Dielectric Relaxation Studies of Ternary Liquid Mixtures of Dimethyl Phthalate with Octanol and Isobutanol in the Microwave Region

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Abstract: The dielectric relaxation time (τ) and dipole moment of the ternary mixtures at different molar concentrations of dimethyl phthalate with octanol in benzene and dimethyl phthalate with isobutanol in benzene have been calculated for three different temperatures 303K, 308K and 313K. Using standard standing wave microwave technique using microwave frequency (9.36GHz). The molecular structure and molecular forces in liquids and solutions in particular have been investigated by dielectric relaxation studies. The nature and strength of the molecular interactions have been established as the main cause for the chemical behavior of compounds.   Different dielectric quantities like dielectric constant (ε'), dielectric loss (ε''), static dielectric constant (ε_0) and dielectric constant at optical frequency (ε_α) have been determined. The relaxation time (τ) has been calculated by both Higasi's method and Cole-Cole method. The complex systems investigated shows the maximum relaxation time values as the concentration and temperature increase by both Higasi's method and Cole-Cole method.

Keywords: Cole–cole method , dielectric constant, dielectric loss, dimethylphthalate, Higasi's method, isobutanol, octanol.

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1. INTRODUCTION

Dimethyl phthalate is used as   a solvent in perfumes, cosmetics, personal care products, and nail polishes and also used in the manufacturing of plastic materials.   Octanol is commonly used alcohol of medical interest particularly in cardiac electrophysiology, and in the study of muscle cells. Isobutanol is used in pharmaceuticals in the formation of monolithic polymers. So the dielectric relaxation studies of these mixtures gain more importance in medical and industrial applications.   Dielectric relaxation studies in the microwave region provide information about various types of molecular association, because microwave detects even weak molecular interactions. Standing wave microwave technique has been used to measure the dielectric constant(ε') and dielectric loss (ε''**)** of dilute solutions of DMP + octanol + benzene and DMP + isobutanol + benzene.

Dielectric relaxation studies of polar molecules in non-polar solvents by microwave absorption have frequently been attempted by so many researchers [1-6]. They studied the association of two polar molecules due to hydrogen bonding from the dielectric relaxation measurements at microwave frequencies. Purcell and Smyth [7] were the first to detect solute - solvent interactions through measurements of relaxation time. The dielectric relaxation studies of ternary mixtures of polar solvents in dilute solutions of non-polar liquids provide valuable information about solute-solute and solute-solvent interactions. Molecular association between triethylamine with alcohols in benzene in the microwave region was studied by this dielectric relaxation behaviour by Kumar et al. [8] using single frequency concentration variation method.

In order to provide the experimental data on ternary mixture, dimethyl phthalate with octanol in benzene and dimethyl phthalate with isobutanol in benzene at various concentrations were studied at microwave region at different temperatures of 303K, 308K and 313K [9]. The study is expected to provide better understanding of the nature of molecular orientation processes.

2. MATERIALS AND METHODS

Dimethyl phthalate with octanol in benzene and dimethyl phthalate with isobutanol in benzene were used. The molar concentrations of the ternary mixture of the octanol and isobutanol with   dimethyl phthalate in benzene are 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6.   The measurement of dielectric constant at an angular frequency (ε') and dielectric loss (ε'') was carried out in the X band microwave frequency at 9.36 GHz.   The static dielectric constant (ε_0) was measured by heterodyne beat method[10] at three different temperatures 303K, 308K and 313K using a dipole meter operated at 220 volts.   The refractive index was measured by Abbe's refractometer [11].   The errors in the measurements of density and refractive index (n_D) are $\pm$ 0.002g/cc and $\pm$ 0.002 respectively. The temperature of all these measurements was maintained at 303K, 308K and 313K using a water circulating thermostat.   The density was measured with a 10ml specific gravity bottle.

