Relaxation phenomena of polar non-polar liquid mixtures under low and high frequency electric field

K DUTTA, S K SIT and S ACHARYYA

Department of Physics, Raiganj College (University College), P.O. Raiganj, Dist. Uttar Dinajpur 733 134, India
Email: koushikduttajsm@rediffmail.com

Abstract. Simultaneous calculation of the dipole moment μ_j and the relaxation time τ_j of a certain number of non-spherical rigid aliphatic polar liquid molecules (j) in non-polar solvents (i) under 9.8 GHz electric field is possible from real ε'_{ij} and imaginary ε''_{ij} parts of the complex relative permittivity ε^*_{ij}. The low frequency and infinite frequency permittivities ε_{0ij} and $\varepsilon_{\infty ij}$ measured by Purohit *et al* [1,2] and Srivastava and Srivastava [3] at 25, 35 and 30°C respectively are used to obtain static μ_s. The ratio of the individual slopes of imaginary σ''_{ij} and real σ'_{ij} parts of high frequency (hf) complex conductivity σ^*_{ij} with weight fractions w_j at $w_j \to 0$ and the slopes of σ''_{ij}–σ'_{ij} curves for different w_js [4] are employed to obtain τ_js. The former method is better in comparison to the existing one as it eliminates polar–polar interaction. The hf μ_js in Coulomb metre (C m) when compared with static and reported μ_ss indicate that μ_ss favour the monomer formations which combine to form dimers in the hf electric field. The comparison among μs shows that a part of the molecule is rotating under X-band electric field [5]. The theoretical μ_{theo}s from available bond angles and bond moments of the substituent polar groups attached to the parent molecules differ from the measured μ_js and μs to establish the possible existence of mesomeric, inductive and electromeric effects in polar liquid molecules.

Keywords. Relaxation time; hf conductivity; dipole moment.

PACS Nos 77.22.Gm; 72.80.Le

1. Introduction

The dielectric relaxation phenomena of dipolar liquid molecules in non-polar solvents under high-frequency electric field have gained much importance to study the structure as well as different molecular interactions like solute–solvent and solute–solute associations [6,7]. Now a days, it is being thought to be an essential tool to investigate the inductive, mesomeric and electromeric moments of the substituent polar groups present in the polar molecule through the time and frequency domain AC spectroscopy [8] or dielectric orientational susceptibility [9] or conductivity measurement technique [10]. The hf conductivity σ_{ij} is concerned with bound molecular charges while the hf susceptibility χ_{ij} contains only

the orientation polarisation of the dipolar molecule. The dipole moment μ_j and the relaxation time τ_j are measured from the conductivity measurements.

Purohit *et al* [1,2] and Srivastava and Srivastava [3] had measured the real ε'_{ij} and imaginary ε''_{ij} parts of the complex relative permittivities ε^*_{ij}, and static or low frequency and infinite frequency relative permittivities ε_{0ij} and $\varepsilon_{\infty ij}$ of some non-spherical rigid aliphatic polar liquid molecules (j) such as chloral (CCl$_3$CHO), ethyl trichloroacetate (CCl$_3$COOCH$_2$CH$_3$), trifluoroethanol (CF$_3$CH$_2$OH), trifluoroacetic acid (CF$_3$COOH) and octanoyl chloride (CH$_3$(CH$_2$)$_6$COCl) in non-polar solvents (i) under 9.8 GHz electric field at 30, 25 and 35°C respectively. They [1–3] used a slotted section of VSWR for ε'_{ij} and ε''_{ij} measurements at 9.8 GHz. The cell containing the experimental liquid in a given solvent was kept vertical and connected to main line by E-plane bend. A short-circuiting reflecting plunger is used to vary the length of the liquid column. The calculation of complex dielectric constant ε^*_{ij} was done by Smyth's method [11]. ε_{0ij} was measured by a Toshniwal Dipole meter and $\varepsilon_{\infty ij}$ from refractive index n^2_{Dij} measurement. The accuracy of measurements for ε'_{ij}, ε''_{ij} and ε_{0ij} are 1%, 5% and 0.5% respectively. The inductive, mesomeric and electromeric moments of the substituent polar groups attached to the parent molecules play a vital role in the formation of solute–solute (dimer) and solute–solvent (monomer) molecular associations. Chloral is widely used in medicine as a drug to induce sleep and relieve pain and in the manufacture of insecticides like DDT. Ethyl trichloroacetate, on the other hand, is used as artificial fragrance of fruits and flowers. Trifluoroethanol and trifluoroacetic acid in C$_6$H$_6$ have a tendency to form either monomer or dimer formations through hydrogen bonding except octanoyl chloride. The liquids were of puram grade of M/s BDH, England but octanoyl chloride was of puram grade of M/s Fluka, AG.

We, therefore, thought to study all these polar molecules from hf complex conductivity σ^*_{ij} in SI units to predict their τ and μ. The molecules have often a tendency to exhibit double relaxation times τ_1 and τ_2 due to rotation of their flexible polar groups attached to parent molecules and the whole molecules themselves [5] under a single-frequency electric field of GHz range at a given temperature. The polar molecules showed double relaxation phenomena in a particular solvent when the measured data are adjusted to chi-squares minimisation [11]. The most effective dispersive region of almost all the polar molecules lies in the neighbourhood of 10 GHz electric field [12]. Moreover, the comparison of hf μ_j obtained from hf conductivity σ_{ij} measurement with the static μ_s from the measured static parameter X_{ij} seems to be interesting to see how far μ_j involved with τ_j agree with μ_s and μ_{theo}. A systematic comparison of τ_js with the reported τs and the estimated τ_1 and τ_2 of the molecules by double relaxation method [11] enables one to conclude that either a part or a whole molecule is rotating under GHz electric field. However, μ_{theo}s were obtained from available bond angles and bond moments of the substituent polar groups attached to the parent molecule [5,11]. Earlier investigations on different polar molecules [10] showed that a part of the molecule is rotating under hf electric field of nearly 3 cm wavelength. The purpose of the present paper is thus to observe how the apparently rigid aliphatic polar molecules behave under static or low frequency and 9.8 GHz electric field.

