

Relaxation phenomena of acrylic esters and phenols in dilute solution of CCl_4 under static and high frequency electric field

S Sahoo¹, T R Middya² & S K Sit^{3*}

¹Department of Electronics & Instrumentation Engineering

²Department of Physics, Jadavpur University, Kolkata, West Bengal, India

³Department of Physics, Dr Meghnad Saha Institute of Technology, P.O: Debhog, Haldia,
Dist: Purba Medinipore 721 657, West Bengal, India

*E-mail: swapansit @ yahoo. co.in

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Double relaxation times τ_2 and τ_1 due to whole molecular rotation and the flexible parts of the binary (jk) polar mixture of p -cresol, p -chlorophenol, 2,4 dichlorophenol and p -bromophenol with methyl methacrylate (MMA) or ethyl methacrylate (EMA) were estimated under 9.37 GHz electric field dissolved in dilute CCl_4 solution at 35°C using high frequency susceptibility data χ_{ijk} 's for different weight fractions w_{jk} 's. Six systems out of eight exhibit τ_2 , τ_1 ; c_2 , c_1 and μ_2 , μ_1 , respectively. The estimated τ_2 's and μ_2 's agree well with the measured and reported values indicating the whole rotation of binary polar mixture under high frequency electric field. Solute-solute and solute-solvent molecular formation through H-bonding are ascertained from $\mu_{av} - x_j$ curves for 0.5 mole fraction x_j of acrylic ester. The associational aspects are taken into consideration in μ_{theo} from the stand point of inductive, mesomeric and electromeric effects within the polar groups of the molecules. Static μ_0 's are calculated and compared with the reported values also.

Keywords: Double relaxation times, Dipole moment, Monomer, Dimer, High frequency susceptibility

1 Introduction

Relaxation phenomena of polar nonpolar liquid mixture yield meaningful information on structural and associational behaviour of polar liquid molecules^{1,2}. The physico-chemical properties of binary or single polar liquid mixture dissolved in non polar solvent under high frequency electric field have been studied by many researchers^{3,4}. In the X-band microwave region, the molecular association is better understood because of the capability of microwave to detect weak molecular association³⁻⁵ in addition to orientational polarisation of the polar molecules.

Faize and Periyaswamy⁶ measured dielectric constant ϵ_{ijk} , dielectric loss ϵ_{ijk}'' , static ϵ_{0ijk} and refractive index $n_{Dijk}^2 (= \epsilon_{\inftyijk})$ of binary (jk) polar mixture dissolved in non polar solvent (i) carbon tetrachloride under 9.37 GHz electric field at 35°C. They prepared variety of binary polar mixtures of methyl methacrylate (MMA) and ethyl methacrylate (EMA) with p -cresol, p -chlorophenol, 2,4 dichlorophenol and p -bromophenol, respectively to get valuable information on the formation of hydrogen bonded complexes dissolved in carbon tetrachloride solution from dielectric study. The acrylic ester thus gained attention of researchers to study the dielectric

properties either in the microwave region⁷ at different temperatures or in pure liquid state at different frequencies⁸ because of their wide industrial importance as adhesive, paints, binders and emulsifiers. Periyaswamy *et al.*⁹ further investigated the nature of H-bonding complex between -OH and C=O groups of alcohols and acrylic esters as it plays a significant role in the study of biopolymer. This study is useful to provide process parameters for efficient design of transesterification process of industrial interest too.

The relaxation behaviour of binary (jk) polar liquid mixture of alkyl methacrylate (MMA & EMA) and phenols under the same molecular environment⁶ to estimate double relaxation times τ_2 and τ_1 as well as dipole moments μ_2 and μ_1 due to whole molecular rotation and flexible part of the molecule based on Debye theory using single frequency susceptibility measurement technique, has been studied. The measurement involved real $\chi'_{ijk} (= \epsilon_{ijk}' - \epsilon_{\inftyijk})$ and imaginary $\chi''_{ijk} (= \epsilon_{ijk}'')$ parts of complex orientational susceptibility χ_{ijk}^* and static orientational susceptibility $\chi_{0ijk} (= \epsilon_{0ijk} - \epsilon_{\inftyijk})$ at different weight fractions w_{jk} 's of acrylic ester (j)

and phenol (k) under same state of molecular environment⁶. The susceptibility measurement yields orientational polarisation¹⁰ alone whereas permittivity measurement is concerned with all type of polarization of polar molecules. The conductivity measurement, on the other hand, is related to bound molecular charge of polar molecules. It is better to use broadband dielectric spectroscopy to get a clear picture of molecular interactions and their effects on molecular dynamics in relation to heteromolecular conformations of acrylic esters and phenols. Keeping all these facts under consideration the static or low frequency dipole moments μ_0 's of the binary polar mixtures are also estimated using Debye theory. The esters are used for the production of copolymer which is needed in fracture repair in small exotic animal species using internal fixation. Phenols are, generally, used as disinfectant or germicides. These *para* compounds sometimes exhibit zero dipole moment¹¹ under high frequency electric field. Earlier¹² study was undertaken on long chain *para* compounds dissolved in benzene under ~ 3 cm wavelength electric field within the framework of Debye model using conductivity measurement technique. It is worthwhile to see how far the single frequency susceptibility measurement technique is appropriate for binary polar mixtures of acrylic esters and phenols dissolved in CCl_4 in predicting τ_2 and τ_1 as well as μ_2 and μ_1 , respectively. The comparison of static μ_0 as well as μ_2 and μ_1 enables one how far frequency of electric field affects μ . Out of eight systems under considerations, six systems exhibit double relaxation phenomena except EMA+ *p*-cresol (V) and EMA+*p*-bromophenol (VIII). The estimated τ_2 and τ_1 from Fig. 1 are placed in Table 1. The values of τ_2 is found to agree well with the reported τ_2 values from Higasi method whereas τ_1 's agree well with the symmetric τ_s . τ 's were also estimated from the ratio of slopes of $\chi''_{ijk} - w_{jk}$ and $\chi'_{ijk} - w_{jk}$ at $w_{jk} \rightarrow 0$ as seen in Figs 2 and 3, respectively. The measured τ 's from linear slope of $\chi''_{ijk} - \chi'_{ijk}$ straight line (Fig. 4) are also placed in Table 1 for comparison. The relative contributions c_1 and c_2 due to τ_1 and τ_2 were calculated for six non-rigid binary polar mixtures. The experimental c_1 and c_2 from the $(\chi'_{ijk} / \chi_{0ijk}) - w_{jk}$ and $(\chi''_{ijk} / \chi_{0ijk}) - w_{jk}$ at $w_{jk} \rightarrow 0$ of Figs 5 and Fig. 6 are calculated and placed in Table 2 along with theoretical c_1 and c_2 . The estimated dipole moments μ_2 and μ_1 due to τ_2 and τ_1

