Indian Journal of Pure & Applied Physics
Vol. 55, March 2017, pp. 207-217

Dielectric relaxation phenomena of alkyl acrylate on complexation with phenol dissolved in carbon tetrachloride under static and high frequency electric field

S Sahoo[a]* & S K Sit[b]

[a]Department of Electronics & Instrumentation Engineering, National Institute of Technology, Silchar 788 010, India
[b]Department of Physics, Dr Meghnad Saha Institute of Technology, Purba Medinipore 721 657, India

Received 13 February 2016; revised 9 September 2016; accepted 29 December 2016

Double relaxation times τ_2 and τ_1 due to whole molecular rotation and the flexible parts of the binary (*jk*) polar mixture of alkyl acrylate (*j*) and phenols CCl_4 (*i*) at 35 ℃ are estimated using susceptibility data under 9.37 GHz electric field. Five systems out of twelve exhibit τ_2, τ_1 and μ_2, μ_1. τ_2's of all systems show gradual increase with the chain length of esters offering hindrance to the rotation of the molecule. The relative contributions c_1 and c_2 due to τ_1 and τ_2 for five systems in terms of $\frac{\chi'_{ijk}}{\chi_{oijk}} - w_{jk}$ and $\frac{\chi''_{ijk}}{\chi_{oijk}} - w_{jk}$ curve at $W_{jk\to 0}$ are estimated along with symmetric τ_s, characteristics τ_{cs} establishing the symmetric distribution of relaxation behavior. The estimated μ's and τ_2's agreed with the reported and measured values. The solute-solute and solute-solvent molecular associations through H-bonding are also as certained.

Keywords: Relaxation time, Dipole moment, Solute-solute association, Solute-solvent association

1 Introduction

Dielectric investigations in polar liquids dissolved in non polar solvents provide meaningful information on structural and associational aspect as well as formation of molecular complexes in GHz electric field under varying conditions of complexation, temperature and environmental factors. It is of considerable interest to researchers because of the capacity of microwaves to detect weak molecular association[1-4]. On the basis of the results, appropriate models[5,6] of liquid mixture involving relaxation process have been formulated. Shyamalamba and Premaswarup[7] studied the dielectric properties of single polar solutes of methyl, ethyl and butyl acrylate under micro wave electric field and compared their result with those of butyrates. Sivagurunathan *et al.*[8] measured the dielectric parameters of binary polar mixture of alkyl acrylate with primary alcohols using TDR technique. They also studied the existence of complex formation in proton donor (alcohols) and proton acceptor (alkyl acrylates) binary polar mixture dissolved in non-polar solvent using FTIR spectroscopic method. The inherent presence of H-bonding in the ester-alcohol polar mixtures is of considerable importance as it relates to the study of biopolymers[9] to provide process parameters for efficient design of transesterification process of industrial interest.

Recently, Khan *et al.*[10] has investigated the binary polar mixtures of methyl acrylate (MA), ethyl acrylate (EA) and butyl acrylate (BA) with p-cresol, p-chlorophenol, 2,4 dichlorophenol and p-bromophenol respectively to get valuable information on the complex formation by constituent polar molecules. They measured dielectric constant ε'_{ijk}, dielectric loss ε''_{ijk}, static ε_{0ijk} and refractive index n_{Dijk}^2 $(= \varepsilon_{\infty ijk})$ of binary (*jk*) polar mixture dissolved in non polar solvent (*i*) carbon tetrachloride under 9.37 GHz electric field at 35 °C to predict relaxation time τ_1 and τ_2 due to intra molecular and overall molecular rotation using slope method of Higasi [11].

Alkyl acrlates are used in various industrial fields like elastomers, adhesives, thickeners, amphoteric surfactants, fibers, plastics, textiles, inks and in chemical synthesis etc. Because of the scientific and industrial importance of acrylates and phenols, we therefore, thought to study further the relaxation behavior of binary (*jk*) polar liquid mixture of alkyl acrylates (MA, EA and BA) and phenols under the same molecular environment[10] to estimate double relaxation times τ_2 and τ_1 as well as dipole moments

---

*Corresponding author (E-mail: swagatdebmsit@yahoo.co.in)

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[12]. The measurement involved real $\chi'_{ijk} = (\varepsilon'_{ijk} - \varepsilon_{\infty ijk})$ and imaginary χ''_{ijk} (=ε''_{ijk}) parts of complex orientational susceptibility χ^*_{ijk} and static orientational susceptibility $\chi_{0ijk} = (\varepsilon_{0ijk} - \varepsilon_{\infty ijk})$ at different weight fractions w_{jk}'s of alkyl acrylate (*j*) and phenol (*k*) under same state of molecular environment[10]. The susceptibility measurement yields orientational polarization[12,13] 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[14]. 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. The static or low frequency dipole moments μ_s's of the binary polar mixtures were also estimated using Debye theory. Earlier study was undertaken on long chain para compounds like Phenols dissolved in benzene sometimes exhibit zero dipole moment[15] 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 alkyl acrylates and phenols dissolved in CCl_4 in predicting τ_2 and τ_1 as well as μ_2 and μ_1 respectively like alkyl methacrylates and phenols[12]. Moreover, τ can be directly estimated from measured χ'_{ijk}s data unlike the method of Higasi[11] which involves estimation of linear slope of ε_{ijk}'s against w_{jk}'s. The linearity relation may not hold good for associating polar mixture even in the lower concentration also. The comparison of static μ_s as well as μ_2 and μ_1 enables one how far frequency of electric field affects μ. Out of twelve systems under observations, five systems exhibit double relaxation phenomena. The estimated τ_2 and τ_1 from Fig. 1 as well symmetric τ_s and characteristic τ_{cs} are placed in Table 1. τ_2's agree well with the reported τ_2 from Higasi method whereas τ_0's agree well with the symmetric τ_s. τ's were also estimated from the ratio of slopes of χ'_{ijk}-w_{jk} and χ''_{ijk}- w_{jk} at $w_{jk\to 0}$ as seen in Figs 2 and 3, respectively. The measured τ's from linear slope of χ''_{ijk}-χ'_{ijk} straight line (Fig. 4) is also