The static or low frequency μ_ss were measured from the linear coefficient of the variation of X_{ij}s with w_js of a polar solute. The variable X_{ij} is, however, related with ε_{0ij} and $\varepsilon_{\infty ij}$ of the polar liquids. The μ_ss are estimated from the measured data of table 1 and placed in table 3 in order to compare with the hf μ_js involved with τ_js measured from eqs (9) and (10) as derived later on. The concentration variations of X_{ij}s are displayed in figure 1 by Newton–Raphson's method with the experimental points placed upon them.

Table 1. Static relative permittivity ε_{0ij}, infinite frequency relative permittivity $\varepsilon_{\infty ij}$, real part ε'_{ij} and imaginary part ε''_{ij} of complex relative permittivity ε^*_{ij} of chloral, ethyl trichloroacetate at 30°C, trifluoroethanol, trifluoroacetic acid at 25°C and octanoyl chloride at 35°C in different non-polar solvents under 9.8 GHz electric field.

System with sl. no. and mol. wt.	Weight fraction w_j	ε_{0ij}	$\varepsilon_{\infty ij}$	Weight fraction w_j	ε'_{ij}	ε''_{ij}
(I) Chloral	0.0255	2.314	2.2350	0.0152	2.26	0.015
in benzene	0.0977	2.441	2.2293	0.0899	2.42	0.035
$M_j = 0.1475$ kg	0.1813	2.622	2.2216	0.1711	2.56	0.057
	0.2511	2.785	2.2147	0.1903	2.60	0.066
	0.3493	3.011	2.2067	0.2510	2.75	0.087
	0.4019	3.189	2.2020	0.3476	2.97	0.116
(II) Chloral	0.0224	1.925	1.9154	0.0224	1.93	0.017
in n-heptane	0.0807	2.048	1.9209	0.0807	2.01	0.029
$M_j = 0.1475$ kg	0.1416	2.140	1.9254	0.1416	2.09	0.036
	0.2003	2.240	1.9301	0.2003	2.19	0.050
	0.2683	2.390	1.9372	0.2683	2.32	0.055
	0.3324	2.516	1.9438	0.3324	2.47	0.080
(III) Ethyl trichloro-	0.0207	2.368	2.2365	0.0207	2.32	0.023
acetate in benzene	0.0498	2.475	2.2344	0.0498	2.38	0.046
$M_j = 0.1915$ kg	0.0802	2.596	2.2317	0.0802	2.44	0.079
	0.1193	2.753	2.2266	0.1193	2.52	0.115
	0.1764	2.996	2.2201	0.1764	2.64	0.194
	0.2444	3.295	2.2126	0.2444	2.82	0.226
(IV) Ethyl trichloro-	0.0266	1.980	1.8837	0.0210	1.92	0.021
acetate in n-hexane	0.0639	2.072	1.8878	0.0595	1.99	0.041
$M_j = 0.1915$ kg	0.0845	2.119	1.8892	0.0649	2.00	0.066
	0.1193	2.223	1.8933	0.1137	2.09	0.093
	0.1683	2.377	1.8988	0.1722	2.24	0.126
				0.2360	2.34	0.190
(V) Trifluoroethanol	0.0030	2.284	2.1994	0.0113	2.332	0.007
in benzene	0.0060	2.301	2.2132	0.0215	2.396	0.041
$M_j = 0.1000$ kg	0.0226	2.405	2.3061	0.0313	2.458	0.073
	0.0311	2.456	2.3537	0.0416	2.515	0.118
	0.0411	2.525	2.4109	0.0523	2.638	0.189
(VI) Trifluoroacetic	0.0066	2.327	2.2370	0.0130	2.315	0.035
acid in benzene	0.0130	2.368	2.2731	0.0271	2.350	0.056
$M_j = 0.1140$ kg	0.0271	2.411	2.3082	0.0391	2.377	0.069
	0.0391	2.449	2.3452	0.0515	2.398	0.084
	0.0515	2.484	2.3671	0.0630	2.420	0.100
	0.0630	2.519	2.3940			
(VII) Octanoyl chloride	0.0183	2.369	2.2218	0.0181	2.306	0.033
in benzene	0.0349	2.444	2.2176	0.0358	2.350	0.076
$M_j = 0.1625$ kg	0.0497	2.526	2.2142	0.0516	2.393	0.111
	0.0648	2.582	2.2110	0.0702	2.439	0.147
	0.0808	2.661	2.2080	0.0802	2.486	0.184