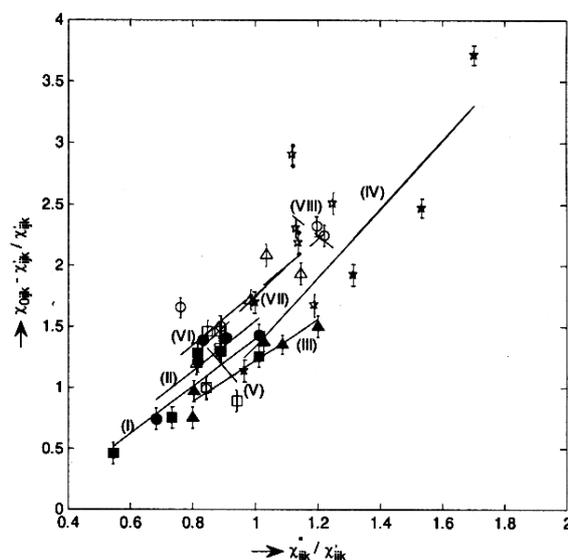


Fig. 1 — Variations of $(\chi_{0ijk} - \chi_{ijk}) / \chi_{ijk}$ against $(\chi''_{ijk} / \chi'_{ijk})$ for different w_{jk} 's of binary polar mixture of phenol & acrylic ester dissolved in CCl_4 at 35°C under 9.37 GHz electric field. (I) —■—, (II) —●—, (III) —▲—, (IV) —★— for *p*-cresol, *p*-chlorophenol, 2,4-dichlorophenol and *p*-bromophenol mixed with MMA, respectively, (V)□..... (VI)○....., (VII)△....., (VIII) ☆..... for *p*-cresol, *p*-chlorophenol, 2,4-dichlorophenol and *p*-bromophenol mixed with EMA, respectively

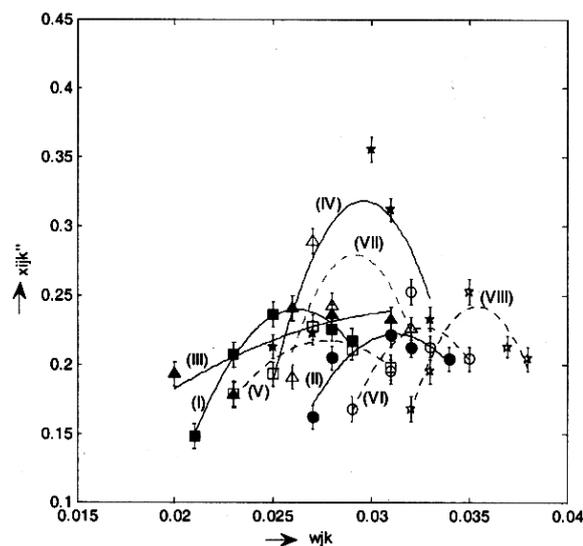


Fig. 2 — Plot of χ''_{ijk} against weight fractions w_{jk} 's of binary polar mixture of phenol & acrylic ester dissolved in CCl_4 at 35°C under 9.37 GHz electric field. (I) —■—, (II) —●—, (III) —▲—, (IV) —★— for *p*-cresol, *p*-chlorophenol, 2,4-dichlorophenol and *p*-bromophenol mixed with MMA, respectively, (V)□..... (VI)○....., (VII)△..... (VIII) ☆..... for *p*-cresol, *p*-chlorophenol, 2,4-dichlorophenol and *p*-bromophenol mixed with EMA, respectively