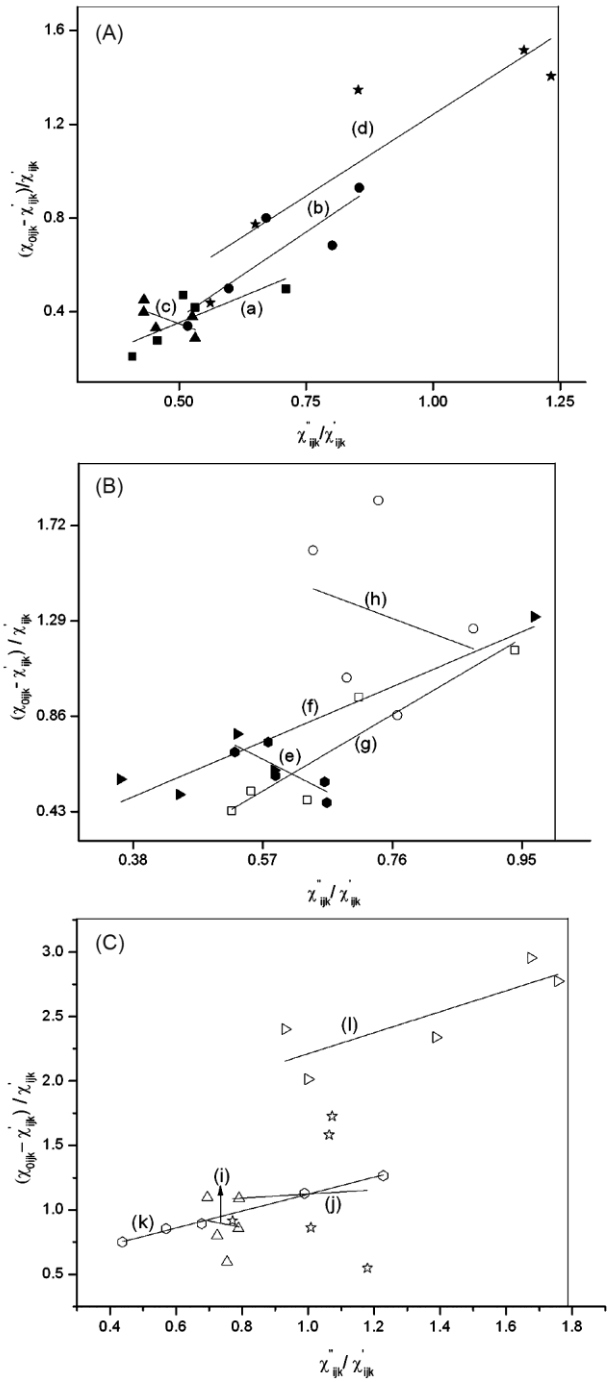

Fig. 1 – The variations of $\frac{\chi_{0ijk}-\chi'_{ijk}}{\chi'_{ijk}}$ against $\frac{\chi''_{ijk}}{\chi'_{ijk}}$ for different w_{jk}'s of binary polar mixture of alkyl acrylate & phenol dissolved in CCl_4 at 35 °C under 9.37 GHz electric field (A) (a) ■, (b) •, (c) ▲, (d) ★ for p-cresol, p-chlorophenol, 2,4-dichlorophenol and p-bromophenol mixed with MA respectively, (B) (e) ⬢, (f) ▶, (g) □, (h) ○ for p-cresol, p-chlorophenol,2,4-dichlorophenol and p-bromophenol mixed with EA, respectively and (C) (i)△, (j) ☆, (k)⬡, (l)▷ for p-cresol, p-chlorophenol, 2,4-dichlorophenol and p-bromophenol mixed with BA, respectively.

Table 1 – Slope and intercept of Eq. (1) , estimated $\tau_2$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 characteristic τ_{cs} of five non rigid binary polar mixture of alkyl acrylate 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 $\frac{\chi_{0ijk}-\chi'_{ijk}}{\chi'_{ijk}}$ against $\frac{\chi''_{ijk}}{\chi'_{ijk}}$ straight line Eq. (1)		Estimated		Most probable $\tau_0=\sqrt{\tau_1\tau_2}$ (ps)	Measured τ from		Reported (from Higasi method)			Estimated symmetric τ_s (ps)	Estimated Characteristic τ_{cs} (ps)
				τ_2 (ps)	τ_1 (ps)		linear slope method (ps)	ratio of slope method (ps)	τ_2 (ps)	τ_1 (ps)	τ_0 (ps)		
(I)Methyl acrylate + p-cresol in CCl_4	3:1	0.89348	-0.09268	13.14	2.04	5.18	6.55	7.06	8.63	7.29	7.93	5.44	8.74
	2:1								10.23	9.98	10.11		
	1:1								15.70	15.07	15.38		
	1:2								13.28	12.16	12.71		
	1:3								11.81	10.88	11.34		
(II) Methyl acrylate + p-chlorophenol in CCl_4	3:1	1.46132	-0.35562	19.58	5.24	10.13	7.03	13.50	11.11	11.36	11.23	10.25	12.80
	2:1								14.12	13.16	13.63		
	1:1								20.11	19.89	20.01		
	1:2								18.36	14.33	16.22		
	1:3								14.41	12.11	13.21		
(III) Methyl acrylate + 2,4-dichlorophenol in CCl_4	3:1	-0.80782	0.75329	9.40	-	-	4.52	3.29	9.15	9.52	9.33	-	-
	2:1								12.31	10.77	11.52		
	1:1								17.68	17.55	17.62		
	1:2								15.64	12.56	14.02		
	1:3								12.20	11.40	11.79		
(IV) Methyl acrylate + p-bromophenol in CCl_4	3:1	1.39118	-0.1493	21.64	1.99	6.56	2.96	14.62	13.19	14.14	13.66	6.94	13.59
	2:1								20.10	15.92	17.89		
	1:1								26.66	22.85	24.68		
	1:2								21.71	19.77	20.72		
	1:3								19.26	18.19	18.76		
(V)Ethyl acrylate + p-cresol in CCl_4	3:1	-1.55585	1.55379	11.74			5.69	7.11	11.99	9.91	10.91	-	-
	2:1								14.42	12.40	13.37		
	1:1								22.23	16.12	18.97		
	1:2								21.72	13.66	17.23		
	1:3								17.03	12.36	14.50		
(VI)Ethyl acrylate + p-chlorophenol in CCl_4	3:1	1.3035	0.00339	22.19			2.47	2.25	17.76	12.19	14.71	-	-
	2:1								19.18	19.03	19.09		
	1:1								26.96	21.38	24.01		
	1:2								24.76	20.65	22.61		
	1:3								22.84	19.08	20.87		
(VII)Ethyl acrylate + 2,4-dichlorophenol in CCl_4	3:1	1.81255	-0.50917	24.89	5.90	12.12	7.32	7.44	14.02	10.39	12.07	12.22	15.62
	2:1								16.02	16.43	16.22		
	1:1								24.53	18.97	21.58		
	1:2								22.50	16.77	19.42		
	1:3								20.82	14.26	17.23		
(VIII) Ethyl acrylate + p-bromophenol in CCl_4	3:1	-1.15107	2.17652	17.12	-	-	5.73	5.73	22.04	18.39	20.97	-	-
	2:1								25.20	23.91	24.54|		
	1:1								35.24	26.71	30.68		
	1:2								27.45	24.11	25.72		
	1:3								24.12	21.03	22.52		
(IX)Butyl acrylate + p-cresol in CCl_4	3:1	-0.50719	1.269	15.31	-	-	8.63	7.20	13.35	11.17	12.21	-	-
	2:1								18.69	13.73	16.02		
	1:1								26.62	22.26	24.34		
	1:2								23.26	17.90	20.40		
	1:3								18.34	15.55	16.89		
(X) Butyl acrylate + p-chlorophenol in CCl_4	3:1	2.2601	-0.76581	31.34	7.05	14.86	3.01	10.16	20.04	13.48	16.44	14.92	19.11
	2:1								27.34	24.11	25.67		
	1:1								31.53	32.72	32.12		
	1:2								27.15	26.97	27.06		
	1:3								25.12	22.48	23.76		

(*Contd*.)

