



MOLECULAR ASSOCIATION OF SUBSTITUTED BENZYL ALCOHOLS AND ETHYL METHACRYLATE IN CARBON TETRACHLORIDE: DIELECTRIC STUDY

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ABSTRACT

The dielectric relaxation of substituted benzyl alcohol (benzyl alcohol, *o*-aminobenzyl alcohol, *o*-methylbenzyl alcohol, *o*-fluorobenzyl alcohol, *o*-chlorobenzyl alcohol, *o*-bromobenzyl alcohol, *o*-iodobenzyl alcohol and *o*-nitrobenzyl alcohol) with Ethyl methacrylate in dilute solution of carbon tetrachloride is measured at 9.37 GHz using Frequency Domain (X-band) technique. Different dielectric parameters like dielectric constant (ϵ'), dielectric loss (ϵ''), dielectric constant at static frequency (ϵ_0), dielectric constant at optical frequency (ϵ_ω) are determined. The relaxation time and activation energy are calculated using the measured dielectric data. All the dielectric parameters that vary with the substituent of benzyl alcohols were observed and discussed.

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INTRODUCTION

Dielectric studies of liquid in pure state or in inert solvents have remained a subject of interest (Gupta *et al.*, 2003) because they provide useful information about the complex formation in solution. The dielectric relaxation studies are useful to investigate intermolecular and intramolecular interactions (Hill *et al.*, 1969). Benzyl alcohol and its substituents are found in the natural products and used for mechanistic investigation (Knop *et al.*, 1972, Matheu *et al.*, 1993 and Faubel *et al.*, 1997). Benzyl alcohol is mainly used in flavour industries, perfumery, artificial essences, cosmetics, paints, lacquers, soap and industrial solvents (Huang *et al.*, 2008). Ethyl methacrylate is an important monomer for a synthetic polymer poly (ethyl methacrylate), which is an excellent substitute for glass and has a wider area of use in dental and industrial applications (Schildknecht *et al.*, 1977). Liakath Ali Khan *et al.*, (2008) have investigated the complex formation of acrylic esters with phenol derivatives in non-polar solvents using frequency domain technique. Singh *et al.*, (2005) have studied the relaxation mechanism of some substituted alcohols using NMR techniques. Singh and Sinha (1985) measured the dielectric constant for benzyl alcohol with 1-hexanol in non-polar solvents. Dharmalingam *et al.*, (2005) have reported the hydrogen bonding between acrylic esters with aliphatic alcohols in non-polar solvents through dielectric studies. Thus the study and knowledge of dielectric properties of the ternary mixtures of polar associating liquids

(aromatic alcohols) with acrylic esters in non-polar solvents is expected to provide useful and vital process parameters for efficient design of transesterification processes of industrial interest. Keeping both the industrial and scientific interest in mind, an attempt has been made in this research paper to study the hydrogen bonding between aromatic alcohols and ester using dielectric method. This study is expected to provide better understanding of the nature of molecular orientation processes.

MATERIALS AND METHODS

Materials

Ethyl methacrylate, benzyl alcohol, *o*-aminobenzyl alcohol, *o*-methylbenzyl alcohol, *o*-fluorobenzyl alcohol, *o*-chlorobenzyl alcohol, *o*-bromobenzyl alcohol, *o*-iodobenzyl alcohol and *o*-nitrobenzyl alcohol with purity > 99% (spectroscopic grade) were purchased from Aldrich and used without any further purification. AR grade carbon tetrachloride was purified by standard method (Weissberger, 1970) and redistilled before use. The physical parameters of all the chemicals used in this study were checked against their literature values.

Dielectric Measurements

The static dielectric constants were measured by heterodyne beat method at 308 K using a commercial instrument, Dipolemeter DM 01 supplied by Wissenschaftlich Technische Werkstatter, Germany, operated at 220 V. The refractive indices were measured by Abbe's refractometer with an accuracy of ± 0.0005 . The percentage of deviation in the

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measurement of refractive index is about $\pm 0.02\%$. The measurements of dielectric constant at an angular frequency (ϵ') and dielectric loss (ϵ''), were carried out in the X-band microwave frequency of 9.37 GHz. The viscosities were measured with the help of Oswald's viscometer. The temperature of all these measurements were maintained at $35 \pm 0.1^\circ\text{C}$ using a water circulating thermostat.