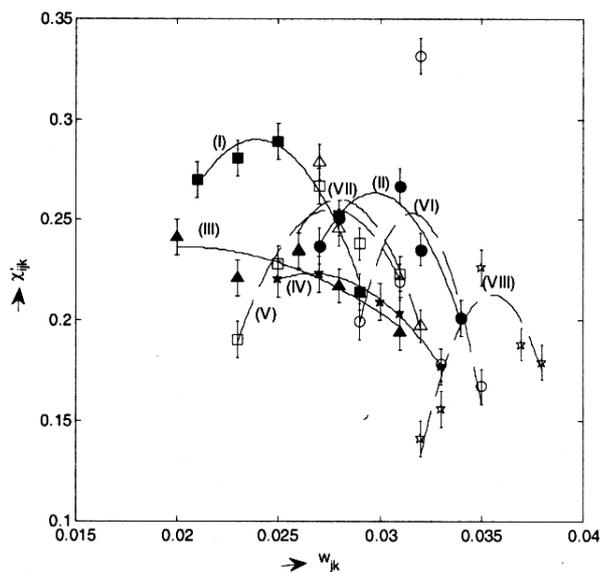


Fig. 3 — Plot of χ'_{ijk} against weight fractions w_{jk} 's of binary polar mixture of phenol & acrylic ester dissolved in CCl_4 at 35°C under 9.37 GHz electric field. (I) —■—, (II) —●—, (III) —▲—, (IV) —★— for *p*-cresol, *p*-chlorophenol, 2,4-dichlorophenol and *p*-bromophenol mixed with MMA, respectively, (V)□....., (VI)○....., (VII)△....., (VIII)☆..... for *p*-cresol, *p*-chlorophenol, 2,4-dichlorophenol and *p*-bromophenol mixed with EMA, respectively

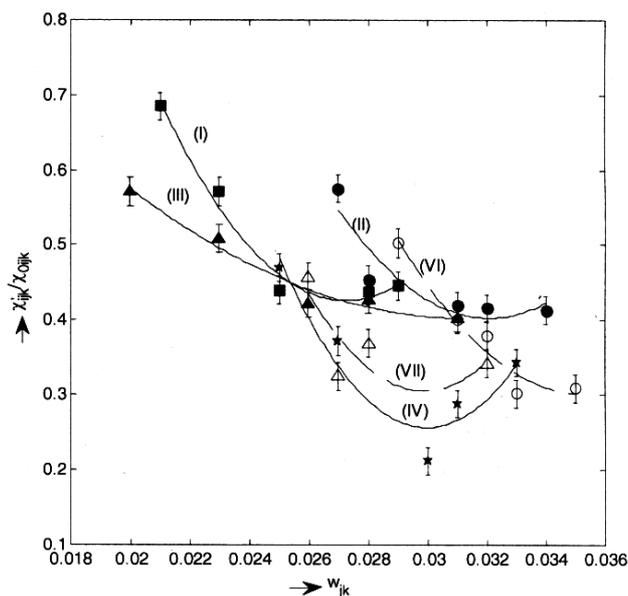


Fig. 5 — Variations of $(\chi'_{ijk}/\chi_{0ijk})$ against w_{jk} 's of binary polar mixture of phenol and acrylic ester dissolved in CCl_4 at 35°C under 9.37 GHz electric field. (I) —■—, (II) —●—, (III) —▲—, (IV) —★— for *p*-cresol, *p*-chlorophenol, 2,4-dichlorophenol and *p*-bromophenol mixed with MMA, respectively, (VI)○....., (VII)△..... for *p*-chlorophenol, 2,4-dichlorophenol mixed with EMA, respectively

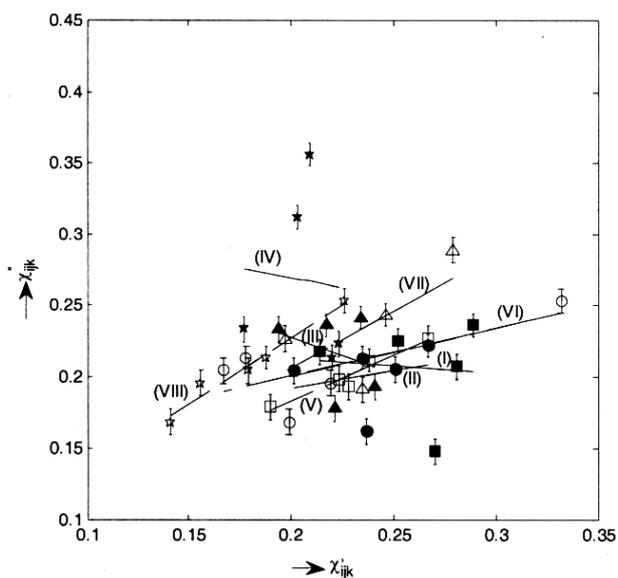


Fig. 4 — Straight line plot of χ''_{ijk} against χ'_{ijk} for different w_{jk} 's of binary polar mixture of phenol & acrylic ester dissolved in CCl_4 at 35°C under 9.37 GHz electric field. (I) —■—, (II) —●—, (III) —▲—, (IV) —★— for *p*-cresol, *p*-chlorophenol, 2,4-dichlorophenol and *p*-bromophenol mixed with MMA, respectively, (V)□....., (VI)○....., (VII)△....., (VIII)☆..... for *p*-cresol, *p*-chlorophenol, 2,4-dichlorophenol and *p*-bromophenol mixed with EMA, respectively

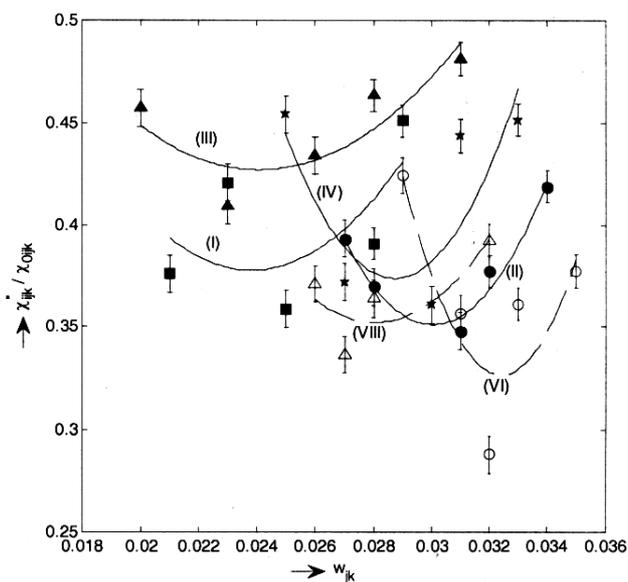


Fig. 6 — Variations of $(\chi''_{ijk}/\chi_{0ijk})$ against w_{jk} 's of binary polar mixture of phenol & acrylic ester dissolved in CCl_4 at 35°C under 9.37 GHz electric field. (I) —■—, (II) —●—, (III) —▲—, (IV) —★— for *p*-cresol, *p*-chlorophenol, 2,4-dichlorophenol and *p*-bromophenol mixed with MMA respectively, (VI)○....., (VII)△..... for *p*-chlorophenol, 2,4-dichlorophenol mixed with EMA, respectively

