurement, a 10ml specific gravity bottle was employed. Its volume at the given temperature was determined using pure water. Density measurements of each sample were made at the required the

losses due to evaporation of the sample were minimized. The viscosities of the mixtures were measured by using Ostwald's viscometer. ε' and ε'' were measured by using a

standard liquid cell supplied by M/s. SISCO Ltd., Allahabad, in conjunction with a X- band microwave set up, at 9.75GHz and temperature 303K,313K and 323K respectively. It is shown in fig 1.The constant temperature was maintained by water – circulating thermostat supplied by Ragga Industries, Chennai, India. The fluctuation in temperature was ± 0.1K.

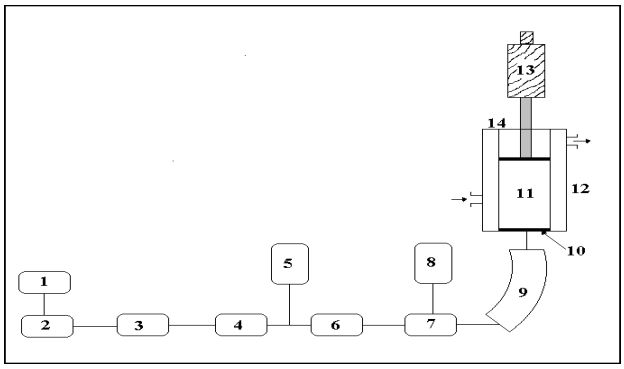

Fig 1.Microwave X – Band Test Bench

1.Power supply 2.Reflex Klystron K – 27 3.Tuner 4.Ferrite isolator 5.Frequency meter 6.Attenuator 7.Slotted line carriage 8.Crystal detector 9. H-Plane bend 10.Teflon window 11.Liquid cell 12.Constant temperature jacket13.Micrometer head 14.Plunger

III. THEORY

The dielectric relaxation time (τ) was calculated using Higasi's method [5-9]. Assuming ε_0, ε' , ε" and ε_∞ vary linearly with weight fraction w_2 of the solute. We have:

;

;

;

The following expression were used for obtaining ε' and ε"

Where λ_d is the wavelength in the dielectric medium, λ_g , the wave guide wavelength, λ_0 , the free space wave length, λ_d, the cut off wavelength and $1/\rho$ is the standing wave ratio obtained by using a short circuited movable plunger. The uncertainties in the measurement of ε' and ε" are 1% and 5% respectively. The relaxation time for various solutions was also obtained in term of two Debye relaxation mechanisms with the help of the following equation for dilute solution of weight fractionw_2

Where τ_1 is a sort of intramolecular relaxation time , τ_2 is dielectric relaxation time for overall rotation of the whole molecule , τ_o is the most probable relaxation time, ω is the angular frequency, τ_1 and τ_2 depending on both the weight factor of such mechanism at a given concentration and temperature.

IV. RESULTS AND DISCUSSION

The values of static permittivity (ε_0),Permittivity at optical frequency (ε_∞), dielectric constant at microwave frequency (ε'),dielectric loss (ε") at microwave frequency, density (ρ) and the coefficient of viscosity (η) of multifunctional additive mixtures 1) 1-butanol in (Benzene tert-butylamine) and 2) 1-propanol + in (Benzene tert-butylamine) are reported in table - 1 at different temperatures 303K,313K and 323K.The table-1 shows that at equimolar concentration, the ε_{0m} value is higher than in pure liquids in benzene. This implies larger relaxation times for mixtures at equimolar concentrations [10].They have reported that larger relaxation time of the solution is due to the longer size of the molecules and suggested that it is due to the intermolecular association exists between solute and solvent molecules. Values of 'α' obtained by Higasi method are reported in table -2.Value of 'α'in the above studied systems at all the three different temperatures is finite. This shows the existence of more than one relaxation processes, due to the mechanism of group rotation (τ_1) and overall molecular rotation (τ_2). Value of 'α is found to decrease with rise of temperature. This may be due to the fact that at high temperature, molecular rotations of solute molecules become faster and uniform in the solution [11]. Kalaivani et al. [12] have pointed out that for rigid molecules the distribution parameter would be larger. They have also pointed out that in amine-nitrile mixtures in benzene, the association between unlike molecules is maximum for 1:1 molar ratio [12]. From table 3, it can be seen that the most probable relaxation time (τ_0) value for the mixtures is greater than the corresponding value of the pure liquids. This trend exists in both the systems taken for investigation

