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Molecular Interaction Studies of Benzyl Alcohols with Methacrylates in Carbon Tetrachloride using Frequency Domain Technique

S. RADHAKRISHNAN[1,2] , K. RAMACHANDRAN[3] and K.SAMUVEL[3]

[1]Research and Development Centre, Bharathiar University, Coimbatore-641 046, Tamilnadu, India.
[2]Department of Physics, Sriram Engineering College, Perumalpattu-602 024, Tamilnadu, India.
[3]Department of Physics, Vadapalani Campus, SRM University, Chennai-600 026, Tamilnadu, India.
*Corresponding author E-mail address: kaviramach76@gmail.com

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ABSTRACT

The dielectric relaxation of benzyl alcohol substitutents (benzyl alcohol, *m*-methylbenzyl alcohol and *m*-nitrobenzyl alcohol) with methyl methacrylate and butyl 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 factor (ε'') at Microwave frequency, static dielectric constant (ε_0) and dielectric constant at infinite dilution (ε_∞) at optical frequency have been determined. From the measured dielectric data, the relaxation time (τ) calculated using Higasi method and activation energies (ΔF_t and ΔF_η) have been determined. All the dielectric parameters that are vary with the substitutent change in benzyl alcohol and chain length of acrylic esters. Suggests that, the proton donating ability is varying with the substitution of benzyl alcohol and proton accepting ability is varying with the chain length of acrylic esters. The relaxation time and molar free energy activation of 1:1 molar ratio is greater than other higher molar ratios (i.e. 3:1, 2:1, 1:2, 1:3) confirm that the existence of most likely 1:1 complex formation between the studied systems and also complex formation formed between free hydroxyl group of substituted benzyl alcohols and carbonyl group of acrylic esters (MMA and EMA).

Keywords: Relaxation time, Activation free energy, Benzyl alcohol, Methyl methacrylate, Butyl methacrylate.

INTRODUCTION

Benzyl alcohol and its substitutents are found in the natural products and used for mechanistic investigation[3, 10, 14]. Benzyl alcohol is used as a general solvent for inks, paints, lacquers, and epoxy resin coatings. It is also a precursor to a variety of esters, used in the soap, perfume, and flavor industries, as well as for pharmaceuticals[7]. It exhibits bacteriostatic and antipruritic properties. It is also used as a photographic developer. Acrylic esters are industrially important chemicals and precursors in the synthesis of polymers[15]. Methacrylates are an important monomer for a synthetic polymer poly, which is an excellent substitute for glass and has a wider area of use in dental and industrial applications[15]. Dielectric studies of liquid in pure state or in inert solvents have remained a subject of interest[4] because they provide useful information about the complex formation in solution. The dielectric relaxation studies are useful to investigate intermolecular and intramolecular interactions[6]. Liakath Ali Khan *et al.*,[12] have investigated the complex formation of acrylic esters with phenol derivatives in non-polar solvents using frequency domain technique. Singh *et al.,*[16] have studied the relaxation mechanism of some substituted alcohols using NMR techniques. Singh and Sinha[17] measured the dielectric constant for benzyl alcohol with 1-hexanol in non-polar solvents. Dharmalingam *et al.,* [1] have reported the hydrogen bonding between acrylic esters with aliphatic alcohols in non-polar solvents through dielectric studies. 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.

Experimental Section and method

Materials

Methyl methacrylate, Butyl methacrylate, benzyl alcohol, *m*-methylbenzyl alcohol, and *m*-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[19] 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 Wissenschaijftlich Technische Werkstatter, Germany, operated at 220 V. The refractive indices were measured by Abbe's refractometer. 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 was maintained at 35 ± 0.1°C using a water circulating thermostat.

