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DIELECTRIC RELAXATION STUDIES OF 1:1 COMPLEXES OF ALKYL METHACRYLATE WITH PHENOLS DERIVATIVES

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ABSTRACT

Dielectric absorption studies of H-bonded complexes of methyl methacrylate (MMA) and butyl methacrylate (BMA) with *p*-cresol, *p*-chlorophenol, 2,4-dichlorophenol and *p*-bromophenol have been studied at microwave frequency 9.37 GHz in dilute solution of carbon tetrachloride at 308K. Different dielectric parameters like dielectric constant ε′ and dielectric loss ε″ at microwave frequency, static dielectric constant ε_o and dielectric constant ε_∞ at optical frequency have been determined. The validity of the single frequency equation of Higasi et al. for multiple relaxation time $\tau_{(1)}$ is found to be function of the hydrogen bonding strength of phenolic hydrogen, whereas the group rotation relaxation time $\tau_{(2)}$ is a function of the steric interaction of proton donor. The relaxation time is maximum at 50:50 mol% ratio.

Keywords: Methyl methacrylate and Butyl methacrylate, Phenol derivatives, Dielectric relaxation, X-band microwave.

INTRODUCTION

Dielectric relaxation investigations, especially in polar liquids dissolved in non-polar solvents have always been of considerable interest to a large number of workers[1-4]. Such studies are very useful in understanding the molecular structure and the molecular forces. Rewar and Bhatnagar[5] have reported the dielectric properties of butyl acrylate, butyl methacrylate and iso-butyl methacrylate in the microwave region at different temperatures. Madhulika khatry and Gandhi[6] have studied the dielectric relaxation behaviour of n-butyl acrylate, allyl-methacrylate, isobutyl-methacrylate and isobutyl-acrylate in non-polar solvent at different temperatures. Dielectric parameters for dimethyl formamide-phenol and dimethyl acetamide-phenol were reported by Tucker[7].

Recently our research group[8–12] has investigated the complex formation of acrylic esters with proton donors (alcohols) in non-polar solvents using FTIR spectroscopic method. The study of the H-bonds of the type O– H···· O=C occupies a position of considerable importance as it relates to the study of biopolymers. Thus the study and knowledge of dielectric properties of the ternary mixtures of acrylic esters with polar associating liquids in non-polar solvents is expected to provide useful and vital process parameters for efficient design of transesterification process of industrial interest. Keeping both the industrial and scientific interests in mind, an attempt has been made in the present work to study the hydrogen bonding between free hydroxyl group of phenol and the carboxyl group of ester using dielectric method. This study is expected to provide better understanding of the nature of molecular orientation process.

EXPERIMENTAL

The static dielectric constant 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 volts. The refractive indices were measured by an Abbe's refractometer. The measurement 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 ± 0.1 °C using a water circulating thermostat. E. Merck variety of methyl methacrylate, butyl methacrylate and 2,4-dichlorophenol, distilled samples of *p*-cresol and *p*-chlorophenol and recrystallized *p*-bromophenol were used. The physical parameters of all the chemicals used here have been checked against their literature values.

The proton donors (phenols) and the acceptors (methacrylates) under study were separately dissolved at the same molar concentration (0.3 mol. L^{-1}) in the solvent carbon tetrachloride. Their dielectric constants were measured separately. Then the two solution were mixed in different proportions but with the total concentration kept at a fixed value and were subjected to the dielectric constant measurements.

As the maximum deviation of dielectric constant for all the systems studied occurs at equimolar ratio of the solutes, it is presumed that the deviation is due to the formation of 1:1 complexes alone.

Dielectric Parameters

According to Higasi method[13], the average relaxation time $\tau_{(1)}$ is described by

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

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

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

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

τ_o may be called the mean relaxation time.