3.THEORY

3.1 Higasi Method

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This method provides multiple relaxation times, one for overall rotation and another for group rotation. Higasi assumed a linear variation of ε_0, ε' and ε'' and ε_α with weight fraction w_2 of the solute and hence one can write,

$$\varepsilon_0 = \varepsilon_{01} + a_0 w_2$$
$$\varepsilon' = \varepsilon'_1 + a' w_2$$
$$\varepsilon' = a'' w_2$$
$$\varepsilon_\alpha = \varepsilon_{\alpha 1} + a_\alpha w_2$$
$$(1)$$

where a_0, a', a'' and a_α are the constants known as Higasi's parameters

Higasi et al. [12] derived a relation connecting τ and α.

$$\tau = \frac{1}{\omega}\left(\frac{A^2+B^2}{C^2}\right)^{\frac{1}{2(1-\alpha)}} \qquad (2)$$

$$(1-\alpha) = \frac{2}{\pi}\tan^{-1}\left(\frac{A}{B}\right) \qquad (3)$$

where τ is the most probable relaxation time, α is the distribution parameter, ω is the angular frequency and

A = a'' (a_0- a_α)
B= $(a_0-a')(a'-a_\alpha) - a'^2$
C= $(a'-a_\alpha)^2 + a''^2$

The Debye equation in terms of a_0, a', a'' and a_α yields two independent equations [13].

$$\tau(1) = \frac{a''}{\omega(a'-a_\infty)} \qquad (4)$$

$$\tau(2) = \frac{(a_0-a')}{\omega a''} \qquad (5)$$

$\tau(1)$ is the molecular relaxation time of the complex as a whole and $\tau(2)$ indicates the relaxation time of the base molecule of alcohols.

$\sqrt{\tau(1)\tau(2)} = \tau$ may be the mean relaxation time and will be calculated.

3.2 Cole-Cole Method

The measured values of ε_0, ε', ε'' and ε_α were fitted in a complex plane plot with a depressed circular arc. The angle made by the diameter drawn through the centre from the ε_α point and the abscissa axis is given by $\left(\frac{\alpha\pi}{2}\right)$. From the Cole-Cole plot the relaxation time τ can be found using the equation.

$$(\omega\tau)^{1-\alpha} = v/u \qquad (6)$$

where ω is the angular frequency, α is the distribution parameter, v is the distance between ε_0 and the experimental point on the Cole-Cole plot and u is the distance between ε_α and that point on the Cole-Cole plot.

The dipole moment is calculated by Higasi's relation

$$\mu = \left(\frac{27 M_2 kT}{\pi N_A d_1}\right)^{\frac{1}{2}}\left(\frac{1}{(2\varepsilon_1+2)}\right) \qquad (7)$$

4. RESULTS AND DISCUSSION

The values of the dielectric constant at high frequency (ε'), the dielectric loss (ε''), the distribution parameter (α), the most probable relaxation time (τ), the relaxation time for overall rotation of the molecule $\tau(1)$, the relaxation time for group rotation $\tau(2)$ and the excess dipole moment for the system-I (benzene + dimethyl phthalate + octanol) and system II (benzene + dimethyl phthalate + isobutanol) for three different temperatures 303 K, 308K, and 313K are reported in Tables 1 to 4.

For system I, the static dielectric constant, the dielectric constant at microwave frequency and dielectric loss are found to increase with the increase of concentration of the mixture. The dielectric constant at optical frequency is found to decrease with increase of concentration of the mixture. For system II, the static dielectric constant, dielectric constant at optical frequency, the dielectric constant at microwave frequency and dielectric loss are found to increase with the increase of concentration of the mixture. The non linear variation of dielectric constant with weight fraction (Figure 1 to 4) for the above two systems indicates the hetero junction between the components [14].

Higasi's parameters were calculated using equation (2) and (3). The relaxation time (τ) and the distribution parameter (α) were also determined by Cole-Cole method using equation (2). The value of τ provides information regarding the orientation of dipoles between the interacting components. The τ values obtained from ternary liquid systems by Cole-Cole method were slightly higher than the values obtained by Higasi's method. This may be attributed to the rigid behavior of solute molecules. Similar results were reported by Krishnan et al. [15] in the studies of alcohols and triethylamine.

The non linear variation of the relaxation time with variation of mole fraction in the mixture predicts the molecular association between the components between the solute - solute. The dipole-dipole interactions are the main cause for molecular association between the components . The different sizes of the relaxing units give rise to a changed environment, but not to a distinguishable change in the multimeric unit responsible for different relaxation times. As the concentration of the solute increases, the relaxation time found to increase for the two systems. Our results are consistent with the interpretation that there is a progressive change in the n-mer and no abrupt change on the dilution. Davidson [16] showed that the relaxation process for any system can be resolved into inter molecular relaxation time $\tau(1)$, and intra molecular relaxation time $\tau(2)$ components only if the ratio of the relaxation time $\left(\frac{\tau(1)}{\tau(2)}\right)$ is greater than 6. In our present investigation, such resolution is found to occur in system I and no such resolution is found to occur in system II owing to the increased overlap of the nearby equal regions. The relaxation time depends on the orientation and size of the molecules. The values of relaxation time were also calculated by Cole-Cole plot method. Similar results were reported by Mushtaq et al.[3].