Theory

According to the method of Higasi *et al.,*[5] 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; α_0, α', α'', and α are defined by the following:

$$\varepsilon_0 = \varepsilon_{01} + a_0 w_2,\ \varepsilon' = \varepsilon_1 + a' w_2,\ \varepsilon'' = a'' w_2,\ \varepsilon_\infty = \varepsilon_{1\infty} + a_\infty w_2$$

in which subscript 1 refers to the pure solvent, 2 refers to the solute, 0 refers to the static frequency, and ¥ 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 ΔFt as well as the viscous flow processes $\Delta F\eta$ has been evaluated using the equations given by Eyring *et al.,*[2]

$$\tau = \frac{h}{kT}\exp\left(\frac{\Delta F_\tau}{RT}\right) \quad , \quad \eta = \frac{Nh}{V}\exp\left(\frac{\Delta F_\eta}{RT}\right)$$

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_o), dielectric constant at angular frequency (ε_∞), the relaxation time due to the individual molecular rotations ($t_{(1)}$), the relaxation time due to the whole or overall molecular rotations ($\tau_{(2)}$), the most probable

Table 1: Static dielectric constant (ε_0), dielectric constant at angular frequency (ε_0), dielectric constant (ε'), dielectric loss (ε''), dielectric relaxation time and activation energies ($\Delta F\tau$, $\Delta F\eta$) for m-methylbenzyl alcohol with acrylic esters in carbon tetrachloride

Esters	Ratio Ester: Alcohol	ε'	ε''	ε_o	ε_∞	Relaxation time (ps)			ΔF_τ kJ/mole	ΔF_η kJ/mole
						$\tau_{(1)}$	$\tau_{(2)}$	$\tau_{(0)}$		
MMA	0:1	2.5116	0.2296	2.7652	2.1298	13.19	18.65	15.69		
	1:3	2.5536	0.2402	2.8526	2.2318	17.34	21.02	19.09		
	1:2	2.5702	0.2745	2.9874	2.2326	18.56	25.66	21.83		
	1:1	2.5889	0.2887	3.1178	2.2461	19.13	30.94	24.32	12.02	13.19
	2:1	2.5713	0.2779	2.9865	2.2319	18.66	25.23	21.70		
	3:1	2.5574	0.2397	2.8528	2.2326	17.09	20.81	18.86		
	1:0	2.2845	0.0306	2.3046	2.1317	7.96	11.09	9.40		
BMA	0:1	2.5116	0.2296	2.7652	2.1298	13.19	18.65	15.69		
	1:3	2.5381	0.2305	2.8392	2.2418	18.68	22.06	20.30		
	1:2	2.5653	0.2608	2.9704	2.2483	19.22	26.23	22.45		
	1:1	2.5692	0.2793	3.0998	2.2507	20.45	32.08	25.61	12.52	14.18
	2:1	2.5642	0.2619	2.9726	2.2454	19.15	26.33	22.46		
	3:1	2.5408	0.2321	2.8372	2.2403	18.44	21.56	19.94		
	1:0	2.2718	0.0204	2.2876	2.1516	10.66	13.08	11.81		

Table 2: Static dielectric constant (ε_0), dielectric constant at angular frequency (ε_0), dielectric constant (ε'), dielectric loss (ε''), dielectric relaxation time and activation energies ($\Delta F\tau$, $\Delta F\eta$) for benzyl alcohol with acrylic esters in carbon tetrachloride