Table 1 –Slope and intercept of Eq. (1) , estimated $\tau_2$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 characteristic τ_{cs} of five non rigid binary polar mixture of alkyl acrylate and phenol dissolved in dilute CCl$_4$ at 35 °C under 9.37 GHz electric field (*Contd.*)

System	Mole fraction x_j of acrylic ester in phenol (k)	Slope & intercept of $\frac{\chi_{oijk}-\chi'_{ijk}}{\chi'_{ijk}}$ against $\frac{\chi''_{ijk}}{\chi'_{ijk}}$ straight line Eq. (1)		Estimated τ_2 (ps)	Estimated τ_1 (ps)	Most probable $\tau_0 = \sqrt{\tau_1\tau_2}$ (ps)	Measured τ from ratio of slope method (ps)	Measured τ from linear slope method (ps)	Reported τ_2 (ps) (from Higasi method)	Reported τ_1 (ps)	Reported τ_0 (ps)	Estimated symmetric τ_s (ps)	Estimated Characteristic τ_{cs} (ps)
(XI) Butyl acrylate + 2,4-dichlorophenol in CCl$_4$	3:1	0.65578	0.46641	18.44	-	-	1.45	2.81	17.41	12.78	14.92	-	-
	2:1								19.26	22.47	20.80		
	1:1								28.95	27.58	28.26		
	1:2								25.47	20.96	23.11		
	1:3								22.24	15.30	18.45		
(XII) Butyl acrylate + p-bromophenol in CCl$_4$	3:1	0.81415	1.39764	28.15	-	-	3.85	7.16	26.67	23.03	24.78	-	-
	2:1								29.80	25.92	27.79		
	1:1								43.59	33.91	38.45		
	1:2								34.01	28.97	31.39		
	1:3								28.46	27.95	28.21		

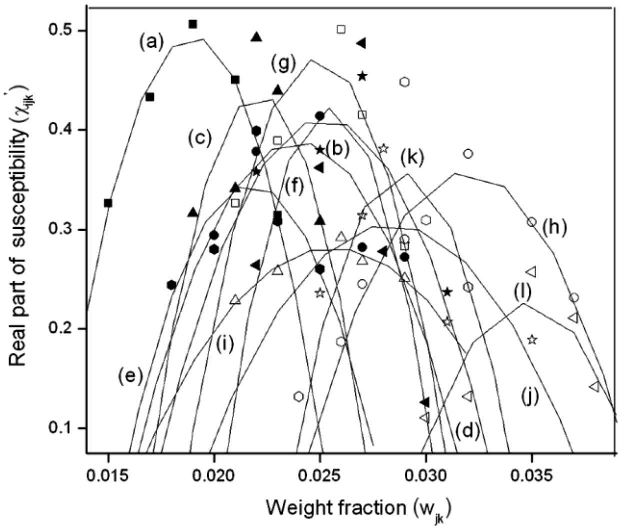

Fig. 2 – The plot of χ'_{ijk} against weight fractions w_{jk}'s of binary polar mixture of alkyl acrylate and phenol dissolved in CCl$_4$ at 35 °C under 9.37 GHz electric field. (a)■, (b)•, (c)▲, (d) ★ for p-cresol, p-chlorophenol , 2,4-dichlorophenol and p-bromophenol mixed with MA (e) ⬢, (f) ▶, (g) □, (h) ○ for p-cresol , p-chlorophenol , 2,4-dichlorophenol and p-bromophenol mixed with EA and (i)△, (j) ☆, (k) ⬢, (l)▷ for p-cresol , p-chlorophenol , 2,4-dichlorophenol and p-bromophenol mixed with BA, respectively

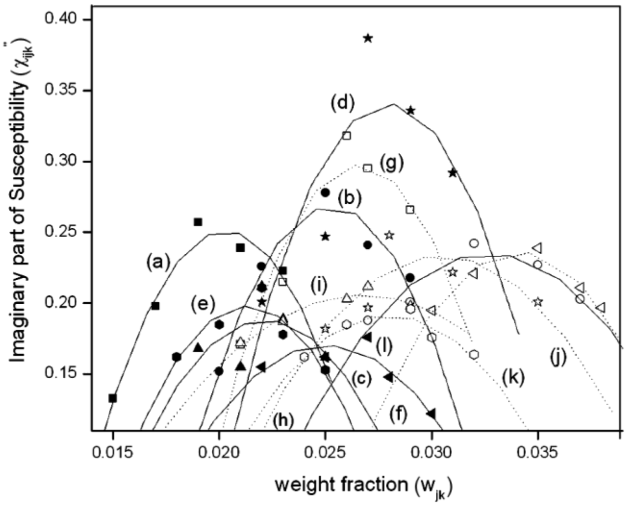

Fig. 3 – The plot of χ''_{ijk} against weight fractions w_{jk}'s of binary polar mixture of alkyl acrylate and phenol dissolved in CCl$_4$ at 35 °C under 9.37 GHz electric field. (a)■, (b)•, (c)▲, (d)★ for p-cresol , p-chlorophenol , 2,4-dichlorophenol and p-bromophenol mixed with MA (e) ⬢, (f) ▶, (g) □, (h) ○ for p-cresol, p-chlorophenol, 2,4-dichlorophenol and p-bromophenol mixed with EA and (i)△, (j) ☆, (k)⬡, (l), ▷ for p-cresol , p-chlorophenol , 2,4-dichlorophenol and p-bromophenol mixed with BA, respectively.

placed in Table 1 for comparison. The relative contributions c_1 and c_2 due to τ_1 and $\tau_2$were calculated for five non rigid binary polar mixtures. The experimental c_1 and c_2 from the $\frac{\chi'_{ijk}}{\chi_{oijk}} - w_{jk}$ and $\frac{\chi''_{ijk}}{\chi_{oijk}} - w_{jk}$ curve at $w_{jk\to 0}$ of Fig. 5 are calculated and placed in Table 2 along with theoretical c_1 and c_2. The symmetric and asymmetric distribution parameter γ and δ are also calculated and placed in Table 2. The estimated dipole moments μ_2 and μ_1 due to τ_2 and τ_1 are placed in Table 3. The plot of most probable or average μ_{av} against mole fractions x_j's of alkyl acrylate reveals the linear dependence of μ_{av} on alkyl chain length of the acrylic ester (Fig. 6). Theoretical μ_{theo}'s (Fig. 7) are also estimated to show the associational behavior and compared with the reported μ's and static μ_s's from slope of X_{ijk} - w_{jk} curve (Fig. 8).