Where ω is the angular frequency a_o, a', a'' and a_∞ are defined by equation (3)

$$\begin{aligned} \varepsilon_o &= \varepsilon_{o1} + a_o w_2 \\ \varepsilon' &= \varepsilon'_1 + a' w_2 \\ \varepsilon_\infty &= \varepsilon_{1\infty} + a_\infty w_2 \end{aligned} \quad (3)$$

in which subscript 1 refers to the pure solvent and 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 energies have been calculated using the Eyring's equation,

$$\tau = (h/ kT) \exp (\Delta F_\tau / RT) \quad (4)$$

$$\eta = (Nh/V) \exp (\Delta F_\eta / RT) \quad (5)$$

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

RESULTS AND DISCUSSION

The ternary systems selected were methacrylate (methyl and butyl) with proton donors (*p*-cresol, *p*-chlorophenol, 2, 4-dichlorophenol and *p*-bromophenol) using carbon tetrachloride as solvent. The relaxation time τ, of methacrylate (methyl and butyl) with proton donors (*p*-cresol, *p*-chlorophenol, 2,4-dichlorophenol and *p*-bromophenol) in carbon tetrachloride at 308K have been provided in Tables 1-8.

A perusal of Tables 1-8 shows that, the value of relaxation time increases with increasing chain length of methacrylate and acidity of Phenols [7-13]. The increase in relaxation time may be due to the increase in effective radius of the rotating unit. The observed higher value of BMA can be attributed to the larger size of BMA molecule in comparison to MMA molecules. In these systems, the complex formation is likely to occur between $H^{\delta+}$ of phenols and $O^{\delta-}$ of C=O group of ester. Oxygen atom is sp^3 hybridized and in the ester structure there is a lot of voids available for O-H to penetrate and enter into complexation components. Carbon tetrachloride is a symmetrical and a non-polar molecule. But each chlorine atom in this molecule is highly polarizable due to its three lone pair of electrons and therefore it can function as an electron donor. Therefore, there is a possibility of interaction between the positive hydrogen of hydroxyl group and a chlorine atom of the carbon tetrachloride molecule. The potential hydrogen bonding nature of the carbon tetrachloride molecule may contribute to increasing the relaxation time[14]. It has been found that two opposing effects namely specific interactions between C=O group of ester and –OH group of phenol and non–specific dispersion interactions, i.e breaking of intermolecular hydrogen bonds in phenols are possibly operative in these mixtures. The relative size of both ester and phenol molecules determines

the predominance of a particular type of interaction over the other. Our results show that the relaxation time is larger at 1:1 mole ratio of methacrylates with phenols. The relaxation time decreases conspicuously for the other mole ratios but are higher than either of the components. Saxena[15] studied the H-bonding in some carbonyl + phenol derivative systems in different compositions. They also observed that the relaxation time of ternary mixtures is always much greater than either of the polar solutes in the inert solvent.

The relaxation time for dilute solution of *p*-cresol, *p*-chlorophenol, 2,4-dichlorophenol and *p*-bromophenol observed in the present study ranges between 14 and 35 ps, with excess of phenols, the relaxation time of methacrylate + phenol system show slight increase. This result is in agreement with the earlier investigations of Tucker[7].

The results also show that the molecular association between methacrylate and phenols is maximum at 50:50 mol% ratio and then decreases at other mol %. From this we conclude that the 1:1 complex is dominant in acrylates-phenol systems. The relaxation time τ increases with increasing acidity of proton donor in complex systems. At high concentration of phenol in the mixtures, there are large numbers of alcohol molecules surrounding the ester molecules. The associative phenol molecules act as proton donors enabling hydrogen bonding with acrylates molecules. Thus dipole-dipole interaction occurs in such a way that the effective dipole moment gets increased and linear α-multimers are formed. The dipole-dipole interaction is the interaction of the –OH group of phenol with C=O of ester. At low concentration of phenol in the mixtures, there are only a small number of phenol molecules to enable dipole-dipole interaction through hydrogen bonding with non-associative acrylates molecules. As a result, weak intermolecular interactions occur.

The relaxation time of methacrylates with 2, 4-dichlorophenol is less than that of methacrylate with other phenol complexes due to steric hindrance and inductive effect. The relaxation time increases with increasing alkyl chain length of ester and acidity of proton donor (phenols), indicating that the degree of cooperation for reorientation of the molecules increases with increasing length and the bulk of cluster increases. The relaxation time increases with increasing chain length with the fact that the relaxation time is directly related to the size of the molecules[16-18]. The molar free energy of activation for viscous flow ΔF_η and the free energy ΔF_τ are calculated and given in Table–9. It is evident from our data that the ΔF_η is > ΔF_τ. This is in agreement with the fact that the process of viscous flow, which involves both the rotational and transnational forms of motion, faced greater interference from neighbors than dielectric relaxation, which takes place by rotation only[19]. Smyth[20] pointed out that the relaxation time of a proton donor increases as the acceptor ability of the solvent environment increases. Similarly for a given proton acceptor, the relaxation time must increase with the proton donor ability of the donor solute. Our results are in accordance with this conclusion.