The percentage of errors in getting X_{ij}–w_j curves were computed from correlation coefficients r for all the systems. The errors introduced in a_1s are very low because rs are very close to unity establishing the fact that X_{ij}s are correlated almost exactly with w_js of table 1. The μ_ss of table 3 are found to be almost equal to hf μ_js except systems V ($-\circ-$) and VI ($-\triangle-$). The μ_js are estimated from the linear coefficient βs of the curves of
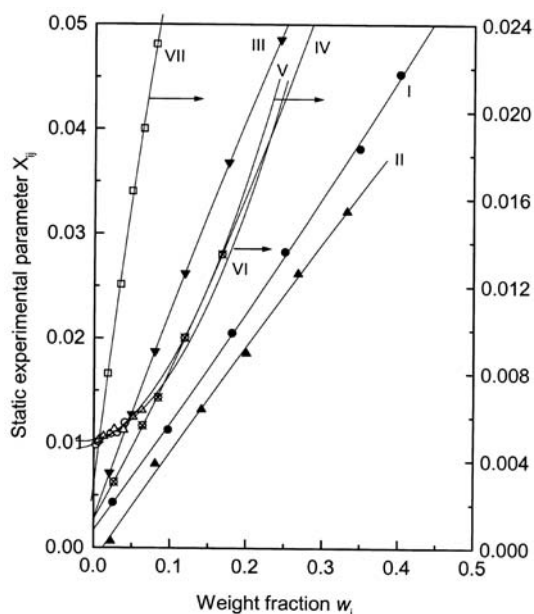
Figure 1. Variation of the measured static experimental parameter X_{ij} with weight fraction w_j of the solutes for I – chloral in benzene ($-\bullet-$); II – chloral in *n*-heptane ($-\blacktriangle-$); III – ethyl trichloroacetate in benzene ($-\blacktriangledown-$); IV – ethyl trichloroacetate in *n*-hexane ($-\otimes-$); V – trifluoroethanol in benzene ($-\circ-$); VI – trifluoroacetic acid in benzene ($-\triangle-$) and VII – octanoyl chloride in benzene ($-\square-$).

hf conductivity σ_{ij}s against w_js of polar liquids at infinite dilution and the estimated τ_js. However, τ_js are obtained from the linear slope of $\sigma_{ij}''-\sigma_{ij}'$ curves of figure 2 and the ratio of individual slopes of σ_{ij}'' and σ_{ij}' with w_j curves at $w_j \to 0$ as shown in figures 3 and 4. The τ_js are placed in table 2 and were used to calculate μ_js of table 3. μ_js from both the methods are found to agree excellently for all the systems except ethyl trichloroacetate and octanoyl chloride in benzene.

The μ_js thus obtained are compared with the theoretical dipole moment μ_{theo} derived from the available bond angles and bond moments of the substituent polar groups of the molecules [5,11] and presented in table 3. In figure 5 conformations of five dipolar molecules are displayed by taking into account the reduced bond length by a factor μ_s/μ_{theo} due to inductive, mesomeric and electromeric effects of the substituent polar groups attached to the parent molecules.

2. Theoretical formulation of X_{ij} to estimate static μ_s

The low frequency or static dipole moment μ_s of a polar solute (j) in a non-polar solvent (i) at any temperature T K is given by [13]:

$$\frac{\varepsilon_{0ij}-1}{\varepsilon_{0ij}+2} - \frac{\varepsilon_{\infty ij}-1}{\varepsilon_{\infty ij}+2} = \frac{\varepsilon_{0i}-1}{\varepsilon_{0i}+2} - \frac{\varepsilon_{\infty i}-1}{\varepsilon_{\infty i}+2} + \frac{N\mu_s^2 c_j}{9\varepsilon_0 k_{\text{B}}T}, \tag{1}$$

Table 2. Slope of σ_{ij}''–σ_{ij}' curves, correlation coefficient r, percentage of error in regression technique, relaxation time τ_j using eq. (9), ratio of slopes of σ_{ij}''–w_j and σ_{ij}'–w_j curves at $w_j \to 0$, percentage of error in σ_{ij}''–w_j and σ_{ij}'–w_j curves, corresponding τ_j using eq. (10) and reported τ for chloral, ethyl trichloroacetate at 30°C, trifluoroethanol, trifluoroacetic acid at 25°C and octanoyl chloride at 35°C in different non-polar solvents under 9.8 GHz electric field.

System with sl.no.	Slope of σ_{ij}''–σ_{ij}' curve	Corrl. coeff. r	% of error	$\tau_j \times 10^{12}$ s from eq. (9)	Ratio of slopes of σ_{ij}''–w_j and σ_{ij}'–w_j curves at $w_j \to 0$	% of error in regression technique σ_{ij}''–w_j curve	σ_{ij}'–w_j curve	$\tau_j \times 10^{12}$ s from eq. (10)	Rept. $\tau \times 10^{12}$ s
(I) Chloral in benzene	6.8735	0.9987	0.07	2.36	6.5416	0.08	0.11	2.48	1.78*
(II) Chloral in n-heptane	8.9472	0.9881	0.65	1.82	8.8940	0.02	1.53	1.83	0.46*
(III) Ethyl trichloroacetate in benzene	2.2289	0.9820	0.98	7.29	1.3768	0.03	0.79	11.80	6.5**
(IV) Ethyl trichloroacetate in n-hexane	2.5845	0.9826	0.95	6.28	3.1959	0.27	0.95	5.08	5.7**
(V) Trifluoroethanol in benzene	1.6508	0.9982	0.11	9.84	3.2082	0.50	0.16	5.06	13.85†
(VI) Trifluoroacetic acid in benzene	1.6337	0.9973	0.16	9.94	2.1001	0.05	0.14	7.73	9.23†
(VII) Octanoyl chloride in benzene	1.2019	0.9989	0.07	3.51	0.8443	0.31	0.38	19.24	18.60‡

*Cole–Cole plot; **Gopalakrishna's method; †Calculated by Gopalakrishna's method; ‡Higasi's method.

where ε_0 is the permittivity of the free space $= 8.854 \times 10^{-12}$ F m^{-1} and all the other symbols carry usual meanings [10].