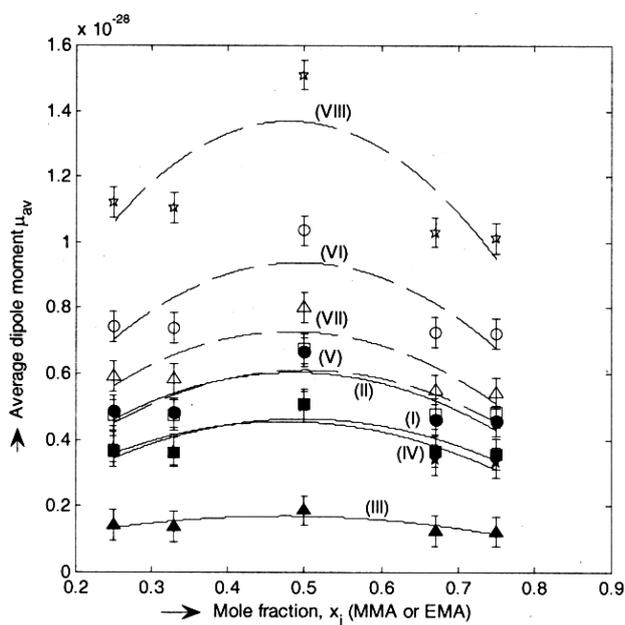


Fig. 7 — Plot of average dipole moment μ_{av} due to τ_0 of binary polar mixture of phenol and acrylic ester dissolved in CCl_4 against mole fraction X_j 's of MMA or EMA at 35°C under 9.37 GHz electric field. (I) —■—, (II) —●—, (III) —▲—, (IV) —★— for *p*-cresol, *p*-chlorophenol, 2,4-dichlorophenol and *p*-bromophenol mixed with MMA respectively, (V).....□....., (VI)○....., (VII)△....., (VIII) ☆..... for *p*-cresol, *p*-chlorophenol, 2,4-dichlorophenol and *p*-bromophenol mixed with EMA, respectively

are placed in Table 3. The plot of most probable or average μ_{av} against mole fractions x_j 's of esters reveal maximum dimerisation at $x_j=0.5$ of ester (Fig. 7). Theoretical μ_{theo} 's (Fig. 8) are also estimated to show the associational behaviour and compared with the reported μ 's and static μ_0 's from slope of $X_{ijk}-w_{jk}$ curve (Fig. 9).

2 Experimental Details

The samples alkyl methacrylates, phenols and CCl_4 are all good quality E Merck grade. They were used after recrystallisation and distillation with purity $>99\%$ to measure ϵ_{ijk}' and ϵ_{ijk}'' using voltage standing wave ratio (VSWR) and Heston *et al*¹³. method at 9.37 GHz electric field⁶. The physical parameters are checked against literature values. ϵ_{0ijk} and n_{Dijk} were measured by Dipole meter DM 01 and Abbe's refractometer, respectively⁶. The accuracy in the measurements of ϵ_{ijk}' and ϵ_{ijk}'' are $\pm 1\%$ and $\pm 5\%$, respectively. The real $\chi_{ijk}' (= \epsilon_{ijk}' - \epsilon_{\infty oijk})$ and imaginary $\chi_{ijk}'' (= \epsilon_{ijk}'')$ parts of complex orientational susceptibility χ_{ijk}^* and static