CONCLUSIONS

The hydrogen bonded complexes of alkyl methacrylate (methyl and butyl) and phenols (*p*-cresol, *p*-chlorophenol, 2,4-dichlorophenol and *p*-bromophenol) have been studied in dilute solution of carbon tetrachloride using dielectric method. From this study it may be concluded that the alkyl chain length of alkyl acrylates and acidity of phenols plays a significant role in the determination of dielectric properties of the above systems studied.

Table-1: Values of dielectric constants and relaxation times for various weight fractions of *p*-cresol with Methyl methacrylate in carbon tetrachloride.

Ratio of *p*-cresol : MMA	Weight fraction W_2	ε'	ε''	ε_o	ε_∞	Relaxation time (ps) using Higasi's method		
						$\tau_{(1)}$	$\tau_{(2)}$	$\tau_{(0)}$
1 : 3	0.021	2.498	0.148	2.622	2.228	11.78	14.15	12.91
1 : 2	0.023	2.512	0.207	2.723	2.231	15.67	17.21	16.43
1 : 1	0.025	2.523	0.236	2.892	2.234	19.58	26.40	22.33
2 : 1	0.028	2.487	0.225	2.811	2.235	18.43	24.32	21.52
3 : 1	0.029	2.451	0.217	2.718	2.237	17.23	20.78	19.27

Table-2: Values of dielectric constants and relaxation times for various weight fractions of *p*-chlorophenol with Methyl methacrylate in carbon tetrachloride.

Ratio of *p*-chlorophenol : MMA	Weight fraction W_2	ε'	ε''	ε_o	ε_∞	Relaxation time (ps) using Higasi's method		
						$\tau_{(1)}$	$\tau_{(2)}$	$\tau_{(0)}$
1 : 3	0.027	2.472	0.162	2.647	2.235	16.19	18.24	17.18
1 : 2	0.028	2.488	0.205	2.792	2.237	22.63	25.04	23.80
1 : 1	0.031	2.508	0.222	2.879	2.241	25.58	28.22	25.79
2 : 1	0.032	2.478	0.213	2.808	2.243	23.54	26.16	23.74
3 : 1	0.034	2.446	0.204	2.732	2.245	20.09	23.67	21.23

Table-3: Values of dielectric constants and relaxation times for various weight fractions of 2,4-dichlorophenol with Methyl methacrylate in carbon tetrachloride.

Ratio of 2,4-dichlorophenol :MMA	Weight fraction W_2	ε'	ε''	ε_o	ε_∞	Relaxation time (ps) using Higasi's method		
						$\tau_{(1)}$	$\tau_{(2)}$	$\tau_{(0)}$
1 : 3	0.020	2.471	0.193	2.652	2.230	13.41	15.84	14.57
1 : 2	0.023	2.453	0.178	2.667	2.232	16.61	20.49	18.45
1 : 1	0.026	2.468	0.241	2.789	2.234	19.76	22.49	21.08
2 : 1	0.028	2.453	0.236	2.745	2.236	19.07	20.89	19.96
3 : 1	0.031	4.432	0.233	2.722	2.238	18.22	21.02	18.59

Table-4: Values of dielectric constants and relaxation times for various weight fractions of *p*-bromophenol with Methyl methacrylate in carbon tetrachloride.

Ratio of *p*-bromophenol :MMA	Weight fraction W_2	ε'	ε''	ε_o	ε_∞	Relaxation time (ps) using Higasi's method		
						$\tau_{(1)}$	$\tau_{(2)}$	$\tau_{(0)}$
1 : 3	0.025	2.456	0.213	2.705	2.236	16.97	19.74	18.30
1 : 2	0.027	2.462	0.223	2.839	2.239	23.10	28.55	25.68
1 : 1	0.030	2.451	0.356	3.229	2.242	29.91	36.90	33.22
2 : 1	0.031	2.446	0.312	2.946	2.243	25.70	29.06	26.37
3 : 1	0.033	2.422	0.233	2.761	2.245	23.73	25.79	24.13

Table-5: Values of dielectric constants and relaxation times for various weight fractions of with *p*-cresol with Butyl methacrylate in carbon tetrachloride.