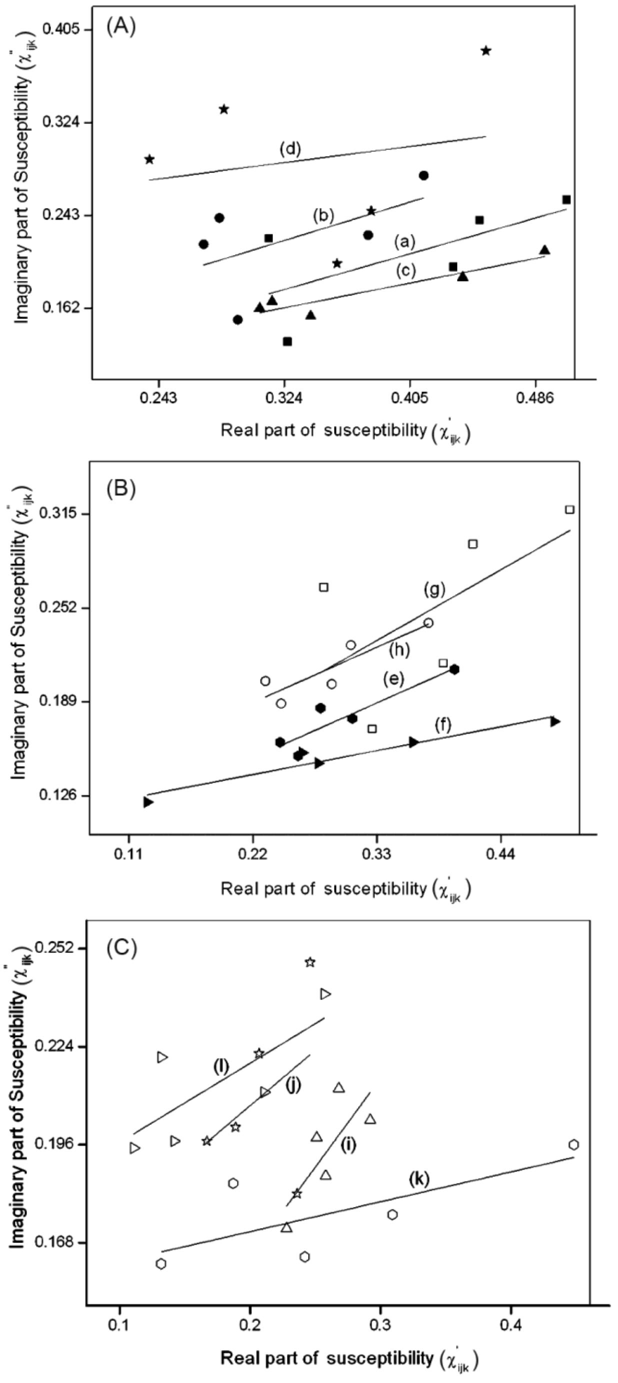

Fig. 4 – The variations of χ''_{ijk} against χ'_{ijk} for different w_{jk}'s of binary polar mixture of alkyl acrylate and phenol dissolved in CCl_4 at 35 °C under 9.37 GHz electric field (A)(a)■, (b)•, (c)▲ (d)★ for p-cresol, p-chlorophenol, 2,4-dichlorophenol and p-bromophenol mixed with MA, respectively, (B) (e) ⬢, (f) ►, (g) ☐, (h) ○ for p-cresol, p-chlorophenol, 2,4-dichlorophenol and p-bromophenol mixed with EA, respectively and (C) (i)△, (j) ☆, (k) ⬡, (l) ▷ for p-cresol, p-chlorophenol, 2,4-dichlorophenol and p-bromophenol mixed with BA, respectively.

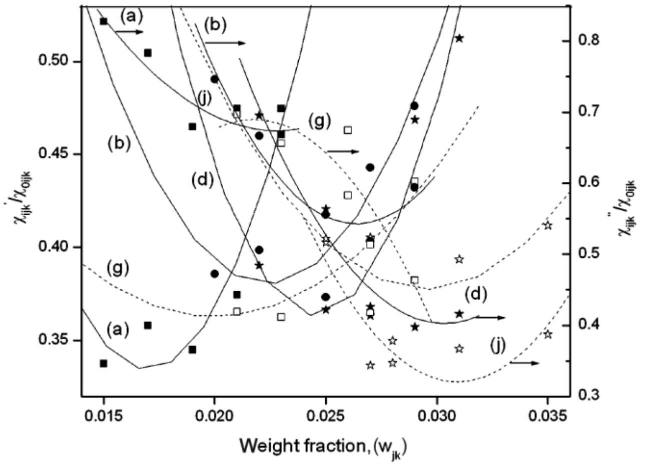

Fig. 5 – Variations of $\frac{\chi'_{ijk}}{\chi_{oijk}}$ as well as $\frac{\chi''_{ijk}}{\chi_{oijk}}$ against w_{jk}'s of binary polar mixtureof alkyl acrylate and phenol dissolved in CCl_4 at 35 °C under 9.37 GHz electric field. (a)■, (b)•, (d)★ , for p-cresol , p-chlorophenol and p-bromophenol mixed with MA (g) ☐ for 2,4-dichlorophenol mixed with EA and (j) ☆ for p-chlorophenol mixed with BA, respectively

2 Experimental Details

The samples alkyl acrylates, 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.*[16] method at 9.37 GHz electric field[10]. The physical parameters are checked against literature values. ε_{0ijk} and n_{Dijk} were measured by Dipolemeter DM 01 and Abbe's refractometer, respectively[10]. The accuracy in the measurements of ε'_{ijk} and ε''_{ijk} are ±1 % and ±5 %, respectively. The real $\chi'_{ijk} = (\varepsilon'_{ijk} - \varepsilon_{\infty ijk})$ and imaginary χ''_{ijk} $(=\varepsilon''_{ijk})$ parts of complex orientational susceptibility χ^*_{ijk} and static orientational susceptibility $\chi_{0ijk} = (\varepsilon_{0ijk} - \varepsilon_{\infty ijk})$ at different w_{jk}'s of solute were estimated by simple normalization of permittivity data. The temperature of the measurements was maintained at 35 ℃ within the accuracy limit of ±0.1 % ℃ by a water circulating thermostat while binary mixtures were prepared.

3 Theoretical Formulations

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

The Bergmann's equations[17] are solved to get a straight line equation in terms of established symbols of χ'_{ijk} , χ''_{ijk} and χ_{0ijk}[12] as:

Table 2 – Relative contributions c_1 and c_2 due to τ_1 and τ_2 for theoretical $\frac{\chi'_{ijk}}{\chi_{oijk}}$ and $\frac{\chi''_{ijk}}{\chi_{oijk}}$ of Fr Ö hlich's equation , experimental c_1 and c_2 of $\frac{\chi'_{ijk}}{\chi_{oijk}}$ and $\frac{\chi''_{ijk}}{\chi_{oijk}}$ at $w_{jk\to 0}$ from Figs 5 and 6, respectively of five non rigid binary polar mixture of alkyl acrylate 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)	Theoretical $\frac{\chi'_{ijk}}{\chi_{0ijk}}$ from Fr Ö hlich's equation[20]	Theoretical $\frac{\chi''_{ijk}}{\chi_{0ijk}}$ from Fr Ö hlich's equation[20]	Relative contributions c_1 (theoretical)	Relative contributions c_2 (theoretical)	Experimental $\frac{\chi'_{ijk}}{\chi_{0ijk}}$ at $w_{jk\to 0}$ from Fig. 5	Experimental $\frac{\chi''_{ijk}}{\chi_{0ijk}}$ at $w_{jk\to 0}$ from Fig. 5	Relative contributions c_1 (experimental)	Relative contributions c_2 (experimental)	Symmetric distribution parameter γ	Asymmetric distribution parameter δ
(I)Methyl acrylate + p-cresol in CCl_4	3:1 2:1 1:1 1:2 1:3	0.8779	0.2893	0.6052	0.4497	2.01869	1.37286	0.2931	2.7650	0.0516	0.6701
(II) Methyl acrylate + p-chlorophenol in CCl_4	3:1 2:1 1:1 1:2 1:3	0.7138	0.4225	0.5193	0.5580	4.25265	1.49546	4.4180	0.5063	0.0388	0.8275
(IV) Methyl acrylate + p-bromophenol in CCl_4	3:1 2:1 1:1 1:2 1:3	0.8008	0.3305	0.6044	0.5367	4.43691	2.68812	2.5978	4.9165	0.0961	0.5799
(VII)Ethyl acrylate +2,4-dichlorophenol in CCl_4	3:1 2:1 1:1 1:2 1:3	0.6413	0.4430	0.4979	0.6200	-1.41525	0.67967	-2.7600	3.2972	0.048	0.8130
(X) Butyl acrylate + p-chlorophenol in CCl_4	3:1 2:1 1:1 1:2 1:3	0.5329	0.4562	0.4588	0.7221	4.94506	1.45545	6.3673	-2.1292	0.0537	0.8137