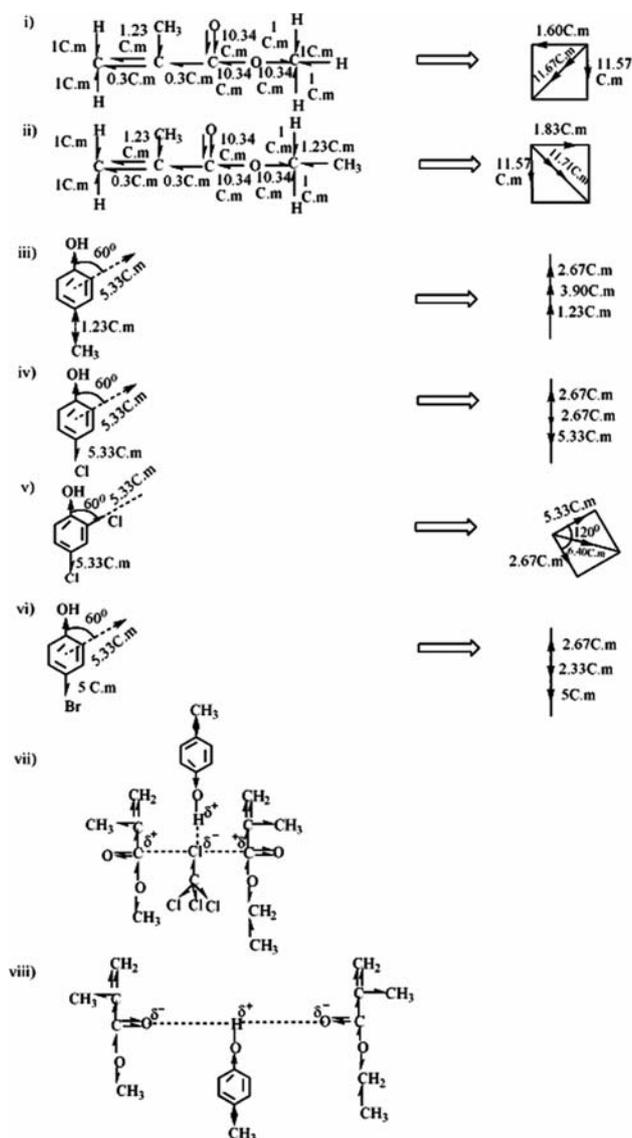


Fig. 8 — Theoretical dipole moments μ_{theo} 's from available bond angles and bond moments (multiples of 10^{-30} C.m) of phenols and acrylic esters along with solute-solvent and solute-solute molecular associations. (i) Methyl methacrylate(MMA), (ii) Ethyl methacrylate (EMA), (iii) *p*-cresol, (iv) *p*-chlorophenol, (v) 2,4-dichlorophenol, (vi) *p*-bromophenol, (vii) solute-solvent molecular association and (viii) solute-solute molecular association

orientational susceptibility $\chi_{0ijk} (= \epsilon_{0ijk} - \epsilon_{\infty oijk})$ at different w_{jk} 's of solute were estimated by simple normalization of permittivity data. The temperature of the measurements was maintained at 35°C within the accuracy limit of $\pm 0.1^\circ\text{C}$ by a water circulating thermostat while binary mixtures were prepared.

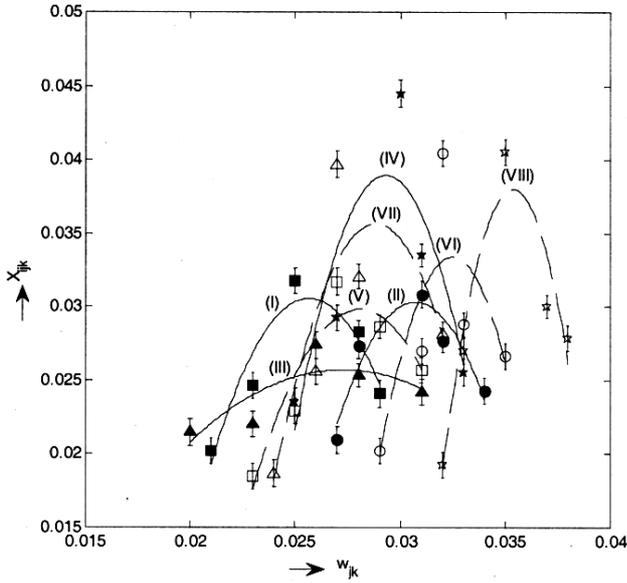


Fig. 9 — Variations of static experimental parameter X_{ijk} against weight fractions w_{jk} 's of binary polar mixture of phenol & acrylic ester dissolved in CCl_4 at 35°C under static electric field. (I) —■— (II)—●— (III)—▲— (IV) —★— for *p*-cresol, *p*-chlorophenol, 2,4-dichlorophenol and *p*-bromophenol mixed with MMA respectively (V).....□..... (VI)○..... (VII)△..... (VIII)..... ☆..... for *p*-cresol, *p*-chlorophenol, 2,4-dichlorophenol and *p*-bromophenol mixed with EMA, respectively

3 Theoretical Formulations

3.1 Relaxation time τ_{jk} and dipole moment μ_{jk} from χ_{ijk} measurement

The Bergmann's equations¹⁴ are solved to get a straight line equation in terms of established symbols¹⁵ of χ'_{ijk} , χ''_{ijk} and χ_{0ijk} as:

$$\frac{\chi_{0ijk} - \chi'_{ijk}}{\chi'_{ijk}} = \omega(\tau_2 + \tau_1) \frac{\chi''_{ijk}}{\chi'_{ijk}} - \omega^2 \tau_1 \tau_2 \quad \dots (1)$$

assuming two separate Debye type dispersions for which $c_1 + c_2 = 1$.

The Eq. (1) is a straight line of variables $(\chi_{0ijk} - \chi'_{ijk}) / \chi'_{ijk}$ against $(\chi''_{ijk} / \chi'_{ijk})$ having slopes of $\omega(\tau_2 + \tau_1)$ and intercepts $\omega^2 \tau_1 \tau_2$ for different w_{jk} 's of solutes under a given angular frequency $\omega (= 2\pi f)$ of electric field as shown in Fig. 1.

The values of τ 's were also estimated from the ratio of slopes of $\left(\frac{d\chi''_{ijk}}{dw_{jk}}\right)_{w_{jk} \rightarrow 0}$ and $\left(\frac{d\chi'_{ijk}}{dw_{jk}}\right)_{w_{jk} \rightarrow 0}$ of $\chi''_{ijk} - w_{jk}$

and $\chi'_{ijk} - w_{jk}$ curves in Figs 2 and 3 to eliminate polar-polar interactions¹⁵:

The slope $\left(\frac{d\chi''_{ijk}}{d\chi'_{ijk}}\right)$ of $\chi''_{ijk} - \chi'_{ijk}$ linear equation of

Fig. 4 can also be used to estimate τ 's from Murthy *et al*¹⁶: All the τ 's including the most probable $\tau_0 = \sqrt{\tau_1 \tau_2}$, measured τ and symmetrical τ_s are placed in Table 1.