Ratio of *p*-cresol : BMA	Weight fraction W_2	ε'	ε''	ε_o	ε_∞	Relaxation time (ps) using Higasi's method		
						$\tau_{(1)}$	$\tau_{(2)}$	$\tau_{(0)}$
1 : 3	0.025	2.388	0.188	2.611	2.234	17.07	20.03	18.49
1 : 2	0.027	2.422	0.201	2.689	2.236	21.48	22.43	21.95
1 : 1	0.029	2.493	0.233	2.948	2.245	26.23	32.98	29.41
2 : 1	0.031	2.486	0.225	2.897	2.248	22.21	30.85	26.18
3 : 1	0.033	2.471	0.204	2.794	2.249	20.63	26.74	23.48

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Table-6: Values of dielectric constants and relaxation times for various weight fractions, *p*-chlorophenol with Butyl methacrylate in carbon tetrachloride.

Ratio of *p*-chlorophenol : BMA	Weight fraction W_2	ε'	ε''	ε_o	ε_∞	Relaxation time (ps) using Higasi's method		
						$\tau_{(1)}$	$\tau_{(2)}$	$\tau_{(0)}$
1 : 3	0.030	2.347	0.172	2.622	2.238	20.60	27.01	23.58
1 : 2	0.032	2.395	0.197	2.857	2.241	26.19	39.62	32.21
1 : 1	0.035	2.475	0.248	3.115	2.248	38.42	43.58	40.92
2 : 1	0.036	2.438	0.221	2.918	2.250	34.08	36.51	35.27
3 : 1	0.039	2.423	0.213	2.832	2.252	31.83	32.42	32.31

Table-7: Values of dielectric constants and relaxation times for various weight fractions of 2,4-dichlorophenol with Butyl methacrylate in carbon tetrachloride.

Ratio of 2,4-dichlorophenol : BMA	Weight fraction W_2	ε'	ε''	ε_o	ε_∞	Relaxation time (ps) using Higasi's method		
						$\tau_{(1)}$	$\tau_{(2)}$	$\tau_{(0)}$
1 : 3	0.026	2.288	0.154	2.501	2.234	19.12	23.36	21.13
1 : 2	0.028	2.355	0.167	2.621	2.235	22.20	26.90	24.44
1 : 1	0.031	2.568	0.211	3.008	2.240	32.39	35.21	33.77
2 : 1	0.032	2.453	0.208	2.822	2.241	24.39	29.96	27.03
3 : 1	0.033	2.378	0.201	2.674	2.243	21.62	24.87	23.19

Table-8: Values of dielectric constants and relaxation times for various weight fractions of *p*-bromophenol with Butyl methacrylate in carbon tetrachloride.

Ratio of *p*-bromophenol : BMA	Weight fraction W_2	ε'	ε''	ε_o	ε_∞	Relaxation time (ps) using Higasi's method		
						$\tau_{(1)}$	$\tau_{(2)}$	$\tau_{(0)}$
1 : 3	0.034	2.311	0.175	2.614	2.239	31.44	29.24	30.32
1 : 2	0.035	2.384	0.188	2.836	2.241	33.42	40.60	36.83
1 : 1	0.038	2.422	0.208	3.228	2.253	40.84	65.43	51.70
2 : 1	0.039	2.401	0.192	2.911	2.256	33.42	44.85	38.72
3 : 1	0.041	2.387	0.187	2.789	2.259	31.58	36.30	33.86

Table-9: The activation energies at 1:1 stoichiometric ratios of Methyl and Butyl methacrylate with phenol derivatives in carbon tetrachloride.

System	Activation energy	
	ΔF_τ (kJ mol^{-1})	ΔF_η (kJ mol^{-1})
Methyl methacrylate + *p*-cresol	12.48	12.96
Methyl methacrylate + *p*-chlorophenol	13.74	14.08
Methyl methacrylate + 2,4-dichlorophenol	12.66	12.89
Methyl methacrylate + *p*-bromophenol	14.05	14.68
Butyl methacrylate + *p*-cresol	13.13	13.87
Butyl methacrylate + *p*-chlorophenol	14.15	14.91
Butyl methacrylate + 2,4-dichlorophenol	13.07	13.64
Butyl methacrylate + *p*-bromophenol	14.43	15.13