at all the studied temperatures. This implies the enchancement of the cluster size. Mixing of two liquids results in the formation of bigger molecular size which enhances the relaxation time (τ_0).The hetero interaction between alcohol and amine molecules is such as to form linear multimer. This shows the existence of strong hetero interaction through H-bonding between dissimilar molecules. In all systems value of τ_0 decreases with rise of temperatures. It indicates that, decrease of τ_0 with increase of temperature may be explained as due to the reduced size of the clusters or due to viscous effect or by both. The relaxation time due to group rotation (τ_1) gives information in both the systems indicates that the existence intramolecular interactions. Value of τ_1 decreases with rise of temperature. This may be due to the hindrance offered due to the thermal agitations. In the mixtures containing 1-propanol, τ_1 value is greater than in mixtures containing 1-butanol. Variation of τ_1 with X_2 for different systems at three temperatures are given in figures from 2-3. Value of τ_2 reflects the overall size of the molecules. τ_2 value shows a non-linear variation with the concentration of alcohol. In all the mixtures the maximum value of τ_2 occurs at equimolar concentration of alcohol. This shows that at these concentrations, the aggregates have a large size.

Temp. (K)	Concentration of 1-Butanol in (Benzene+Tert.Butylamine)	ε_0	ε_∞	ε'	ε''	ρ g/cc	η x 10 -2 Pa-s
303	0	2.6960	2.1860	2.5063	0.1843	0.8411	1.5270
	0.33	2.7500	2.1798	2.4854	0.1849	0.8484	1.5740
	0.50	2.8310	2.1674	2.4554	0.1842	0.8528	1.5890
	0.67	2.7770	2.1641	2.4803	0.1870	0.8603	1.5830
	1	2.7230	2.1518	2.4836	0.1792	0.8680	1.5730
313	0	2.6690	2.1768	2			
	0.33	2.6960	2.1742	2			
	0.50	2.7770	2.1556	2			
	0.67	2.7500	2.1442	2			
	1	2.6960	2.1412	2			
323	0	2.6420	2.1677	2			
	0.33	2.6690	2.1615	2			
	0.50	2.7500	2.1494	2			
	0.67	2.7230	2.1383	2.4823	0.1853	0.7962	1.0850
	1	2.6690	2.1366	2.4875	0.1774	0.8015	1.0630

Table.1 Values of ε_m, ε_∞ , ε', ε'', ρ and η at different temperatures.

Temp. (K)	Concentration of n-Propanol in (Benzene+ Tert. Butylamine)	ε_0	ε_∞	ε'
303	0	2.6960	2.1860	2.5063
	0.33	2.7770	2.1851	2.4763
	0.50	2.9120	2.1798	2.4375
	0.67	2.8310	2.1706	2.4621
	1	2.7770	2.1624	2.4783
313	0	2.6690	2.1768	2.5070
	0.33	2.7230	2.1753	2.4774
	0.50	2.8580	2.1665	2.4384
	0.67	2.7770	2.1603	2.4630
	1	2.7500	2.1474	2.4820
323	0	2.6420	2.1677	2.5078
	0.33	2.6960	2.1647	2.4789
	0.50	2.8310	2.1556	2.4391
	0.67	2.7500	2.1474	2.4641
	1	2.7230	2.1383	2.4840

Table.2 Values of ε_0, τ_0 , τ_1, and τ_2 at different temperatures.