The relative contributions c_1 and c_2 due to τ_1 and τ_2 can be measured from Bergmann's equation^{14,15} as:

$$c_1 = \frac{\left(\frac{\chi'_{ijk}}{\chi_{0ijk}} \alpha_2 - \frac{\chi''_{ijk}}{\chi_{0ijk}}\right) (1 + \alpha_1^2)}{\alpha_2 - \alpha_1} \quad \dots (2)$$

$$c_2 = \frac{\left(\frac{\chi''_{ijk}}{\chi_{0ijk}} - \frac{\chi'_{ijk}}{\chi_{0ijk}} \alpha_1\right) (1 + \alpha_2^2)}{\alpha_2 - \alpha_1} \quad \dots (3)$$

where $\alpha_1 = \omega\tau_1$ and $\alpha_2 = \omega\tau_2$ provided $\alpha_2 > \alpha_1$. The other symbols and terminologies are explained elsewhere¹⁵. The six systems out of eight under consideration show non rigid behaviour. A continuous distribution of τ between two discrete values of τ_1 and τ_2 is, therefore, expected using Fröhlich's equations¹⁷. The theoretical values of c_1 and c_2 are calculated from $(\chi'_{ijk} / \chi_{0ijk})$ and $(\chi''_{ijk} / \chi_{0ijk})$ of Fröhlich's equation¹⁷. They are compared with the experimental c_1 and c_2 from the graphical plots of $(\chi'_{ijk} / \chi_{0ijk})$ and $(\chi''_{ijk} / \chi_{0ijk})$ against w_{jk} at $w_{jk} \rightarrow 0$ as seen in Figs 5 and 6. All the c 's are placed in Table 2 for six systems.

Again, the imaginary part of dielectric orientational susceptibility χ''_{ijk} as a function of w_{jk} of solutes can be written as¹⁵:

$$\chi''_{ijk} = \frac{N \rho_{ijk} \mu_{jk}^2}{27 \epsilon_0 M_{jk} K_B T} \left(\frac{\omega \tau_{jk}}{1 + \omega^2 \tau_{jk}^2} \right) (\epsilon_{ijk} + 2)^2 w_{jk} \quad \dots (4)$$

On differentiation of Eq. (4) w.r. to w_{jk} and at $w_{jk} \rightarrow 0$ which after simplification yields:

Table 1 — Reports slope & intercept of Eq. (1), estimated τ_2 and τ_1 due to whole molecular rotation and flexible parts of the polar molecule, measured τ from ratio of slopes and linear slope method, reported τ 's from Higasi method, symmetric τ_s and as well as symmetric distribution parameter γ of six non rigid binary polar mixture of acrylic ester and phenol dissolved in dilute CCl_4 at 35°C under 9.37 GHz electric field

System	Mole fraction x_j of acrylic ester in phenol(k)	Slope & intercept of $\frac{\chi_{ijk} - \chi'_{ijk}}{\chi_{ijk}}$ against $\frac{\chi_{ijk}}{\chi'_{ijk}}$ straight line Eq. (1)		Estimated		Most probable $\tau_0 = \sqrt{\tau_1 \tau_2}$ in pico sec	Measured τ from linear slope method		Reported		Estimated symmetric τ_s in pico sec	Symmetric Distribution parameter γ
		$\frac{\chi_{ijk} - \chi'_{ijk}}{\chi_{ijk}}$	intercept	τ_2 in pico sec	τ_1 in pico sec		in pico sec	in pico sec	τ_2 in pico sec	τ_1 in pico sec		
(I)MMA +p-cresol in CCl_4	0.25								14.15	11.78		
	0.33								17.21	15.67		
	0.50	1.93289	-0.54545	27.00	5.83	12.55	-	22.80	26.40	19.58	8.77	-0.9651
	0.67								24.32	18.43		
	0.75								20.78	17.23		
	0.25								18.24	16.19		
(II)MMA +p-chlorophenol in CCl_4	0.33								25.04	22.63		
	0.50	2.03448	-0.4973	29.73	4.83	11.98	3.93	14.39	28.22	25.58	4.15	-0.9452
	0.67								26.16	23.54		
	0.75								23.67	20.09		
	0.25								15.84	13.41		
	0.33								20.49	16.61		
(III)MMA +2,4-dichlorophenol in CCl_4	0.50	1.68008	-0.46847	22.54	6.00	11.63	-	25.85	22.49	19.76	13.75	-0.7333
	0.67								20.89	19.07		
	0.75								21.02	18.22		
	0.25								19.74	16.97		
	0.33								28.55	23.10		
	0.50	2.81425	-1.48788	35.82	11.98	20.72	-	102.32	36.90	29.91	11.85	-0.9654
(IV)MMA +p-bromophenol in CCl_4	0.67								29.06	25.70		
	0.75								25.79	23.73		
	0.25								15.85	13.62		
	0.33								19.77	16.30		
	0.50	-3.03552	3.90273	16.54	-	-	10.81	10.20	29.46	19.46	-	-
	0.67								27.78	20.97		
(V)EMA +p-cresol in CCl_4	0.75								25.16	18.21		
	0.25								19.80	17.79		
	0.33								28.40	23.35		
	0.50	2.16969	-0.39485	33.45	3.41	10.68	5.70	9.60	36.51	24.55	7.14	-0.9527
	0.67								32.66	23.98		
	0.75								30.96	24.78		
(VI)EMA +p-chlorophenol in CCl_4	0.25								18.81	16.89		
	0.33								24.88	18.02		
	0.50	2.4447	-0.70725	35.83	5.69	14.28	13.71	31.00	33.83	23.13	9.24	-0.9750
	0.67								29.32	21.84		
	0.75								28.11	20.19		
	0.25								23.62	21.33		
(VII)EMA +2,4-dichlorophenol in CCl_4	0.33								33.86	25.74		
	0.50	-2.04101	4.69295	23.34	-	-	15.84	17.82	43.78	33.38	-	-
	0.67								34.25	29.97		
	0.75								32.37	26.31		
	0.25								33.82	25.30		
	0.33								22.45	22.45		
(VIII)EMA +p-bromophenol in CCl_4	0.50								34.78	33.38		
	0.67								38.23	38.23		
	0.75								32.04	29.97		