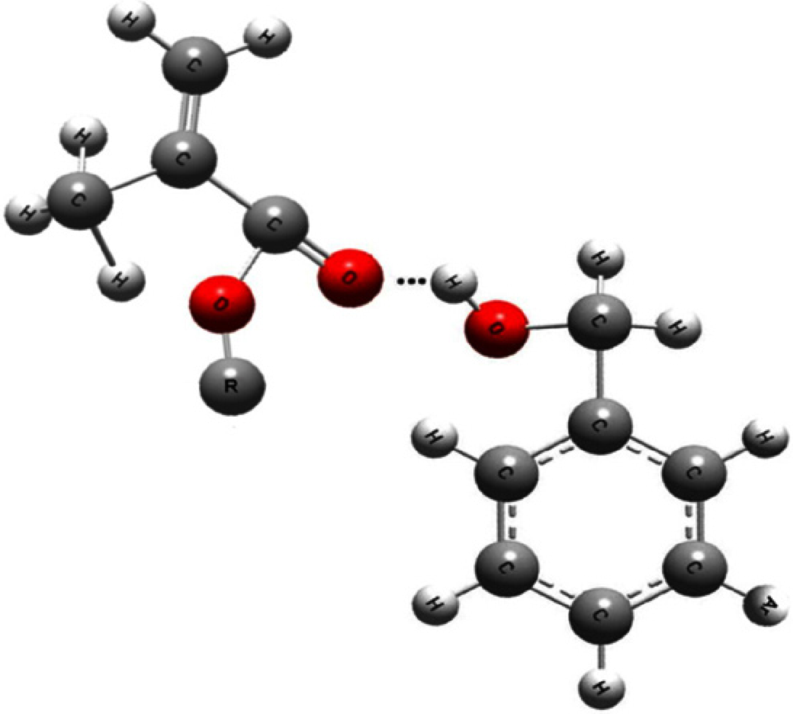
Esters	Ratio Ester: Alcohol	ε'	ε''	ε_o	ε_∞	Relaxation time (ps)			ΔF_τ kJ/mole	ΔF_η kJ/mole
						$\tau_{(1)}$	$\tau_{(2)}$	$\tau_{(0)}$		
MMA	0:1	2.4537	0.1689	2.6834	2.1891	16.14	22.96	19.25		
	1:3	2.5012	0.2023	2.7917	2.2484	20.72	24.25	22.41		
	1:2	2.5216	0.2422	2.9302	2.2528	22.61	28.49	25.38		
	1:1	2.5398	0.2617	3.0686	2.2679	24.02	34.12	28.63	13.21	14.81
	2:1	2.5221	0.2435	2.9324	2.2557	23.04	28.45	25.60		
	3:1	2.5034	0.2041	2.7947	2.2495	20.76	24.10	22.37		
	1:0	2.2845	0.0306	2.3046	2.1317	7.96	11.09	9.40		
BMA	0:1	2.4537	0.1689	2.6834	2.1891	16.14	22.96	19.25		
	1:3	2.4632	0.1723	2.7632	2.2593	25.08	29.40	27.16		
	1:2	2.4861	0.2084	2.8795	2.2634	26.11	31.88	28.85		
	1:1	2.5009	0.2273	3.0207	2.2709	27.01	38.62	32.30	13.59	14.54
	2:1	2.4831	0.2075	2.8766	2.2618	26.27	32.02	29.00		
	3:1	2.4657	0.1764	2.7628	2.2584	24.95	28.44	26.64		
	1:0	2.2718	0.0204	2.2876	2.1516	10.66	13.08	11.81		

Table 3: Static dielectric constant (ε_o), dielectric constant at angular frequency (ε_o), dielectric constant (ε'), dielectric loss (ε''), dielectric relaxation time and activation energies ($\Delta F\tau$, $\Delta F\eta$) for m-nitrobenzyl alcohol with acrylic esters in carbon tetrachloride

Esters	Ratio Ester: Alcohol	ε'	ε''	ε_o	$\varepsilon_{¥}$	Relaxation time (ps) $\tau_{(1)}$	$\tau_{(2)}$	$\tau_{(0)}$	$\Delta F\tau$ kJ/mole	$\Delta F\eta$ kJ/mole
MMA	0:1	2.3548	0.0217	2.4132	2.2576	39.40	45.44	42.32		
	1:3	2.3741	0.0603	2.5542	2.2627	43.33	50.43	46.75		
	1:2	2.3846	0.0901	2.6641	2.2638	46.24	52.38	49.22		
	1:1	2.4047	0.1176	2.8108	2.2778	50.92	58.31	54.49	15.75	16.64
	2:1	2.3851	0.0937	2.6786	2.2632	46.54	52.89	49.61		
	3:1	2.3742	0.0622	2.5551	2.2628	44.69	49.11	46.85		
	1:0	2.2845	0.0306	2.3046	2.1317	7.96	11.09	9.40		
BMA	0:1	2.3548	0.0217	2.4132	2.2576	39.40	45.44	42.32		
	1:3	2.3689	0.0411	2.4984	2.2671	49.93	53.21	51.54		
	1:2	2.3797	0.0532	2.5708	2.2754	54.78	60.66	57.64		
	1:1	2.3979	0.0737	2.6745	2.2888	58.70	63.37	60.99	16.68	17.51
	2:1	2.3793	0.0502	2.5603	2.2761	55.40	60.88	58.08		
	3:1	2.3696	0.0405	2.5002	2.2682	50.66	54.45	52.52		
	1:0	2.2718	0.0204	2.2876	2.1516	10.66	13.08	11.81		