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

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

Equation (1) is a straight line of variables $\frac{\chi_{oijk}-\chi'_{ijk}}{\chi'_{ijk}}$ against $\frac{\chi''_{ijk}}{\chi'_{ijk}}$ 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 displayed in Fig. 1.

τ's were also estimated from the ratio of slopes of $\left(\frac{d\chi'_{ijk}}{w_{jk}}\right)_{w_{jk\to o}}$ and $\left(\frac{d\chi''_{ijk}}{w_{jk}}\right)_{w_{jk\to o}}$ of χ'_{ijk}- w_{jk} and χ''_{ijk}- w_{jk} curves in Figs 2 and 3 to eliminate polar- polar interactions[12].

The slope $\left(\frac{d\chi''_{ijk}}{d\chi'_{ijk}}\right)$ of χ''_{ijk} -χ'_{ijk} linear equation of Fig. 4 can also be used to estimate τ's from Murthy *et al.*[18]. All the τ's including the most probable $\tau_0 = \sqrt{\tau_1\tau_2}$, measured τ's, symmetrical τ_s and asymmetric τ_{cs} 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[17,19] as :

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

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

where $\alpha_1 = \omega\tau_1$ and $\alpha_2 = \omega\tau_2$ provided $\alpha_2 > \alpha_1$. The other symbols and terminologies are explained elsewhere[19]. The five systems out of twelve under consideration show non rigid behavior. A continuous distribution of τ between two discrete values of τ_1 and τ_2 is, therefore, expected using Fr ö hlich's equations[20]. The theoretical values of c_1 and c_2 are

Table 3 – Slope of X_{ijk}- w_{jk}, χ'_{ijk}- w_{jk} curve, estimated dipole moments μ_2,μ_1 due to τ_2,τ_1 and static μ_s, measured μ's due to τ from linear slopes and ratio of slopes method respectively, reported μ's due to Higasi method , theoretical dipole moment of Mithyl acrylate, Ethyl acrylate and Butyl acrylate with phenols dissolved in CCl$_4$ at 35 °C temperature at 9.37 GHz electric field

System	Mole fraction x_j of alkyl acrylate in phenol(k)	Slope of X_{ijk}- w_{jk} curve at $w_{jk\to0}$	Slope of χ'_{ijk}-w_{jk} curve at $w_{jk\to0}$	Average molecular weight $M_{jk}=M_jx_j + M_kx_k$	Estimated			Estimated $\mu_0\times10^{30}$ C.m	Measured		Reported $\mu\times10^{30}$ C.m from Gopala krishna method[22]	Theoretical dipole moment $\mu_{theo}\times10^{30}$ C.m	Free Energy of activation ΔF_τ (kJ mol^{-1})
					$\mu_2\times10^{30}$ C.m	$\mu_1\times10^{30}$ C.m	$\mu_{av}\times10^{30}$ C.m		$\mu\times10^{30}$ from τ of linear slope	$\mu\times10^{30}$ from τ of ratio of slope			
(I)Methyl acrylate + p-cresol in CCl$_4$	3:1	28.88429	416.97143	0.0896	60.46	48.17	50.00	52.97	51.26	51.80	46.42	9.48	8.97
	2:1			0.0907	60.84	48.47	50.31|	53.30	51.58	52.11	46.71	3.90	
	1:1			0.0931	61.64	49.10	50.97	54.00	52.25	52.79	47.32		
	1:2			0.0955	62.42	49.73	51.62	54.68	52.91	53.46	47.92		
	1:3			0.0966	62.79	50.02	51.92	55.00	53.22	53.78	48.20		
(II) Methyl acrylate + p-chlorophenol in CCl$_4$	3:1	28.89801	261.3471	0.0967	60.03	41.16	45.80	55.04	42.57	50.25	44.72	9.48	10.68
	2:1			0.1001	61.07	41.88	46.60	56.00	43.31	51.12	45.50	2.67	
	1:1			0.1073	63.24	43.37	48.25	57.98	4.85	52.93	47.11		
	1:2			0.1145	65.33	44.80	49.84	59.90	46.33	54.86	48.67		
	1:3			0.1179	66.29	45.46	50.58	60.78	47.01	55.49	49.38		
(III) Methyl acrylate + 2,4-dichlorophenol in CCl$_4$	3:1	44.61214	625.98571	0.1053	72.61	-	-	-	65.74	64.71	58.64	9.48	10.49
	2:1			0.1115	74.70				67.63	66.57	60.33	6.40	
	1:1			0.1245	78.96				71.49	70.37	63.76		
	1:2			0.1376	83.00				75.15	73.97	67.03		
	1:3			0.1438	84.84				76.81	75.61	68.51		
(IV) Methyl acrylate + p-bromophenol in CCl$_4$	3:1	30.41277	281.76414	0.1078	69.85	43.42	46.23	59.62	43.78	56.90	49.22	9.48	9.57
	2:1			0.1148	72.06	44.80	47.70	61.51	45.16	58.71	50.78	2.33	
	1:1			0.1295	76.56	47.59	50.67	65.35	47.98	62.37	53.95		
	1:2			0.1443	80.81	50.24	53.49	68.98	50.65	65.83	56.94		
	1:3			0.1513	82.73	51.43	54.76	70.62	51.85	67.40	58.30		
(V)Ethyl acrylate + p-cresol in CCl$_4$	3:1	32.8252	348.28969	0.1021	56.72	-	-	60.28	49.21	50.59	46.30	9.53	11.06
	2:1			0.1028	56.90	-	-	60.47	49.37	50.74	46.44	3.90	
	1:1			0.1041	57.28	-	-	60.87	49.69	51.08	46.75		
	1:2			0.1055	57.65	-	-	61.27	50.02	51.41	47.06		
	1:3			0.1061	57.83	-	-	61.45	50.17	51.57	47.20		
(VI)Ethyl acrylate + p-chlorophenol in CCl$_4$	3:1	42.94718	726.14003	0.1072	113.59	-	-	70.65	69.77	69.64	64.54	9.53	12.69
	2:1			0.1095	114.78			71.40	70.50	70.38	65.22	2.67	
	1:1			0.1143	117.29			72.96	72.04	71.92	66.64		
	1:2			0.1192	119.75			74.49	73.55	73.42	68.04		
	1:3			0.1215	120.88			75.19	74.25	74.12	68.68		
(VII)Ethyl acrylate + 2,4-dichlorophenol in CCl$_4$	3:1	27.94167	536.32143	0.1158	109.41	65.29	75.76	59.23	67.15	67.33	59.85	9.53	11.12
	2:1			0.1209	111.76	66.69	77.39	60.51	68.60	68.77	61.13	6.40	
	1:1			0.1316	116.60	69.57	80.74	63.13	71.57	71.75	63.77		
	1:2			0.1422	121.24	72.35	83.95	65.64	74.42	74.61	66.31		
	1:3			0.1473	123.36	73.61	85.43	66.79	75.77	75.92	67.47		
(VIII) Ethyl acrylate + p-bromophenol in CCl$_4$	3:1	48.54468	319.37904	0.1183	68.30	-	-	78.91	50.77	50.77	46.40	9.53	12.03
	2:1			0.1242	69.96	-	-	80.83	52.00	52.00	47.53	2.33	
	1:1			0.1366	73.37	-	-	84.77	54.53	54.53	49.84		
	1:2			0.1489	76.62	-	-	88.53	56.95	56.95	52.05		
	1:3			0.1548	78.11	-	-	90.25	58.06	58.06	53.06		
(IX)Butyl acrylate + p-cresol in CCl$_4$	3:1	23.69167	135.55952	0.1232	43.04	-	-	56.24	35.86	34.72	31.74	9.67	11.47
	2:1			0.1216	42.76			55.87	35.63	34.50	31.53	3.90	
	1:1			0.1182	42.16			55.08	35.12	34.01	31.09		
	1:2			0.1147	41.54			54.28	34.61	33.52	30.64		
	1:3			0.1131	41.25			53.90	34.37	33.28	30.42		
(X) Butyl acrylate + p-chlorophenol in CCl$_4$	3:1	16.4859	174.67146	0.1283	77.72	40.10	49.21	47.88	37.61	43.15	39.20	9.67	11.66
	2:1			0.1283	77.73	40.10	49.21	47.88	37.62	43.16	39.21	2.67	
	1:1			0.1284	77.75	40.11	49.23	47.90	37.63	43.17	39.21		
	1:2			0.1284	77.77	40.12	49.24	47.91	37.64	43.18	39.22		
	1:3			0.1285	77.78	40.13	49.24	47.91	37.64	43.19	39.23		