$$\mu_{jk} = \left[\frac{27\epsilon_0 M_{jk} K_B T \beta}{N \rho_i (\epsilon_i + 2)^2 b} \right]^{1/2} \quad \dots (5)$$

where $b=1/(1+\omega^2 \tau_{jk}^2)$ is the dimensionless parameter and β is the slope of $\chi'_{ijk} - w_{jk}$ curve at $w_{jk} \rightarrow 0$ as shown in Fig. 3. The most probable or average μ_{av} are plotted against different x_j 's of MMA or EMA in phenol as shown in Fig. 7. All the μ 's along with theoretical dipole moment μ_{theo} (Fig. 8) from available bond angles and bond moments are placed in Table 3.

3.2 Estimation of static dipole moment μ_0

The low frequency or static dipole moment μ_0 's of binary polar mixture (jk) in a non polar solvent (i) at any temperature T K is given by¹⁸:

$$\frac{\epsilon_{0ijk} - 1}{\epsilon_{0ijk} + 2} - \frac{\epsilon_{\inftyijk} - 1}{\epsilon_{\inftyijk} + 2} = \frac{\epsilon_{0i} - 1}{\epsilon_{0i} + 2} - \frac{\epsilon_{\infty i} - 1}{\epsilon_{\infty i} + 2} + \frac{N \mu_0^2 c_{jk}}{9 \epsilon_0 K_B T} \quad \dots (6)$$

where all the symbols carry usual significance¹⁹.

On simplification of Eq. (6) and introducing w_{jk} in place of c_{jk} , one gets μ_0 as:

$$\mu_0 = \left[\frac{27 \epsilon_0 M_{jk} K_B T a_1}{N \rho_i} \right]^{1/2} \quad \dots (7)$$

where a_1 is the slope of static experimental parameter¹⁸ $X_{ijk} - w_{jk}$ curve of Fig. 9 at $w_{jk} \rightarrow 0$. All the terms are expressed in SI units with usual meanings¹⁸. All μ_0 along with a_1 's are placed in Table 3.

4 Results and Discussion

Eight binary polar mixtures of *p*-cresol, *p*-chlorophenol, 2,4 dichlorophenol and *p*-bromophenol with methyl methacrylate (MMA) or ethyl methacrylate (EMA) dissolved in CCl_4 solution under identical molecular environment⁶ were used to measure χ'_{ijk} 's of solution at different w_{jk} 's under 9.37 GHz electric field. Double relaxation times τ_2 and τ_1 due to end over end rotation as well as flexible part of the molecule are derived from straight line Eq. (1) analytically. Six systems exhibit reasonable values of τ_2 and τ_1 except systems (V) and (VIII) which show single relaxation behaviour. The graphs of

$(\chi'_{0ijk} - \chi'_{ijk}) / \chi'_{ijk}$ against $(\chi''_{ijk} / \chi'_{ijk})$ of Fig. 1 for different w_{jk} 's of solutes are drawn by adopting MATLAB programming technique using least squares fitting of the experimental data within the error bar. It is evident that graphs are not perfectly linear demanding accurate measurement of experimental data in the low concentration region. The values of τ were also estimated from ratio of slopes of $\chi''_{ijk} - w_{jk}$ and $\chi'_{ijk} - w_{jk}$ curves of Figs 2 and 3, respectively. All the graphs of χ''_{ijk} and χ'_{ijk} against w_{jk} 's are parabolae and highly convex in nature exhibiting the maximum value at a certain w_{jk} 's of solutes. This indicates that maximum absorption of high frequency electric energy occurs leading to maximum polarization of polar mixture. The parabolae are all best fitted through the experimental points within the error bar revealing the uniqueness of the method. The values of τ were also estimated from slope of $\chi''_{ijk} - \chi'_{ijk}$ linear equation of Fig. 4. It is evident from Fig. 4 that the least squares fitted straight lines are not perfectly linear with the experimental points except system (V). It fails to yield τ for system (I), (III) and (IV), respectively. This fact reveals that ratio of slopes method is more applicable rather than linear slope method for the molecular systems under investigation. The estimated τ_2 and τ_1 are compared with the most probable $\tau_0 = \sqrt{\tau_1 \tau_2}$ and measured τ 's from ratio of slope and linear slope. The values of τ_2 agree well with τ from ratio of slopes and Higasi's method except MMA+*p*-bromophenol (IV) and EMA+*p*-chlorophenol (VI) dissolved in CCl_4 solution. This indicates that the rotation of the whole binary polar mixture is responsible for the systems under high frequency electric field. The little disagreement of τ in two cases may be due to steric hinderness offered during rotation of polar molecules. The values of τ were estimated assuming the polar mixture obeying symmetric distribution of relaxation behaviour. The values of τ_s are found to be low and agree well with τ_1 despite the symmetric distribution parameter γ 's are negative. The relative contributions c_1 and c_2 due to τ_1 and τ_2 were estimated from Fröhlich's equation¹⁷ as well as graphical plot of $(\chi'_{ijk} / \chi'_{0ijk})$ and $(\chi''_{ijk} / \chi'_{0ijk})$ against w_{jk} at $w_{jk} \rightarrow 0$ of Figs 5 and 6. The theoretical values of $c_1 + c_2$ for six systems are $\cong 1$. The