Theory

According to the method of Higasi *et al.*, (1971) the individual relaxation time $\tau_{(1)}$ is described by

$$\tau_{(1)} = \frac{a''}{\omega(a' - a_\infty)}$$

While the overall dielectric relaxation $\tau_{(2)}$ is given by

$$\tau_{(2)} = \frac{a_o - a'}{\omega a''}$$

and the most probable relaxation time $\tau_{(0)}$ is given by,

$$\tau_{(0)} = \sqrt{\tau_{(1)}\tau_{(2)}}$$

Where, ω is the angular frequency; a_0 , a' , a'' , and a^∞ are defined by the following:

$$\epsilon_0 = \epsilon_{01} + a_0 w_2$$

$$\epsilon' = \epsilon'_{1} + a' w_2$$

$$\epsilon'' = a'' w_2$$

$$\epsilon_\infty = \epsilon_{1\infty} + a_\infty w_2$$

in which subscript 1 refers to the pure solvent, 2 refers to the solute, 0 refers to the static frequency, and $\square\square$ refers to the infinite or optical frequency measurements, and w_2 is the weight fraction of the solute. The molar free energy of activation, for both dielectric relaxation ΔF_τ as well as the viscous flow processes ΔF_η has been evaluated using the equations given by Eyring *et al.*, (1941)

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

$$\eta = \frac{N h}{V} \exp\left(\frac{\Delta F_\eta}{RT}\right)$$

Where h is Plank's constant, k is Boltzmann constant, N is Avogadro's number, and V is the molar volume

RESULTS AND DISCUSSION

The value of dielectric constant (ϵ'), dielectric loss (ϵ''), dielectric constant at static frequency (ϵ_0), dielectric constant at angular frequency (ϵ_∞), the relaxation time due to the individual molecular rotations ($\tau_{(1)}$), the relaxation time due to the whole or overall molecular rotations ($\tau_{(2)}$), the most probable relaxation time ($\tau_{(0)}$) and the free energy of activation for dielectric relaxation process (ΔF_τ) and viscous flow (ΔF_η) of proton donors (*o*-aminobenzyl alcohol, *o*-methylbenzyl alcohol, benzyl alcohol, *o*-fluorobenzyl alcohol, *o*-chlorobenzyl alcohol, *o*-bromobenzyl alcohol, *o*-iodobenzyl alcohol and *o*-nitrobenzyl alcohol) with proton acceptor (Ethyl

methacrylate) in carbon tetrachloride at 308 K are shown in Table 1 and 2. In Table 1, it is observed that the values of $\tau_{(2)}$ are significantly higher than $\tau_{(1)}$ and $\tau_{(0)}$ for all the systems. Higher values of $\tau_{(2)}$ indicate that the contribution of intermolecular or overall molecular relaxation is larger in comparison to intramolecular or individual molecular relaxation in the systems (Khameshara *et al.*, 1983). In the present study, it has been observed that the relaxation time of ternary mixtures (benzyl alcohol derivatives with ema in CCl_4) is much greater than the binary mixture (benzyl alcohol derivatives with CCl_4 or ema with CCl_4). This result indicates that there is a hydrogen bond formation between the hydrogen atom in O-H group of substituted benzyl alcohols and the oxygen atom in C=O group of ethyl methacrylate, and is shown in Fig 1.

For a given ethyl methacrylate, the relaxation times and activation energies values are increasing in the order: *o*-aminobenzyl alcohol < *o*-methylbenzyl alcohol < benzyl alcohol < *o*-fluorobenzyl alcohol < *o*-chlorobenzyl alcohol < *o*-bromobenzyl alcohol < *o*-iodobenzyl alcohol < *o*-nitrobenzyl alcohol. This change in relaxation times and activation energies values indicates that the proton donating ability of proton donor varies with the substitution in benzyl alcohol. This may be due to acidity of benzyl alcohol increasing in the same sequence. By changing the type and number of substituents in benzyl ring, the acidity can be regulated almost continuously. Further, the relaxation time and activation energies value decreases for electron donating groups (i.e., amino and methyl) and increases for electron withdrawing groups (i.e., fluoro, Chloro, bromo, iodo and nitro) when compared with benzyl alcohol. This is because, the electron donating substituents make the bond breaking process easier, whereas the electron withdrawing groups make the bond making process easier. This is well reflected with a lower relaxation times and activation energies values for electron donating groups and higher relaxation times and activation energies values for electron withdrawing groups with ethyl methacrylate. Therefore, the strong hydrogen bond would be expected to form between *o*-nitrobenzyl alcohol with ethyl methacrylate in carbon tetrachloride and weakest hydrogen bond between *o*-aminobenzyl alcohol with ethyl methacrylate in carbon tetrachloride as reflected by the higher relaxation time for former systems and lower relaxation time for lesser systems. The relaxation time values for *o*-nitrobenzyl alcohol with ethyl methacrylate are found to be greater than that for all other substituted benzyl alcohols, which reveals that, the tendency of complex formation of *o*-nitrobenzyl alcohol is relatively larger than other substituted benzyl alcohols. Similar results of methacrylates with phenol derivatives were carried out by Liakath Ali Khan *et al.*, (2010)

