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Dielectric Relaxation Studies of Ternary Liquid Mixtures of Dimethyl Phthalate with Triethylamine in the Microwave Region

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ABSTRACT: 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. The dielectric behavior of Triethylamine with Dimethyl Phthalate has been studied at microwave frequency 9.36 GHz at different temperatures 303K, 308K and 313K. 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 system investigated shows the maximum relaxation time values at temperatures by both Higasi's method and Cole-Cole method.

KEYWORDS: Dielectric constant, Dielectric loss, Optical frequency, Higasi's method, Cole–cole method, Dimethylphthalate, Trimethylamine.

I. INTRODUCTION

The dielectric relaxation behaviour of mixtures of polar molecules under varying conditions of complexation, temperature and environmental factors has evoked considerable interest. Based on the results, models of relaxation process in liquid mixtures have been formulated. So many researchers [1-6] 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 S. Kumar et al [8] using single frequency concentration variation method.

In order to provide the experimental data on ternary mixture, dimethyl Phthalate with triethylamine 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.

II. MATERIALS AND METHODS

Dimethyl Phthalate with triethylamine in benzene was used. The molar concentrations of the ternary mixture of the triethylamine 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 [10] method 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 20ml specific gravity bottle.

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III. THEORY

Higasi Method

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.

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

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

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

$A = a''(a_0 - a_\alpha)$

$B = (a_0 - a')(a' - a_\alpha) - a'^2$

$C = (a' - a_\alpha)^2 + a''^2$

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

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

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

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

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

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.

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

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 free energy of activation due to dielectric relaxation (ΔF_τ) and viscous flow (ΔF_η) have been calculated using the following Eyring's [14] equations

$$\tau = \left(\frac{h}{kT}\right)\exp(\Delta F_\tau / RT) \quad (7)$$

$$\eta = \frac{N_A h}{V}\exp(\Delta F_\eta / RT) \quad (8)$$

where h is Planck's constant, k is Boltzmann constant, N is Avogadro number and V is molar volume.

The dipole moment is calculated by Higasi's relation

$$\mu = \left(\frac{27\, M_2 kT}{\pi N_A d_1}\right)^{\frac{1}{2}}\left(\frac{1}{(2\varepsilon_1+2)}\right) \quad (9)$$

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IV. RESULTS AND DISCUSSION

The values of the dielectric constants 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 benzene + dimethyl phthalate + triethylamine at temperatures 303 k, 308k, and 313k are reported in Table 1.

The static dielectric constant, the dielectric constant at optical frequency, the dielectric constant and dielectric loss at microwave frequency decrease with the increase of concentration of the mixture. The variation of the dielectric constant with concentration indicates the hetro junction between the components [15].

Higasi's parameters were calculated using equation (2) and (3). The relaxation time (τ) and the distribution parameter (α) were also determined by the Cole-Cole method using equation (2). Davidson [16] showed that the relaxation process for any system can be resolved into inter molecular relaxation time τ(1), and intra molecular relaxation time τ(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, no such resolution is found to occur owing to the increased overlap of the nearby equal regions. 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. Our results are consistent with the interpretation that there is a progressive change in the n-mer and no abrupt change on the dilution.

Table 1 Values of dielectric constants and Higasi's parameters at different temperatures

Temperature	w_2	ε_o	ε_α	ε'	ε''	a_0	a'	a''	a_α
303 K	0.011	2.718	2.246	2.574	0.046	40.380	30.909	6.909	1.093
	0.022	2.715	2.242	2.571	0.046	19.954	15.025	3.440	0.852
	0.033	2.712	2.235	2.568	0.046	13.176	9.687	2.256	0.359
	0.044	2.708	2.233	2.565	0.046	9.763	6.996	1.687	0.215
	0.056	2.706	2.227	2.563	0.046	7.752	5.275	1.328	0.064
	0.067	2.703	2.225	2.561	0.046	6.396	4.100	1.103	0.031
308 K	0.011	2.702	2.241	2.564	0.045	39.398	29.602	6.808	1.088
	0.022	2.693	2.239	2.560	0.045	19.234	14.346	3.394	0.930
	0.033	2.685	2.219	2.555	0.045	12.544	9.025	2.256	0.018
	0.044	2.678	2.217	2.551	0.045	9.223	6.366	1.665	-0.026
	0.056	2.669	2.212	2.547	0.045	7.195	4.773	1.328	-0.107
	0.067	2.660	2.210	2.541	0.045	5.844	3.623	1.088	-0.120
313 K	0.011	2.698	2.212	2.559	0.043	39.489	28.314	6.355	-0.294
	0.022	2.691	2.211	2.554	0.043	19.370	13.233	3.213	-0.187
	0.033	2.683	2.204	2.552	0.043	12.635	8.092	2.136	-0.330
	0.044	2.675	2.202	2.550	0.043	9.268	5.583	1.575	-0.300
	0.056	2.666	2.196	2.544	0.043	7.231	4.069	1.256	-0.346
	0.067	2.659	2.192	2.540	0.043	5.904	3.061	1.044	-0.336