(*Contd.*)

Table 3 – Slope of X_{ijk}- w_{jk}, χ'_{ijk}- w_{jk} curve, estimated dipole moments μ_2,μ_1 due to τ_2,τ_1 and static μ_s, measured μ's due to τ from linear slopes and ratio of slopes method respectively, reported μ's due to Higasi method , theoretical dipole moment of Mithyl acrylate, Ethyl acrylate and Butyl acrylate with phenols dissolved in CCl_4 at 35 °C temperature at 9.37 GHz electric field (*Contd*.)

System	Mole fraction x_j of alkyl acrylate in phenol(k)	Slope of X_{ijk}- w_{jk} curve at $w_{jk\to0}$	Slope of χ'_{ijk}-w_{jk} curve at $w_{jk\to0}$	Average molecular weight $M_{jk}=M_jx_j + M_kx_k$	Estimated $\mu_2\times10^{30}$ C.m	$\mu_1\times10^{30}$ C.m	$\mu_{av}\times10^{30}$ C.m	Estimated $\mu_0\times10^{30}$ C.m	Measured $\mu\times10^{30}$ from τ of linear slope	$\mu\times10^{30}$ from τ of ratio of slope	Reported $\mu\times10^{30}$ C.m from Gopala krishna method[22]	Theoretical dipole moment $\mu_{theo}\times10^{30}$ C.m	Free Energy of activation ΔF_τ (kJ mol^{-1})
(XI) Butyl acrylate + 2,4-dichlorophenol in CCl_4	3:1	43.72415	623.38095	0.1369	106.68	-	-	80.55	72.54	73.26	68.54	9.67	12.22
	2:1			0.1397	107.76			81.36	73.27	74.00	69.23	6.40	
	1:1			0.1456	110.02			83.07	74.81	75.55	70.69		
	1:2			0.1515	112.23			84.74	76.31	77.07	72.11		
	1:3			0.1543	113.26			85.52	77.01	77.78	72.77		
(XII) Butyl acrylate + p-bromophenol in CCl_4	3:1	64.4886	420.75803	0.1394	115.98	-	-	98.71	61.44	65.02	58.59	9.67	13.30
	2:1			0.1430	117.46			99.97	62.22	65.85	59.33	2.33	
	1:1			0.1506	120.55			102.60	63.86	67.59	60.90		
	1:2			0.1801	131.83			112.20	69.83	73.91	66.59		
	1:3			0.1939	136.78			116.42	72.46	76.69	69.09		

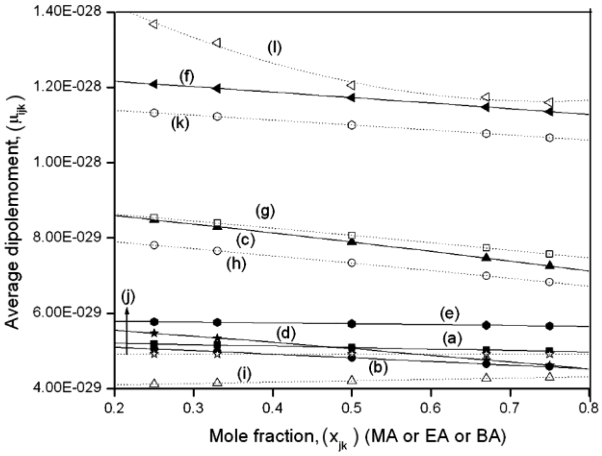

Fig. 6 – The plot of average dipole moment μ_{av} due to τ_0 of binary polar mixture of alkyl acrylate and phenol dissolved in CCl_4 against mole fraction X_j's of MA, EA and BA at 35 °C under 9.37 GHz electric field. (a)■, (b)•, (c)▲, (d)★ for p-cresol , p-chlorophenol , 2,4-dichlorophenol and p-bromophenol mixed with MA (e) ⬢, (f) ▶, (g) □, (h) ○ for p-cresol , p-chlorophenol , 2,4-dichlorophenol and p-bromophenol mixed with EA and (i)△, (j) ☆, (k)⬡, (l)▷ for p-cresol , p-chlorophenol , 2,4-dichlorophenol and p-bromophenol mixed with BA, respectively

calculated from of $\frac{\chi'_{ijk}}{\chi_{oijk}}$ and $\frac{\chi''_{ijk}}{\chi_{oijk}}$ of Fröhlich's equation. They are compared with the experimental c_1 and c_2 from the graphical plots of $\frac{\chi'_{ijk}}{\chi_{oijk}}$ and $\frac{\chi''_{ijk}}{\chi_{oijk}}$ against w_{jk} at $w_{jk\to0}$ as seen in Fig. 5. All the c's are placed in Table 2 for five systems.