The significant alpha values of the mixtures also suggest that beside the molecular reorientation in the mixture, there is a large probability of the group rotations due to breaking and

reforming of hydrogen bonds in dilute solution. $\tau(1)$ may be due to individual molecular rotation where as $\tau(2)$ may be due to over all intermolecular rotation.

The excess dipole moment is a qualitative index for the presence of a hydrogen bond in the ternary system. The excess dipole moment of the mixture is calculated using the following equation

$$\Delta\mu = \mu_{ab} - \mu_a - \mu_b \qquad (8)$$

The excess dipole moment may be attributed to the proton - transfer in this bond. Similar results were reported by Thenappan [17] for the mixture of amines and alcohols in benzene and by Subramanian [18] for the mixtures of alcohols and nitriles in benzene /1, 4 dioxane.

The values of $\Delta\mu$ are found to be negative for all the concentrations and temperatures. This shows the absence of ionic structures [19,20]. The negative value of $\Delta\mu$ also indicates the presence of hydrogen bonds between the partners.

V. ACKNOWLEDGEMENT

System I : Dimethyl phthalate + octanol + benzene
Table 1: Values of dielectric constants and Higasi's parameters at different temperatures

Temp.	w_2	ε_o	ε_α	ε'	ε''	a_0	a'	a''	a_α
303 K	0.11	3.3555	2.2192	3.3071	0.9170	93.244	89.077	79.060	-0.360
	0.21	3.4985	2.2150	3.3193	0.9245	52.827	45.094	39.885	-0.360
	0.34	3.5190	2.2118	3.3236	0.9287	35.833	30.208	26.729	-0.334
	0.39	3.5909	2.1996	3.3301	0.9312	28.447	22.813	20.114	-0.514
	0.52	3.6631	2.1960	3.3573	0.9481	24.021	18.734	16.395	-0.473
	0.60	3.6941	2.1937	3.3711	0.9553	20.478	15.820	13.776	-0.429
308 K	0.11	3.5137	2.2091	3.3261	0.9170	107.407	91.226	79.060	-0.768
	0.21	3.5989	2.2067	3.3537	0.9245	57.415	46.837	39.885	-0.487
	0.34	3.6309	2.2037	3.3717	0.9287	39.225	31.764	26.729	-0.410
	0.39	3.6950	2.1913	3.3811	0.9312	30.825	24.043	20.114	-0.577
	0.52	3.8453	2.1889	3.4175	0.9481	27.276	19.878	16.395	-0.503
	0.60	3.9856	2.1801	3.4481	0.9553	24.770	17.018	13.776	-0.547
313 K	0.11	3.6263	2.1972	3.3380	0.9170	117.542	92.684	79.060	-1.534
	0.21	3.7126	2.1910	3.3718	0.9245	62.537	47.834	39.885	-1.036
	0.34	3.7330	2.1889	3.3763	0.9287	42.307	32.041	26.729	-0.751
	0.39	3.7964	2.1851	3.3924	0.9312	33.123	24.395	20.114	-0.646

0.52	3.9054	2.1759	3.4104	0.9481	28.402	19.842	16.395	-0.676
0.60	4.1020	2.1671	3.4808	0.9853	26.520	17.562	14.209	-0.691

Table 2 : Values of relaxation time, distribution parameter and activation energy at different temperatures