The molar concentration c_j can be expressed in terms of weight fraction w_j of the polar solute by

$$c_j = \frac{\rho_{ij} w_j}{M_j}.$$

The weight W_i and volume V_i of a non-polar solvent is mixed with a polar solute of weight W_j and volume V_j to give the solution density ρ_{ij}, where

$$\rho_{ij} = \frac{W_i + W_j}{V_i + V_j} = \frac{W_i + W_j}{(W_i/\rho_i) + (W_j/\rho_j)} = \frac{\rho_i \rho_j}{\rho_j w_i + \rho_i w_j} = \rho_i (1 - \gamma w_j)^{-1}. \quad (2)$$

The weight fractions w_i and w_j of the solvent and the solute are

$$w_i = \frac{W_i}{W_i + W_j} \quad \text{and} \quad w_j = \frac{W_j}{W_i + W_j}$$

Table 3. Values of coefficients of $X_{ij} = a_0 + a_1 w_j + a_2 w_j^2$ and $\sigma_{ij} = \alpha + \beta w_j + \gamma w_j^2$ curves, static and hf dipole moment μ_s and μ_j, theoretical dipole moment μ_{theo}, reported dipole moment μ and estimated μ_1 and μ_2 of the flexible part and the whole molecule by double relaxation method for chloral, ethyl trichloroacetate at 30°C, trifluoroethanol, trifluoroacetic acid at 25°C and octanoyl chloride at 35°C in different non-polar solvents under 9.8 GHz electric field.

System with sl. no. and mol. wt.	Coeff. of X_{ij}–w_j curve a_0, a_1, a_2	Coeff. of σ_{ij}–w_j curve α, β, γ	$\mu_s \times 10^{30}$ (C m)	$\mu_j^a \times 10^{30}$ (C m)	$\mu_j^b \times 10^{30}$ (C m)	$\mu_{theo} 10^{30}$ (C m)	Rept. $\mu \times 10^{30}$ (C m)	$\frac{\mu_s}{\mu_{theo}}$	Corrc. $\mu_{theo} 10^{30}$ (C m)	$\mu_1 \times 10^{30}$ (C m)	$\mu_2 \times 10^{30}$ (C m)
(I) Chloral in benzene $M_j = 0.1475$ kg	0.0017 0.0992 0.0207	1.2206 0.9559 0.5611	5.28	5.27	5.27	10.02	4.87	0.53	5.31	5.27	19.32
(II) Chloral in *n*-heptane $M_j = 0.1475$ kg	−0.0013 0.1053 0.0144	1.0419 0.5311 1.1538	6.17	4.85	4.85	10.02	6.00	0.62	6.21	4.83	9.07
(III) Ethyl trichloroacetate in benzene $M_j = 0.1915$ kg	0.0028 0.2049 −0.0719	1.2468 0.9425 1.0703	8.65	6.46	7.29	10.50	6.50	0.82	8.61	–	11.07
(IV) Ethyl trichloroacetate in *n*-hexane $M_j = 0.1915$ kg	0.0027 0.1299 0.1231	1.0198 1.1260 −0.0323	7.96	8.71	8.52	10.50	8.67	0.76	7.97	8.13	14.53
(V) Trifluoroethanol in benzene $M_j = 0.1000$ kg	0.0047 0.0144 0.2276	1.2535 1.3716 41.238	1.64	5.93	5.31	2.78	9.98	0.59	1.64	–	–
(VI) Trifluoroacetic acid in benzene $M_j = 0.1140$ kg	0.0049 0.0077 0.2279	1.2430 1.5621 −5.3871	1.28	6.77	6.40	8.47	5.58	0.15	1.27	–	8.77
(VII) Octanoyl chloride in benzene $M_j = 0.1625$ kg	0.0028 0.2870 −0.4601	1.2396 0.8981 6.9372	9.54	6.99	8.33	11.62	9.14	0.82	9.55	–	7.02

μ_j^a = hf dipole moment using τ_j of eq. (9).
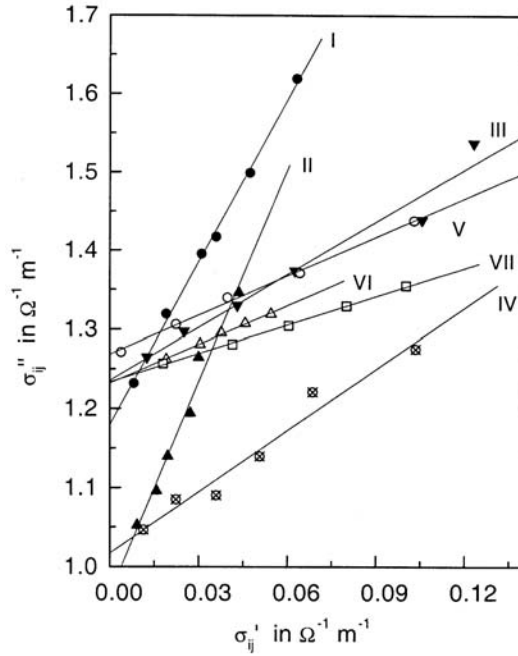μ_j^b = hf dipole moment using τ_j of eq. (10).

Figure 2. Linear plot of σ_{ij}'' against σ_{ij}' for different weight fraction w_j for I – chloral in benzene ($-\bullet-$); II – chloral in *n*-heptane ($-\blacktriangle-$); III – ethyl trichloroacetate in benzene ($-\blacktriangledown-$); IV – ethyl trichloroacetate in *n*-hexane ($-\otimes-$); V – trifluoroethanol in benzene ($-\circ-$); VI – trifluoroacetic acid in benzene ($-\triangle-$) and VII – octanoyl chloride in benzene ($-\square-$).

such that $w_i + w_j = 1$ and $\gamma = (1 - \rho_i/\rho_j)$ where ρ_i and ρ_j are the densities of pure solvent and pure solute respectively in SI units.