Again, the imaginary part of dielectric orientational susceptibility χ''_{ijk} as a function of w_{jk} of solutes can be written as[19]:

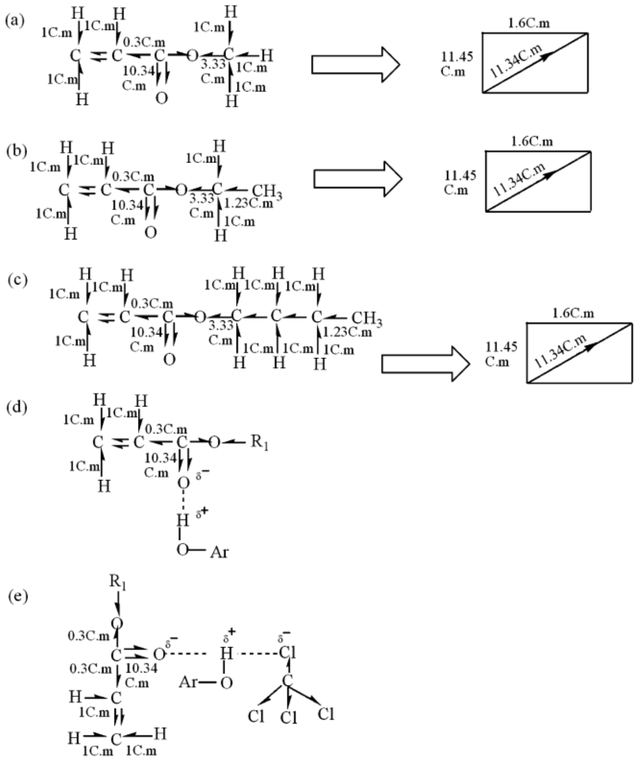

Fig. 7–Theoretical dipole moments μ_{theo}'s from available bond angles and bond moments (multiples of 10^{-30}C.m) of alkyl acrylate and phenol along with solute-solvent and solute-solute molecular associations. (a) methyl acrylate (MA), (b) ethyl acrylate (EA), (c) butyl acrylate (BA), (d) solute-solute molecular association and (e) solute-solvent molecular association .

$$\chi''_{ijk} = \frac{N\rho_{ijk}\mu_{jk}^2}{27\varepsilon_0 M_{jk}K_BT}\left(\frac{\omega\tau_{jk}}{1+\omega^2\tau_{jk}^2}\right)(\varepsilon_i+2)^2 w_{jk} \qquad \dots (4)$$

On differentiation of Eq. (4) with respect to w_{jk} and at $w_{jk\to0}$ which after simplification yields:

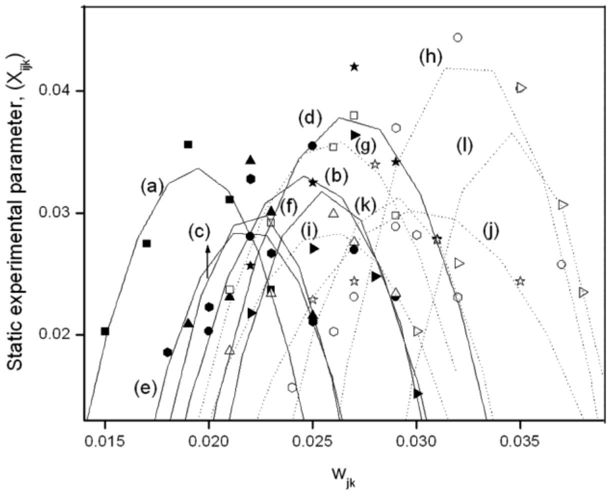

Fig. 8 – Variations of static experimental parameter X_{ijk} against weight fractions w_{jk}'s of binary polar mixture of alkyl acrylate and phenol dissolved in CCl_4 at 35 °C under 9.37 GHz electric field. (a)■, (b)•, (c)▲, (d)★, for p-cresol, p-chlorophenol, 2,4-dichlorophenol and p-bromophenol mixed with MA (e) ⬢, (f) ►, (g) □, (h) ○,for p-cresol, p-chlorophenol, 2,4-dichlorophenol and p-bromophenol mixed with EA and (i)△, (j) ☆(k), ⬡, (l)▷, for p-cresol, p-chlorophenol, 2,4-dichlorophenol and p-bromophenol mixed with BA, respectively

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

where $b = \frac{1}{(1+\omega^2 \tau_{jk}^2)}$ is the dimensionless parameter and β is the slope of χ'_{ijk}- w_{jk} curve at $w_{jk \to 0}$ as shown in Fig. 2. The most probable or average μ_{av} are plotted against different x_j's of MA, EA or BA in phenol as displayed in Fig. 6. All the μ's alongwith theoretical dipole moment μ_{theo} (Fig. 7) 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 is given by[5]:

$$\frac{\varepsilon_{oijk}-1}{\varepsilon_{oijk}+2} - \frac{\varepsilon_{\infty ijk}-1}{\varepsilon_{\infty ijk}+2} = \frac{\varepsilon_{oi}-1}{\varepsilon_{oi}+2} - \frac{\varepsilon_{\infty i}-1}{\varepsilon_{\infty i}+2} + \frac{N \mu_0^2 c_{jk}}{9 \varepsilon_0 K_B T} \qquad \ldots (6)$$

where all the symbols carry usual significance[21].

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

$$\mu_0 = \left[\frac{27 \varepsilon_0 M_{jk} K_B T a_1}{N \rho_i}\right]^{1/2} \qquad \ldots (7)$$

where a_1 is the slope of static experimental parameter[5] X_{ijk}- w_{jk} curve of Fig. 8 at $w_{jk \to 0}$. All the terms are expressed in SI units with usual meanings[5]. All the μ_0 alongwith a_1's are placed in Table 3.