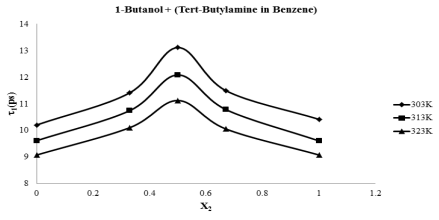

Fig.2 Variation of τ_1 with X_2

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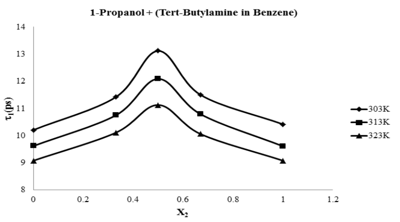

Fig.3. Variation of τ_1 with X_2

System	X_2	α			τ_0 (ps)			τ_1 (ps)			τ_2 (ps)		
		303 K	313 K	323 K	303 K	313 K	323 K	303 K	313 K	323 K	303 K	313 K	323 K
1-Butanol in (Benzene+ Tert. Butylamine)	0	0.16	0.12	0.09	11.82	10.50	9.45	10.21	9.62	9.08	16.97	14.67	12.28
	0.33	0.24	0.18	0.16	15.14	12.35	10.75	10.63	10.18	9.51	23.27	18.50	16.08
	0.50	0.32	0.30	0.29	24.15	18.78	16.36	11.44	10.67	10.19	33.61	28.83	26.46
	0.67	0.28	0.28	0.26	16.66	13.93	12.24	10.49	9.63	9.24	[illegible]	23.77	21.41
	1	0.25	0.24	0.19	12.91	11.21	9.91	9.55	9.02	8.06	22.01	19.56	16.86
1-Propanol in (Benzene+ Tert-Butylamine)	0	0.16	0.13	0.09	11.82	10.50	9.45	10.21	9.62	9.08	16.97	14.67	12.28
	0.33	0.26	0.22	0.20	18.34	14.55	12.61	11.42	10.78	10.11	26.62	21.85	19.30
	0.50	0.33	0.33	0.33	36.43	28.96	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	0.67	0.31	0.29	0.28	23.13	18.20	[illegible]	11.50	10.79	10.06	32.41	27.75	23.44
	1	0.28	0.27	0.26	16.79	13.9[illegible]	12.84	10.42	9.61	9.08	26.56	23.94	21.53

As concentration of alcohol increases, number of alcohol molecules also increases. This may be the reason for the enhancement of hetero association. Beyond equimolar concentration self-association among like molecules may lead to the reduction in size which may be the reason for the decrease of τ_2 values. τ_1 and τ_2 values for all the mixtures at all the studied temperatures have a non-linear variation with concentration of alcohol. This non-linear variation confirms the solute-solute interaction [13]. It was concluded that high viscosities provide larger droplet diameters and high penetration of the fuel jet. It leads hinders vaporization, favoring the formation of large diameter droplets and causing incomplete combustion due to the high penetration of the fuel jet, hindering cold starts and increasing the emission of unburned hydrocarbons (HCs) and particulate matter (PM). But at high temperature the size of the molecules reduced. It shows that shortened ignition delay and improved the combustion process [14]. It can be concluded that the addition of oxygenates and corrosion inhibitor had reduced the Hydrocarbon(HC), Particulate Matter (PM), Carbon Monoxide (CO) emissions to a significant with bringing much change in the performance [15].

V.CONCLUSION

1. The hetero interaction between the molecules of alcohol and amine have been identified by the dielectric relaxation process.
2. Combustion quality depends upon the structure of the fuel and its additive molecules.
3. Most of the oxygenated additive mixtures showed improved combustion phases, decrease in cylinder temperature due to high latent heat of evaporation.
4. Multifunctional fuel additives in fuel blends decreases the ignition delay, improved premixed combustion duration and combustion stability.

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