Now eq. (1) may be written as

$$\frac{\varepsilon_{0ij} - \varepsilon_{\infty ij}}{(\varepsilon_{0ij} + 2)(\varepsilon_{\infty ij} + 2)} = \frac{\varepsilon_{0i} - \varepsilon_{\infty i}}{(\varepsilon_{0i} + 2)(\varepsilon_{\infty i} + 2)} + \frac{N\rho_i\mu_s^2}{27\varepsilon_0 M_j k_B T} w_j (1 - \gamma w_j)^{-1}$$

or

$$X_{ij} = X_i + \frac{N\rho_i\mu_s^2}{27\varepsilon_0 M_j k_B T} w_j + \frac{N\rho_i\mu_s^2}{27\varepsilon_0 M_j k_B T} \gamma w_j^2 + \cdots. \tag{3}$$

Equation (3) can be expressed by the following polynomial equation of w_j:

$$X_{ij} = a_0 + a_1 w_j + a_2 w_j^2 + \cdots. \tag{4}$$

Now equating the coefficients of first power of w_j of eqs (3) and (4), one gets the static μ_s where

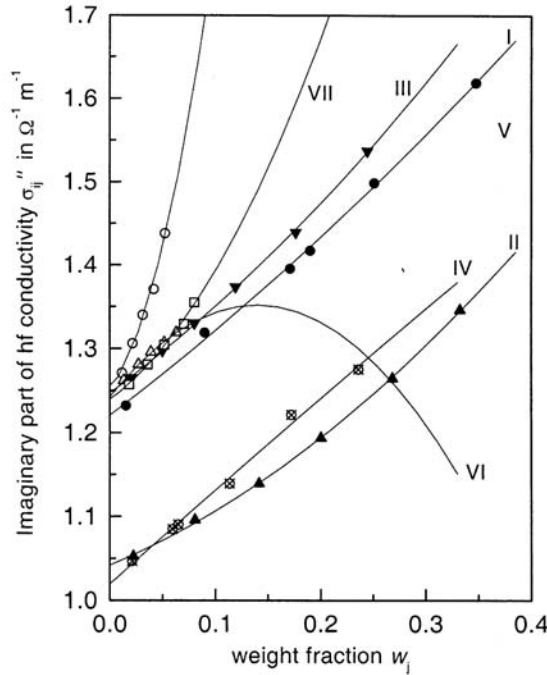$$\mu_s = \left(\frac{27\varepsilon_0 M_j k_B T a_1}{N\rho_i} \right)^{1/2}, \tag{5}$$

Figure 3. Variation of the imaginary part of hf complex conductivity σ_{ij}'' with weight fraction w_j for I – chloral in benzene $(-\bullet-)$; II – chloral in n-heptane $(-\blacktriangle-)$; III – ethyl trichloroacetate in benzene $(-\blacktriangledown-)$; IV – ethyltrichloroacetate in n-hexane $(-\otimes-)$; V – trifluoroethanol in benzene $(-\circ-)$; VI – trifluoroacetic acid in benzene $(-\triangle-)$ and VII – octanoyl chloride in benzene $(-\square-)$.

where a_1 is the slope of X_{ij}–w_j curve of figure 1. But μ_s from the coefficients of higher powers of w_j of eqs (3) and (4) are not reliable as they are involved with various effects of solvent, relative density, solute–solute association, internal field, macroscopic viscosity etc. μ_s from eq. (5) along with a_1 are placed in table 3 to compare with hf μ_js as well as μ_1 and μ_2 from double relaxation method and μ_{theo} from the available bond angles and bond moments.

3. Formulation of hf conductivity σ_{ij} to estimate τ_j and hf μ_j

The hf complex conductivity σ_{ij}^* of a polar–non-polar liquid mixture for a given weight fraction w_j is [13] related to $\varepsilon_{ij}^* = \varepsilon_{ij}' - j\varepsilon_{ij}''$ by

$$\sigma_{ij}^* = \sigma_{ij}' + j\sigma_{ij}'' = \omega\varepsilon_0\varepsilon_{ij}'' + j\omega\varepsilon_0\varepsilon_{ij}', \tag{6}$$

where $\omega\varepsilon_0\varepsilon_{ij}'' = \sigma_{ij}'$ and $\omega\varepsilon_0\varepsilon_{ij}' = \sigma_{ij}''$ are the real and imaginary parts of complex conductivity and j is a complex number $= \sqrt{-1}$.

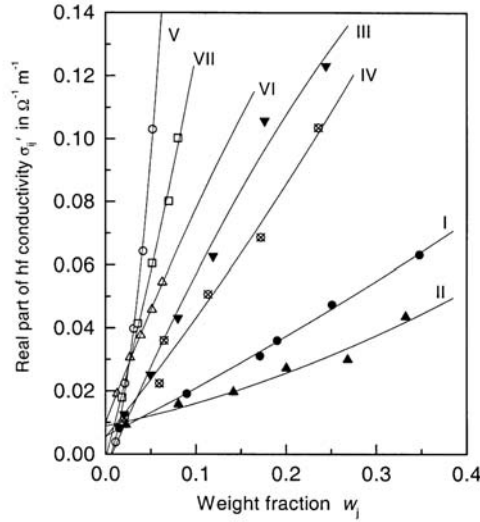The total hf conductivity σ_{ij} is given by

Figure 4. Variation of the real part of hf complex conductivity σ'_{ij} with weight fraction w_j for I – chloral in benzene $(-\bullet-)$; II – chloral in n-heptane $(-\blacktriangle-)$; III – ethyl trichloroacetate in benzene $(-\blacktriangledown-)$; IV – ethyl trichloroacetate in n-hexane $(-\otimes-)$; V – trifluoroethanol in benzene $(-\circ-)$; VI – trifluoroacetic acid in benzene $(-\triangle-)$ and VII – octanoyl chloride in benzene $(-\square-)$.

$$\sigma_{ij} = \omega\varepsilon_0(\varepsilon''^2_{ij} + \varepsilon'^2_{ij})^{1/2}. \tag{7}$$

Again, σ''_{ij} is related to σ'_{ij} by

$$\sigma''_{ij} = \sigma_{\infty ij} + \frac{1}{\omega\tau_j}\sigma'_{ij} \tag{8}$$

$\sigma_{\infty ij}$ is the constant conductivity at infinite dilution of $w_j = 0$ and τ_j is the relaxation time of a dipolar liquid.