4 Results and Discussion

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. Five systems (a, b, d, g & j) exhibit reasonable values of τ_2 and τ_1 signifying non-rigid systems where as seven other systems (c, e, f, h, i, k & l) having single relaxation behavior treated as rigid systems. The graphs of $\frac{\chi_{oijk}-\chi'_{ijk}}{\chi'_{ijk}}$ against $\frac{\chi''_{ijk}}{\chi'_{ijk}}$ of Fig. 1 for different w_{jk}'s of solutes are drawn by adopting least squares fitting technique of the experimental data. It is evident that graphs are not perfectly linear demanding accurate measurement of experimental data in the low concentration region. τ's were also estimated from ratio of slopes of χ'_{ijk}- w_{jk} and χ''_{ijk} - w_{jk} curves of Figs 2 and 3, respectively. All the graphs of χ''_{ijk} and χ'_{ijk} against w_{jk}'s are parabola 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 parabola is all best fitted through the experimental points revealing the uniqueness of the method. τ's were also estimated from slope of χ''_{ijk}-χ'_{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 (f). This fact reveals that ratio of slopes method avoids polar-polar interaction compare to 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. τ_2's of seven systems having single relaxation and τ_0's of five system having double relaxation behaviour agree well with τ from ratio of slopes and Higasi's method. This indicates double relaxation phenomenon yield macroscopic as well as microscopic relaxation times[19] for the five systems (a, b, d, g, j) and rotation of the whole binary polar mixture for other seven systems (c, e, f, h, i, k, l) showing their molecular non-rigidity under high frequency electric field. It is evident from Table 1 that the value of relaxation time τ's increases with increasing chain length of acrylates and acidity of phenol derivatives[10,12]. Relaxation time increases may be due to increase in effective radius of the rotating unit. Higher value of τ's of butyl acrylate (BA) shown in Table 1 signifies the larger size of the BA molecule in comparison to ethyl acrylate (EA) and methyl acrylate (MA)[10]. The estimated symmetric τ_s's and characteristics relaxation time sτ_{cs}'s of the five systems possessing double relaxation times are placed in the last two columns of Table 1. Unlike τ_{cs}'s,τ_s's agree with the estimated $\tau_0 = \sqrt{\tau_1 \tau_2}$ and reported τ's. This reveals the fact that the binary polar mixture obey the symmetric (Cole – Cole) distribution of relaxation behavior rather than asymmetric (Cole – Davidson) distribution. This is in accord with the fact that the values of symmetric distribution parameter γ's are very small in comparison to the asymmetric distribution parameter δ's shown in Table 3 validating the symmetric distribution of relaxation behavior in them. The relative contributions c_1 and c_2 due to $\tau_1$and τ_2 were estimated from Fr ö hlich's equation[20] as well as graphical plot of $\frac{\chi'_{ijk}}{\chi_{oijk}}$and $\frac{\chi''_{ijk}}{\chi_{oijk}}$ against w_{jk} at $w_{jk\to 0}$ of Fig. 5 and placed in Table 3. The theoretical values of $c_1 + c_2$ for five systems are $\cong 1$. The experimental $c_1 + c_2$ are, however, greater than 1 reveals the possible existence of more than two Debye type dispersions in the binary polar mixture[19] even if c_2's are negative for system (j) probably due to inertia of flexible part[21] of polar molecules. The graphical plot reveals that the $\frac{\chi'_{ijk}}{\chi_{oijk}} - w_{jk}$ and $\frac{\chi''_{ijk}}{\chi_{oijk}} - w_{jk}$ curves of Fig. 5 are all parabola in nature exhibiting a minimum at a certain w_{jk}'s of solutes. Like $\frac{\chi'_{ijk}}{\chi_{oijk}} - w_{jk}$ curve, $\frac{\chi''_{ijk}}{\chi_{oijk}} - w_{jk}$ curves are also concave in nature with the increase of w_{jk} which is consistent with the earlier observation[21]. 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 χ'_{ijk}- w_{jk} curve at $w_{jk\to 0}$ 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 method[22]. In order to study the behavior of polar mixtures in the broadband frequency spectrum, the static dipole moment μ_0's are also estimated using Debye equation[19]. It appears from Table 3 that μ's exhibit high value for butyl acrylate (*j*) and phenol (*k*) mixture in CCl_4 in comparison to ethyl acrylate (EA) and methyl acrylate (MA) like earlier observation in the estimation of τ[10]. 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 moment get increased. The plot of average μ_{av} in terms of most probable τ_0 against x_j's of alkyl acrylate as shown in Fig. 6 supports the above fact. This indicates double relaxation phenomenon yield macroscopic as well as microscopic relaxation times[19] for five systems (a, b, d, g, j) and rotation of the whole binary polar mixture for other seven systems (c, e, f, h, i, k, l) showing their molecular non-rigidity. It is also observed from Table 3 that estimated μ_{av} for five systems (a, b, d, g, j) and μ_2 for other seven systems (c, e, f, h, i, k, l) agree well with the measured μ's and static μ_0's as well as reported μ due to Gopalakrishna's method except system (a). 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 behavior of the component polar mixtures is displayed in Fig. 7(d). This may arise due to interaction between $H^{\delta+}$ of –OH group in phenol and $O^{\delta-}$ of C=O group in esters. Oxygen atom in C=O is sp^3 hybridized. The –OH group of phenol enter into empty space of ester molecule for complexation and provide 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 nonpolar 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 $H^{\delta+}$of –OH group of phenol or $C^{\delta+}$ of C=O group of ester to form molecular association (Fig. 7(e)). The associational aspects as well as the theoretical dipole moment of methyl acrylate (MA), ethyl acrylate (EA) and butyl acrylate (BA) with p-cresol, p-chlorophenol, 2, 4 dichlorophenol and p-bromophenol[12] are all displayed in Fig. 7. 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. 8 at $w_{jk\to 0}$.

5 Conclusions

Relaxation phenomena of alkyl acrylate and phenols dissolved in CCl_4 solution over a broad

frequency range of zero to 9.37 GHz electric field were studied using least squares fitting of experimental data point to explore structural and associational behavior. 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. The study 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.

References

1 Kumlar W D & Porter CW, *J Am Chem Soc*, 56 (1934) 2549.
2 Rabinovitz M & Pines A, *J Am Chem Soc*, 91 (1969) 1585.
3 Nour Abd El & Messieh Abd El, *J Mol Liq*, 79 (1999) 235.
4 Sahoo S & Sit S K, *Indian J Phys*, 84 (2010) 1549.
5 Sahoo S, Middya T R & Sit S K, *Indian J Pure Appl Phys*, 50 (2012) 175.
6 Sahoo S, Dutta K, Acharyya S & Sit S K, *Indian J Pure Appl Phys*, 45 (2007) 529.
7 Symalamba K & Premaswarup D, *Indian J Pure Appl Phys*, 3 (1965) 267.
8 Sivagurunathan P, Dharmalingam K & Ramachandran K, *Mol Phys*,18 (2006) 2835.
9 Sivagurunathan P, Dharmalingam K & Ramachandran K, *Spectrochim Acta*, 64 (2006) 127.
10 AliKhan F L, Sivagurunathan P & Asghar J, *Indian J Pure Appl Phys*, 46 (2008) 54.
11 Higasi K, Koga Y & Nakamura M, *Bull Chem Soc Japan*, 44 (1971) 988.
12 Sahoo S, Middya T R & Sit S K, *Indian J Pure Appl Phys*, 53 (2015) 725.
13 Ghosh N, Sit S K , Bothra A K & Acharyya S, *J Phys D: Appl Phys*, 34 (2001) 379.
14 Sahoo S, Middya T R & Sit S K, *Pramana J Phys*, 4 (2014) 579.
15 Ghosh N , Basak R C, Sit S K & Acharyya S, *J Mol Liq*, 85 (2000) 375.
16 Heston N M, Franklin A D, Henely E L & Smyth C P, *J Am Chem Soc*,72 (1950) 3443.
17 Bergmann K, Roberti D M & Smyth C P, *J Phys Chem*, 64 (1960) 665.
18 Murthy M B R, Patil R L & Deshpande D K, *Indian J Phys*, 63B (1989) 491.
19 Sahoo S & Sit S K, *Mater Sci Eng B*, 163 (2009) 31.
20 Hill N, Price A H & Davies M, *Dielectric properties & molecular behaviour*, (Von-Nostrand, NewYork), 1969.
21 Dutta K, Sit S K & Acharyya S, *Pramana J Phys*, 57 (2001) 775.
22 Gopalakrishna K V, *Trans Faraday Soc*, 33 (1957) 767.