The decrease in τ (1) and τ(2) with dilution is assigned to the reduction in the sizes of the n-mers due to the intervention caused by the solvent . The coupling between the dipoles is also reduced by the solvent, enabling the dipoles to rotate more freely. Similar results were reported by the Dannhauser et al. [17] and Cambell et al[18].

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

Temperature	w_2	Relaxation Time(pico second)				Distribution Parameter		Activation Energy (kJ/mol)		Excess dipole moment
		Higasi's Method			Cole-Cole plot	Higasi	cole-cole			
		τ_1	τ_2	τ	τ	α	α	$\Delta F\tau$	$\Delta F\eta$	$\Delta\mu$
303 K	0.011	4.079	23.320	9.753	11.339	0.449	0.656	10.361	13.135	-1.68
	0.022	4.129	24.377	10.032	11.650	0.461	0.665	10.432	15.071	-2.53
	0.033	4.115	26.312	10.406	12.068	0.484	0.679	10.524	16.213	-2.81
	0.044	4.233	27.900	10.867	12.492	0.496	0.689	10.633	16.995	-2.95
	0.056	4.335	31.726	11.727	13.251	0.528	0.710	10.824	17.703	-3.03
	0.067	4.613	35.404	12.779	13.999	0.546	0.725	11.041	18.204	-3.09
308 K	0.011	4.210	24.477	10.151	11.753	0.459	0.668	10.461	13.244	-1.69
	0.022	4.304	24.498	10.268	11.811	0.456	0.666	10.490	15.245	-2.55
	0.033	4.262	26.539	10.635	12.282	0.481	0.685	10.579	16.451	-2.81
	0.044	4.430	29.197	11.373	12.896	0.502	0.698	10.747	17.253	-2.96
	0.056	4.629	31.036	11.987	13.292	0.512	0.701	10.880	17.954	-3.05
	0.067	4.947	34.724	13.107	14.089	0.530	0.719	11.104	18.451	-3.10
313 K	0.011	3.779	29.917	10.633	12.628	0.532	0.711	10.578	13.334	-1.55
	0.022	4.073	32.491	11.504	13.316	0.543	0.725	10.776	15.419	-2.48
	0.033	4.314	36.181	12.494	14.020	0.562	0.740	10.984	16.669	-2.78
	0.044	4.553	39.809	13.463	14.585	0.576	0.749	11.172	17.480	-2.93
	0.056	4.841	42.835	14.399	15.077	0.583	0.755	11.341	18.188	-3.02
	0.067	5.227	46.347	15.565	15.620	0.586	0.760	11.536	18.655	-3.09

The τ values obtained from the Cole –Cole plot are 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 S. Krishnan et al. in the studies of alcohols and triethylamine [19].

For all the concentrations and temperatures studied, the free energy of activation (ΔF_τ) is less than the corresponding values of the viscous flow (ΔF_η). This is in agreement with the fact [20-21] that the process of viscous flow involves greater interference by neighbours than does dielectric relaxation as the latter takes place by rotation only whereas the viscous flow involves both the rotational and translational forms of motion.

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

$$\Delta\mu = \mu_{ab} - \mu_a - \mu_b \quad (10)$$

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The excess dipole moment may be attributed to the proton - transfer in this bond. Similar results were reported by Thenappan [22] for the mixture of amines and alcohols in benzene and by Subramainian [23] for the mixtures of alcohols and nitriles in benzene /1,4 dioxane . The values of relaxation times, distribution parameters, activation free energies and excess dipole moments at various temperatures are reported in Table 2.

The values of $\Delta\mu$ are found to be negative for all the concentrations and temperatures . This shows the absence of ionic structures[24, 25]. The negative value of $\Delta\mu$ also indicates the presence of hydrogen bonds between the partners.

V. ACKNOWLEDGEMENT

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