Table 1 shows that, the relaxation times of all studied systems are larger at 1:1 molar ratio than other higher molar ratios (3:1, 2:1, 1:2, 1:3). This indicates that the 1:1 complex formation is the predominant value in substituted benzyl alcohol - ethyl methacrylate systems. Similar results were reported by Malathi *et al.*, (2003) in some carbonyl + phenol derivative systems. The molar free energy of activation for viscous flow (ΔF_τ) and the free energy (ΔF_η) calculated for proton donors (*o*-aminobenzyl alcohol, *o*-methylbenzyl alcohol, benzyl alcohol, *o*-fluorobenzyl alcohol, *o*-chlorobenzyl alcohol, *o*-bromobenzyl alcohol, *o*-iodobenzyl alcohol and *o*-nitrobenzyl alcohol) with proton acceptor (Ethyl methacrylate) in carbon

Table 1. Values of dielectric constants and relaxation times for Substituted Benzyl alcohols with Ethyl methacrylate in carbon tetrachloride.

Ratio of benzyl alcohol:ethyl methacrylate	ϵ'	ϵ''	Relaxation time (ps) using Higasi's method				
			ϵ_0	ϵ_∞	$\tau_{(1)}$	$\tau_{(2)}$	$\tau_{(0)}$
<i>o</i> -Aminobenzyl alcohol							
1:3	2.5982	0.2852	2.8926	2.1814	14.64	17.43	15.98
1:2	2.6123	0.3142	3.0342	2.1939	16.05	22.67	19.08
1:1	2.6241	0.3368	3.1576	2.2056	17.20	26.75	21.45
2:1	2.6114	0.3127	3.0357	2.1901	15.84	22.91	19.05
3:1	2.5974	0.2841	2.8969	2.1823	14.66	17.80	16.16
<i>o</i> -Methylbenzyl alcohol							
1:3	2.5554	0.2432	2.8523	2.2316	17.41	20.61	18.94
1:2	2.5712	0.2718	2.9811	2.2334	18.37	25.47	21.63
1:1	2.5842	0.2904	3.1156	2.2412	19.22	30.90	24.37
2:1	2.5732	0.2724	2.9805	2.2331	18.24	25.25	21.46
3:1	2.5541	0.2413	2.8521	2.2316	17.37	20.85	19.03
Benzyl alcohol							
1:3	2.4865	0.1876	2.7775	2.2575	22.45	26.19	24.25
1:2	2.5072	0.2212	2.8958	2.2592	23.33	29.67	26.31
1:1	2.5163	0.2413	3.0389	2.2683	25.45	36.57	30.51
2:1	2.5078	0.2209	2.8958	2.2594	23.24	29.66	26.25
3:1	2.4855	0.1887	2.7784	2.2572	22.70	26.21	24.39
<i>o</i> -Fluorobenzyl alcohol							
1:3	2.4433	0.1385	2.6957	2.2613	24.85	30.77	27.66
1:2	2.4587	0.1653	2.8068	2.2624	25.75	35.56	30.26
1:1	2.4792	0.1897	2.9221	2.2731	27.10	39.42	32.69
2:1	2.4582	0.1647	2.8071	2.2621	25.70	35.77	30.32
3:1	2.4441	0.1382	2.6926	2.2599	24.23	30.36	27.13
<i>o</i> -Chlorobenzyl alcohol							
1:3	2.4241	0.1172	2.6581	2.2608	26.25	33.71	29.75
1:2	2.4327	0.1358	2.7421	2.2619	27.66	38.47	32.62
1:1	2.4472	0.1632	2.8668	2.2731	31.97	43.42	37.26
2:1	2.4329	0.1361	2.7439	2.2612	27.42	38.59	32.53
3:1	2.4219	0.1176	2.6572	2.2601	26.87	33.79	30.13
<i>o</i> -Bromobenzyl alcohol							
1:3	2.3841	0.0721	2.5648	2.2621	35.70	42.32	38.87
1:2	2.3987	0.1023	2.6741	2.2633	36.37	45.46	40.66
1:1	2.4198	0.1281	2.8093	2.2776	39.84	51.34	45.23
2:1	2.3981	0.1034	2.6732	2.2628	36.84	44.93	40.68
3:1	2.3852	0.0732	2.5645	2.2620	35.02	41.36	38.06
<i>o</i> -Iodobenzyl alcohol							
1:3	2.3794	0.0674	2.5584	2.2622	38.84	44.85	41.74
1:2	2.3907	0.0956	2.6598	2.2634	40.97	47.53	44.13
1:1	2.4126	0.1204	2.7924	2.2778	43.35	53.27	48.05
2:1	2.3924	0.0982	2.6573	2.2629	39.86	45.55	42.61
3:1	2.3801	0.0687	2.5561	2.2622	38.67	43.26	40.90
<i>o</i> -Nitrobenzyl alcohol							
1:3	2.3725	0.0581	2.5392	2.2627	44.80	48.45	46.59
1:2	2.3837	0.0876	2.6487	2.2638	46.23	51.08	48.59
1:1	2.4034	0.1097	2.7753	2.2781	49.53	57.25	53.25
2:1	2.3831	0.0889	2.6485	2.2633	47.06	50.41	48.71
3:1	2.3735	0.0598	2.5402	2.2628	44.29	47.07	45.66