| Temp. | w_2 | Relaxation Time(pico second) | | | | Distribution Parameter | | Excess dipole moment |
| | | Higasi's Method | | | Cole-Cole plot | Higasi | cole-cole | |
		τ_1	τ_2	τ	τ	α	α	$\Delta\mu$
303 K	0.11	15.039	0.897	3.672	9.17	0.623	0.412	1.479
	0.21	14.928	3.298	7.017	9.70	0.457	0.322	0.820
	0.34	14.888	3.580	7.301	9.77	0.388	0.311	-0.071
	0.39	14.669	4.765	8.361	10.06	0.289	0.265	-0.511
	0.52	14.522	5.486	8.926	10.26	0.254	0.237	-0.813
	0.60	14.424	5.752	9.109	10.32	0.238	0.226	-1.075
308 K	0.11	14.620	3.482	7.135	9.63	0.611	0.309	1.244
	0.21	14.338	4.512	8.043	9.84	0.328	0.267	1.084
	0.34	14.133	4.748	8.192	9.84	0.317	0.254	0.161
	0.39	13.899	5.736	8.929	10.08	0.288	0.216	-0.324
	0.52	13.686	7.677	10.250	10.74	0.173	0.149	-0.558
	0.60	13.343	9.573	11.302	11.38	0.116	0.085	-0.726
313 K	0.11	14.275	5.349	8.738	10.11	0.334	0.237	3.466
	0.21	13.885	6.271	9.331	10.29	0.218	0.198	0.851
	0.34	13.867	6.534	9.518	10.38	0.209	0.189	0.386
	0.39	13.665	7.382	10.043	10.62	0.197	0.158	-0.146
	0.52	13.594	8.882	10.989	11.21	0.162	0.111	-0.442
	0.60	13.243	10.726	11.918	11.86	0.115	0.052	-0.567

System II : Dimethyl phthalate + isobutanol+ benzene

Table 3 : Values of dielectric constants and Higasi's parameters at different temperatures

Temp.	w_2	ε_o	ε_α	ε'	ε''	a_0	a'	a''	a_α
303 K	0.12	3.0618	2.2252	2.9442	0.4476	67.921	57.787	38.596	0.154
	0.21	3.4509	2.2189	3.2396	0.5743	50.771	41.656	24.775	-0.193
	0.33	3.5704	2.2150	3.2922	0.4927	37.311	29.303	14.179	-0.240
	0.42	3.6321	2.2118	3.3206	0.6150	29.337	22.607	13.285	-0.251
	0.51	3.7147	2.2094	3.4542	0.9117	24.914	20.409	15.767	-0.242
	0.60	3.7665	2.2061	3.3813	1.0396	21.523	17.987	14.992	-0.249
308 K	0.12	3.1521	2.2240	2.9520	0.1890	76.226	58.978	16.295	0.515
	0.21	3.4529	2.2073	3.2638	0.8023	51.119	42.958	34.612	-0.461
	0.33	3.6684	2.2109	3.3114	0.6368	40.304	30.029	18.329	-0.205
	0.42	3.8345	2.2037	3.4721	0.8811	33.838	26.009	19.032	-0.308
	0.51	3.9748	2.1978	3.5232	0.7998	29.516	21.706	13.831	-0.349
	0.60	4.0529	2.1966	3.5596	0.8999	25.740	18.626	12.977	-0.308
313 K	0.12	3.3653	2.2186	3.0911	0.4482	95.040	71.402	38.647	0.311
	0.21	3.6108	2.2026	3.2707	0.5683	58.145	43.471	24.516	-0.537

	0.33	3.6865	2.1966	3.3200	0.6692	40.971	30.423	19.261	-0.529
	0.42	3.9622	2.1940	3.4914	0.5227	36.704	26.534	11.291	-0.455
	0.51	4.1781	2.1901	3.5918	0.6323	33.117	22.978	10.933	-0.431
	0.60	4.2347	2.1874	3.5825	0.4639	28.433	19.029	6.690	-0.397

Table 4 : Values of relaxation time, distribution parameter and activation energy at different temperatures