Equation (8) on differentiation with respect to σ'_{ij} yields

$$\frac{\mathrm{d}\sigma''_{ij}}{\mathrm{d}\sigma'_{ij}} = \frac{1}{\omega\tau_j}, \tag{9}$$

which provides a convenient method to obtain τ_j of a polar molecule [4]. It is, however, better to use the ratio of the individual slopes of variation of σ''_{ij} and σ'_{ij} with w_j in order to avoid the polar–polar interaction at $w_j \to 0$ in a given solvent to get τ_j from

$$\frac{(\mathrm{d}\sigma''_{ij}/\mathrm{d}w_j)_{w_j \to 0}}{(\mathrm{d}\sigma'_{ij}/\mathrm{d}w_j)_{w_j \to 0}} = \frac{1}{\omega\tau_j}, \tag{10}$$

where $\omega = 2\pi f$ and f is the frequency of the applied hf electric field.

In hf region of GHz range, it is generally observed that $\sigma''_{ij} \approx \sigma_{ij}$ as evident from figures 3 and 6 and hence eq. (8) becomes
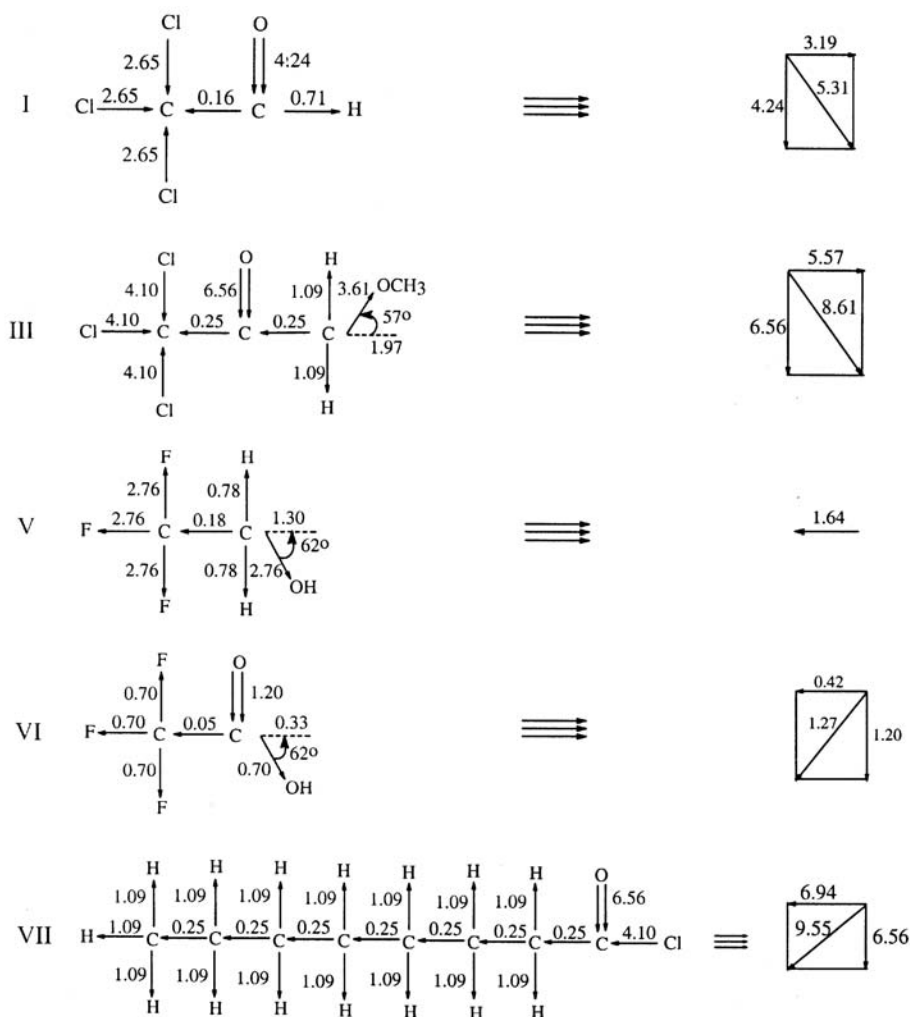
Figure 5. Conformational structures of the molecules by taking into account the reduced bond moments in multiples of 10^{-30} C m. I – chloral, III – ethyl trichloroacetate, V – trifluoroethanol, VI – trifluoroacetic acid, VII – octanoyl chloride.

$$\sigma_{ij} = \sigma_{\infty ij} + \frac{1}{\omega \tau_j} \sigma'_{ij}$$

or

$$\beta = \frac{1}{\omega \tau_j} \left(\frac{d\sigma'_{ij}}{dw_j} \right)_{w_j \to 0} . \tag{11}$$

Here $\beta = (d\sigma_{ij}/dw_j)_{w_j \to 0}$ is the slope of σ_{ij}–w_j curves of figure 6 at $w_j \to 0$.