relaxation time ($\tau_{(0)}$) and the free energy of activation for dielectric relaxation process ($\Delta F\tau$) and viscous flow ($\Delta F\eta$) of proton donors (*m*-methylbenzyl alcohol, benzyl alcohol and *m*-nitrobenzyl alcohol) with proton acceptor (methyl methacrylate and butyl methacrylate) in carbon tetrachloride at 308 K are shown in Tables 1, 2 and 3. A perusal of Tables 1, 2 and 3 show that the values of e', e" and e_o for substituted benzyl alcohols with carbon tetrachloride systems decrease in the order: *m*-methylbenzyl alcohol > benzyl alcohol > *m*-nitrobenzyl alcohol. This may be due to induced dipole moment of substituted benzyl alcohols increasing in the same sequence. In Table 1to 3, 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[9]. In the present study, it has been observed that the relaxation time of ternary mixtures (benzyl alcohol derivatives with MMA or BMA in ccl_4) is much greater than the binary mixture (benzyl alcohol derivatives with ccl_4 or MMA with ccl_4 or BMA 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 methacrylates, and is shown in Fig 1.

For a given methyl methacrylate, the relaxation times and activation energies values are increasing in the order: *m*-methylbenzyl alcohol < benzyl alcohol < *m*-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 substitutents 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., methyl) and increases for electron withdrawing groups (i.e., nitro) when compared with benzyl alcohol. This is because, the electron donating substitutents 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 methacrylates. Therefore,



Ar = CH_3 (methylbenzyl alcohol),
H (benzyl alcohol),
NO_2 (nitrobenzyl alcohol).
R = CH_3 (methyl methacrylate),
C_4H_9 (butyl methacrylate)

Fig. 1: Hydrogen bonding between *meta* substituted benzyl alcohols and acrylic esters

the strong hydrogen bond would be expected to form between *m*-nitrobenzyl alcohol with methacrylates in carbon tetrachloride and weakest hydrogen bond between *m*-methylbenzyl alcohol with methacrylates in carbon tetrachloride as reflected by the higher relaxation time for former systems and lower relaxation time for lesser systems. Similar results of methacrylates with phenol derivatives were carried out by Liakath Ali Khan *et al.,*[11].

Table1 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 - methacrylates systems. Similar results were reported by Malathi *et al.,*[13] in some carbonyl + phenol derivative systems.

The molar free energy of activation for viscous flow ($\Delta\mathbf{F}\tau$) and the free energy ($\Delta\mathbf{F}\eta$) calculated for proton donors (*m*-methylbenzyl alcohol, benzyl alcohol and *m*-nitrobenzyl alcohol) with proton acceptor (methyl methacrylate and butyl methacrylate) in carbon tetrachloride are presented in Table 2. It is evident from the data that the $\Delta\mathbf{F}\eta$ is $>\Delta\mathbf{F}\tau$. 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[8]. Smyth *et al.,*[18] pointed out that the relaxation time of a proton donor increases as the acceptor ability of the solvent environment increases. All the results are in complete accordance with this conclusion.

The values of $\tau_{(1)}$, $\tau_{(2)}$, $\tau_{(0)}$, $\Delta F\tau$ and $\Delta F\eta$ for acrylic esters with carbon tetrachloride are shown in Tables 1-3. They follow in the order: methyl methacrylate < butyl methacrylate. This indicates that the relaxation time varies in accordance with the size, shape and viscosity of the molecules. Further, the values of $\tau_{(1)}$, $\tau_{(2)}$, $\tau_{(0)}$, $\Delta F\tau$ and $\Delta F\eta$ for proton donors (substituted benzyl alcohols) with acrylic esters in carbon tetrachloride increase in the order: methyl methacrylate < butyl methacrylate for alkyl methacrylates. This trend suggests that the proton accepting ability of acrylic esters increases with increasing chain length i.e. butyl group of alkyl methacrylate has higher proton accepting ability than that of methyl groups of alkyl methacrylate. This is probably due to electron contribution of the butyl group to C=O group which is significantly greater than that from methyl group.

CONCLUSION

The complex formation between substituted benzyl alcohols with methyl methacrylate and butyl methacrylate in carbon tetrachloride has been carried out using dielectric method. From this study, it may be concluded that the proton donating ability of substituted benzyl alcohols and the proton accepting ability of acrylic esters vary linearly with the substitution in benzyl alcohols and carbon chain length of acrylic esters and 1:1 complex formation is more predominant than other higher order complexes.

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