| Temp.	w_2	Relaxation Time(pico second)				Distribution Parameter		Excess dipole moment
		Higasi's Method			Cole-Cole plot	Higasi	cole-cole	
		τ_1	τ_2	τ	τ	α	α	$\Delta\mu$
303 K	0.12	11.393	4.467	7.134	8.28	0.529	0.191	0.933
	0.21	10.071	6.260	7.940	8.32	0.507	0.102	0.239
	0.33	8.165	9.607	8.857	8.46	0.488	0.054	-0.402
	0.42	9.888	8.618	9.231	9.12	0.461	0.024	-0.839
	0.51	11.066	8.619	9.766	9.78	0.434	0.023	-1.108
	0.60	15.727	6.303	9.956	11.08	0.417	0.038	-1.330
313 K	0.12	4.742	18.007	9.240	9.67	0.346	0.233	1.276
	0.21	13.561	4.011	7.376	9.65	0.323	0.068	0.304
	0.33	10.313	9.537	9.917	9.72	0.299	0.009	-0.219
	0.42	12.303	6.998	9.279	9.82	0.276	0.138	-0.552
	0.51	10.669	9.606	10.123	10.00	0.253	0.018	-0.794
	0.60	11.660	9.326	10.428	11.43	0.230	0.052	-1.025
323 K	0.12	9.248	10.405	9.810	9.39	0.161	0.047	1.986
	0.21	9.477	10.183	9.824	9.49	0.138	0.032	0.650
	0.33	10.587	9.317	9.932	9.80	0.115	0.023	-0.136
	0.42	7.117	15.324	10.444	9.97	0.092	0.223	-0.359
	0.51	7.946	15.776	11.196	10.75	0.068	0.206	-0.555
	0.60	5.859	23.916	11.837	11.83	0.045	0.402	-0.828
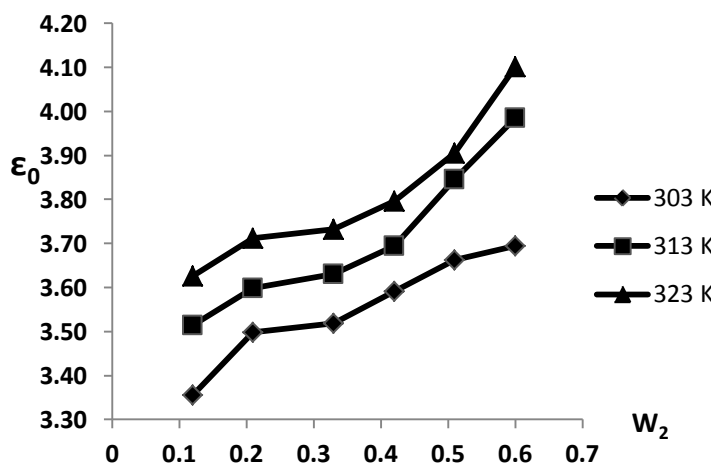
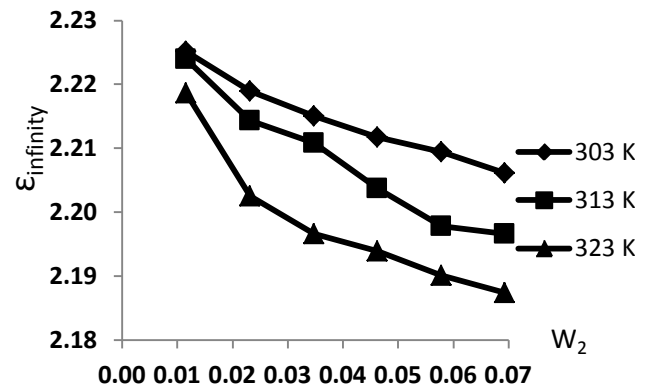Fig:1 Variation of dielectric constant with weight fraction for the system - I

Figure:2 Variation of dielectric constant at optical frequency with weight fraction for the system - I
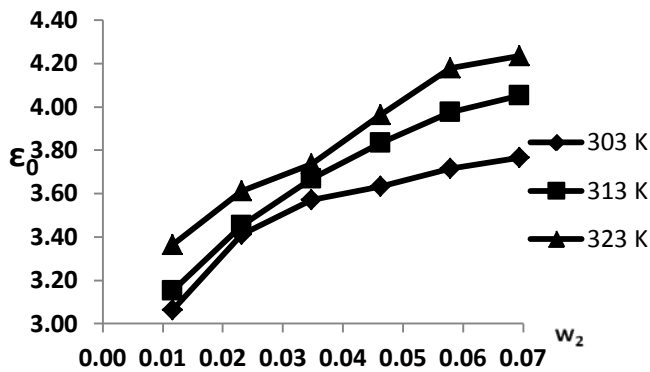
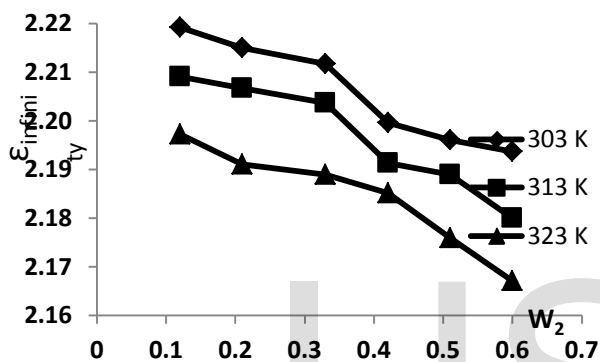Fig:3 Variation of dielectric constant with weight fraction for the system - II

Fig:4 Variation of dielectric constant at optical frequency with weight fraction for the system - II

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