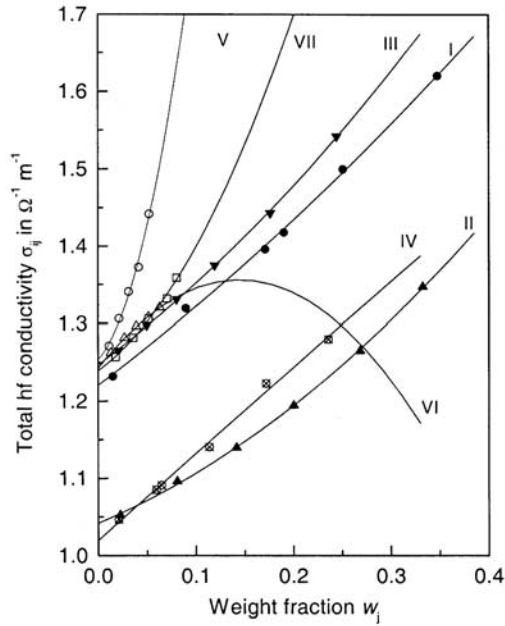The real part σ'_{ij} of a polar–non-polar liquid mixture of w_j at T K is [13] given by

Figure 6. Variation of the total hf conductivity σ_{ij} with weight fraction w_j for I – chloral in benzene $(-\bullet-)$; II – chloral in *n*-heptane $(-\blacktriangle-)$; III – ethyl trichloroacetate in benzene $(-\blacktriangledown-)$; IV – ethyl trichloroacetate in *n*-hexane $(-\otimes-)$; V – trifluoroethanol in benzene $(-\circ-)$; VI – trifluoroacetic acid in benzene $(-\triangle-)$ and VII – octanoyl chloride in benzene $(-\square-)$.

$$\sigma'_{ij} = \frac{N\rho_{ij}\mu_j^2}{27M_j k_{\mathrm{B}}T}\left(\frac{\omega^2\tau}{1+\omega^2\tau^2}\right)(\varepsilon_{0ij}+2)(\varepsilon_{\infty ij}+2)w_j,$$

$$\left(\frac{\mathrm{d}\sigma'_{ij}}{\mathrm{d}w_j}\right)_{w_j\to 0} = \frac{N\rho_i\mu_j^2}{3M_j k_{\mathrm{B}}T}\left(\frac{\varepsilon_i+2}{3}\right)^2\left(\frac{\omega^2\tau}{1+\omega^2\tau^2}\right). \tag{12}$$

Now, comparing eqs (11) and (12) one gets the hf μ_j from:

$$\mu_j = \left[\frac{27M_j k_{\mathrm{B}}T\beta}{N\rho_i(\varepsilon_i+2)^2\omega b}\right]^{1/2}, \tag{13}$$

where

$$b = 1/(1+\omega^2\tau_j^2) \tag{14}$$

is a dimensionless parameter involved with τ_js obtained from eqs (9) and (10). The other symbols used in eq. (13) are: N = Avogadro's number, ρ_i = density of the solvent, ε_i = relative permittivity of the solvent, M_j = molecular weight of the solute and k_{B} = Boltzmann constant. All are expressed in SI units. All the computed hf μ_js in terms of βs and bs are presented in table 3. They are compared with μ_1 and μ_2 of the flexible part and the whole molecule by the double relaxation method [5] as entered in table 3. The computed τ_js are, however, placed in table 2 to compare with those by other methods and freshly calculated Gopalakrishna's method [14] for the last three systems.

4. Results and discussion

The dipole moments μ_ss of the polar molecule under static or low frequency electric field are estimated from the slope a_1 of the X_{ij}–w_j curves of figure 1. X_{ij} is related to static and infinite frequency relative permittivities ε_{0ij} and $\varepsilon_{\infty ij}$ of eq. (1) at different w_js of polar solutes presented in table 1. All the curves of X_{ij} against w_j were, however, drawn by best-fitted regression analysis made on available experimental data extracted from table 1 in order to plot figure 1. Each system which consists of a polar solute in different non-polar solvents usually shows almost the same slopes as seen in figure 1. This signifies the almost same polarity of the molecules under investigation [15]. Polarisations are found to be slightly larger for ethyl trichloroacetate in benzene, *n*-hexane and octanoyl chloride in benzene in comparison to other molecules. The increase in polarisation is due to the increase in dipole moment, which means that dimerisation takes place in such a manner that in the dimeric molecule, the dipoles are inclined at an angle less than 90° so that the dipole moment is more than that of the monomer. The correlation coefficients rs in getting the coefficients of X_{ij}–w_j curves of figure 1 were very close to unity, i.e., 0.9993, 0.9978, 0.9999, 0.9998, 0.9693, 0.9574 and 0.9980 for seven systems of tables and figures respectively and hence percentage of errors in terms of rs were very small.

The relaxation time τ_j of the molecule is estimated by using the linear slope of σ_{ij}''–σ_{ij}' curve of Murthy *et al* [4] and the ratio of individual slopes of σ_{ij}''–w_j and σ_{ij}'–w_j at $w_j \to 0$. It is evident from table 2 that τ_js agree well in both the methods except ethyl trichloroacetate (III), trifluoroethanol (V) and octanoyl chloride (VII) all in benzene. This behaviour is explained on the basis of solute–solute (dimer) molecular association in the higher concentration region that turns into solute–solvent (monomer) association due to rupture of the dimer. In such case it is better to use the ratio of individual slopes of σ_{ij}'' and σ_{ij}' in Ω^{-1} m^{-1} against w_j at infinite dilution as seen in figures 3 and 4 where polar–polar interaction is almost avoided completely to compute τ_j. The curves of σ_{ij}''–σ_{ij}' in figure 2 are not perfectly linear with the experimental data according to eq. (9) for the systems III ($-\blacktriangledown-$), IV ($-\otimes-$) and V ($-\circ-$). In such cases polar–polar interaction in the higher concentration region or solute–solvent association in the lower concentration region may be the cause for such non-linear behaviour. The almost parallel nature of the curves I and II; III and IV in figure 3 indicates the same polarity of the molecules of chloral and ethyl trichloroacetate in different solvents. The higher magnitude of σ_{ij}'' in Ω^{-1} m^{-1} in benzene for each solute of figure 3 may reveal the solute–solute (dimer) interaction of the polar molecules. Curve VI (trifluoroacetic acid in benzene) of figure 3 is found to increase gradually to show maximum at $w_j = 0.1401$. This type of behaviour may be due to transition of phase [16] occurred after a certain concentration of the solute. Like systems II and IV in *n*-heptane and *n*-hexane, the other curves of figure 3 for solvent benzene meet at a point on the ordinate axis $1.2206 \le \sigma_{ij}'' \le 1.2526$ at $w_j = 0$ exhibiting the probable solvation effect of polar solute in the same non-polar solvent. It is evident from figure 3 that all the curves are almost same as total hf conductivity σ_{ij} in Ω^{-1} m^{-1} plotted against w_j in figure 6. This indicate the validity of the approximation $\sigma_{ij}'' \approx \sigma_{ij}$ in eq. (11). All the curves of σ_{ij}' in figure 4 increase gradually with w_j and become closer to yield $\sigma_{ij}' \approx 0$ at $w_j = 0$. This is explained on the basis of the fact that absorption of hf electric energy increases with concentration. The magnitude of absorption is maximum for trifluoroethanol in benzene (V) and minimum for chloral in *n*-heptane (II) although concentration of polar solute of the latter system is higher than the former.