Table 2. Activation energies at 1:1 stoichiometric ratios of Substituted Benzyl alcohols + Ethyl methacrylate systems in Carbon tetrachloride at 308 K

Alcohol	Activation energy	
	ΔF_τ kJ/mole	ΔF_η kJ/mole
<i>o</i> -Aminobenzyl alcohol	11.62	13.38
<i>o</i> -Methylbenzyl alcohol	12.13	13.72
Benzyl alcohol	12.32	14.07
<i>o</i> -Fluorobenzyl alcohol	12.97	14.52
<i>o</i> -Chlorobenzyl alcohol	13.38	14.97
<i>o</i> -Bromobenzyl alcohol	13.82	15.32
<i>o</i> -Iodobenzyl alcohol	14.26	15.61
<i>o</i> -Nitrobenzyl alcohol	14.78	15.97

tetrachloride are presented in Table 2. It is evident from the data that the ΔF_η is $> \Delta F_\tau$. This is in agreement with the fact that the process of viscous flow, which involves both the rotational and translational forms of motion faces greater interference

from neighbours than dielectric relaxation, which takes place by rotation only (Kalaivani *et al.*, 2004). Smyth *et al.*, (1981) pointed out that the relaxation time of a proton donor increases as the acceptor ability of the solvent environment

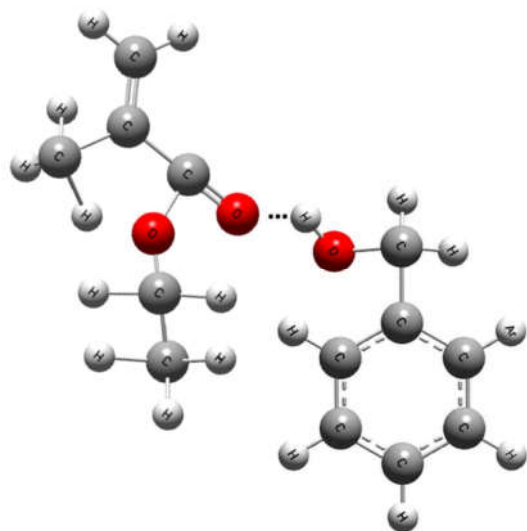


Fig 1. Hydrogen bonding between Substituted Benzyl alcohols and Ethyl methacrylate.

Ar = NH₂ (*o*-Aminobenzyl alcohol), CH₃ (*o*-Methylbenzyl alcohol), H (Benzyl alcohol), F (*o*-Fluorobenzyl alcohol), Br (*o*-Bromobenzyl alcohol), Cl (*o*-Chlorobenzyl alcohol), I (*o*-Iodobenzyl alcohol), NO₂ (*o*-Nitrobenzyl alcohol).

increases. All the results are in complete accordance with this conclusion.

Conclusion

The complex formation between substituted benzyl alcohols with ethyl methacrylate in carbon tetrachloride has been carried out using dielectric method. From this study, it may be concluded that the degree of complex formation varies with substituent of benzyl alcohols and 1:1 complex formation is more predominant than other higher order complexes.

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