experimental $c_1 + c_2$ are, however, greater than 1 even if c_2 's are negative for some systems probably due to inertia of flexible part¹⁹ of polar molecules. The graphical plot reveals that the $(\chi'_{ijk} / \chi_{0ijk}) - w_{jk}$ and $(\chi''_{ijk} / \chi_{0ijk}) - w_{jk}$ curves are all parabolae in nature exhibiting a minimum at a certain w_{jk} 's of solutes. Like $(\chi'_{ijk} / \chi_{0ijk}) - w_{jk}$ curve, $(\chi''_{ijk} / \chi_{0ijk}) - w_{jk}$ curves are also concave in nature with the increase of w_{jk} which is consistent with the earlier observation¹⁹. This is probably due to solute-solute (dimer) or solute-solvent (monomer) molecular complex formation through H-bonding in the higher concentration region.

The dipole moments μ_2 and μ_1 due to τ_2 and τ_1 are estimated in terms of slope β of $\chi'_{ijk} - w_{jk}$ curve at $w_{jk} \rightarrow 0$ as shown in Fig. 3. They are placed in Table 3 along with measured μ 's from linear slope and ratio of slopes as well as reported values from Gopalakrishna's method²⁰. In order to study the behaviour of polar mixtures in the broadband frequency spectrum, the static dipole moment μ_0 's are also estimated using Debye equation¹⁷. It appears from Table 3 that the values of μ exhibit high value at 0.50 mole fraction x_j of alkyl acrylate (j) and phenol (k) mixture in CCl_4 like earlier observation⁶ in the estimation of τ . This is explained on the basis of the fact that solute-solute (dimer) molecular association or complex formation in ternary mixture through H-bond is predominant to yield larger size of the rotating unit to exhibit larger μ . At higher concentration, the phenols act as proton donor enabling hydrogen bonding with alkyl acrylates. Thus, the dipole-dipole interaction occurs in such a way that the effective dipole moments get increased. The plot of average μ_{av} in terms of most probable τ_0 against x_j 's of alkyl methacrylate as shown in Fig. 7 supports the above fact. It is also observed that estimated μ_2 agree well with the measured μ 's and static μ_0 's as well as reported μ due to Gopalakrishna's method revealing the fact that the whole binary polar mixture is rotating under high frequency electric field.

The theoretical dipole moment μ_{theo} 's are calculated from available bond angles and bond moments assuming the planar structure of the molecules. There also exist a difference in electron affinity between two adjacent atoms of a polar group causing inductive, mesomeric and electromeric effects in them. The

solute-solute associational behaviour of the component polar mixtures are displayed in Fig. 8 (viii). This may arise due to interaction between $\text{H}^{\delta+}$ of $-\text{OH}$ group in phenol and $\text{O}^{\delta-}$ of $\text{C}=\text{O}$ group in esters. Oxygen atom in $\text{C}=\text{O}$ is sp^3 hybridized. The $-\text{OH}$ group of phenol enters into empty space of ester molecule for complexation and provides information on H-bonding between interacting components. Solute-solvent (monomer) molecular association is also possible in the ternary mixture due to potential hydrogen bonding of CCl_4 molecule as each chlorine atom in non-polar solvent CCl_4 is highly polar due to its three lone pair electron. Therefore, there is a probability of interaction between electron donor chlorine atom with $\text{H}^{\delta+}$ of $-\text{OH}$ group of phenol or $\text{C}^{\delta+}$ of $\text{C}=\text{O}$ group of ester to form molecular association [Fig. 8(viii)]. The associational aspects as well as the theoretical dipole moment of p -cresol, p -chlorophenol, 2,4-dichlorophenol and p -bromophenol in methyl methacrylate (MMA) or ethyl methacrylate (EMA) are all shown in Fig. 8. The static dipole moment μ_0 's are estimated and placed in Table 3 in terms of slope of $X_{ijk} - w_{jk}$ curve of Fig. 9 at $w_{jk} \rightarrow 0$.

5 Conclusions

Relaxation phenomena of acrylic esters and phenols dissolved in CCl_4 solution over a broad frequency range of zero to 9.37 GHz electric field have been studied by introducing MATLAB programming technique using least squares fitting of experimental data point within the error bar to explore structural and associational behaviour. Double relaxation times τ_2 and τ_1 as well as μ_2 and μ_1 are estimated from single frequency measurement of χ_{ijk} 's for different w_{jk} 's at 9.37 GHz and compared with reported and measured μ_0 under static electric field. Only six binary polar mixture out of eight exhibits double relaxation behaviour signifying the non-rigidity of their flexible parts unlike systems EMA+ p -cresol (V) and EMA+ p -bromophenol(VIII) showing mono-relaxation behaviour. It is also evident that μ_{ijk} 's yield high value for $x_j=0.5$ of acrylates (j) and phenol (k) in CCl_4 solution because of larger size of the rotating unit arising out of solute-solute molecular association through H-bonding. The study further reveals that the whole rotation of the polar mixture is possible under hf electric field. The solute-solute (dimer) and solute-solvent (monomer) molecular association are ascertained in terms of μ_{theo} 's taking inductive, mesomeric and electromeric effects within the polar groups of the molecules.

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