The high-frequency dipole moments μ_js of the polar liquids are estimated in terms of slope β of σ_{ij}–w_j curve of figure 6 and dimensionless parameter bs in order to show them in table 3. They are compared with μ_s, μ_1, μ_2 and reported μs respectively. All the curves of total hf conductivity σ_{ij} in $\Omega^{-1}\,m^{-1}$ against w_j of figure 6 are parabolic as evident from the coefficients α, β and γ of table 3. This indicates that conductivity of the mixture with the absorption of hf electric energy increases with w_js of the solute except for system VI. These curves when extrapolated beyond the experimental data exhibit maximum σ_{ij} at $w_j = 0.1401$ and then decreases gradually like σ_{ij}''–w_j curves of figure 3 probably due to the transition of phase [16] occurred at that concentration. This type of behaviour invariably demands experimental measurement beyond the concentration of polar liquid already taken up.

The hf μ_js are found to agree well with the static μ_s for chloral, ethyl trichloroacetate and octanoyl chloride in benzene, n-heptane and n-hexane (systems I, II, III, IV, and VII). It reveals the fact that dimerisation takes place both in static and hf electric fields probably the available data of relative permittivities are in higher concentration regions. The μ_js of trifluoroethanol and trifluoroacetic acid are higher than μ_s indicating the strong solute–solvent association due to hydrogen bonding. The μ_js when compared with μ_1 and μ_2 by double relaxation method indicate that chloral in benzene, n-heptane and ethyl trichloroacetate in n-hexane show double relaxation phenomena in X-band electric field. This is due to slow and rapid rotations of the whole molecules and the flexible parts attached to the parent molecules respectively. The other systems show the mono relaxation behaviour due to their solvation effect with benzene.

Assuming planar structure for molecules, the theoretical dipole moments μ_{theo}s for the polar molecules were estimated from the available bond angles and bond moments of C$\leftarrow$Cl, C$\leftarrow$C, C$\rightarrow$F, C$\Leftarrow$O, C$\rightarrow$OH and C$\rightarrow$OCH$_3$ of 5.00, 0.30, 4.67, 8.00, 4.67 and 4.40 times of 10^{-30} Coulomb metre (C m) making angles $62°$ and $57°$ with the bond axis by C$\rightarrow$OH and C$\rightarrow$OCH$_3$ groups only and were shown elsewhere [5,11]. μ_{theo}s thus obtained are placed in table 3. A little disagreement among the estimated μ_s and μ_j with μ_{theo} occurs due to inductive, mesomeric and electromeric effects of the substituent polar groups attached to the parent molecules under static or hf electric field. The so-called mesomeric moments have significant values. This is caused by the permanent polarisation of different substituent groups acting as pusher or puller of electron towards or away from C-atoms of the compounds. The larger values of μ_{theo}s from the available bond angles and bond moments in comparison to μ_s indicate that the bond length of the substituent polar groups of the dipolar molecules are reduced by a factor μ_s/μ_{theo}. The reduction in bond moments evidently occurs in all polar liquids by a factor μ_s/μ_{theo} lying in the range 0.5 to 0.8 except trifluoroacetic acid (0.15) to conform to the exact μ_s. The structural conformations of five compounds with reduced bond lengths, in agreement with μ_j or μ_s are sketched in figure 5.

5. Conclusion

A convenient and useful method is suggested to calculate the relaxation time τ_j and hf dipole moment μ_j under the most effective dispersive region of 10 GHz electric field along with the static μ_s in SI units of some non-spherical rigid aliphatic polar molecules in non-polar solvents. The existing method by using the slope of hf σ_{ij}''–σ_{ij}' curves of Murthy *et al* [4] to obtain τ_j when compared with those from the ratio of the slopes of the individual

variations of σ_{ij}''–w_j and σ_{ij}'–w_j at $w_j \rightarrow 0$ reveals the fact that both methods yield almost the same τ_js both in higher and lower concentrations of dipolar molecules. The latter method to get τ_j is a significant improvement over the former one as it eliminates the polar-polar interaction almost completely in a given solvent. The slope βs of hf $\sigma_{ij} - w_j$ curves are used to calculate hf μ_js in terms of τ_js by the latter method. The comparison of μ_j and μ_s with μ_1 and μ_2 of the flexible part and the whole molecules by double relaxation method and μ_{theo} from available bond angles and bond moments of the substituent polar groups seems to be interesting to offer a deep insight into the dielectric relaxation. The μ_js and μ_s are almost equal in some cases only to show that μ_s are little affected by frequency of the electric field in higher concentration region while lower μ_ss than μ_js in the lower concentration region support monomer and dimer formation in the static and hf electric field respectively. Moreover, the X_{ij}–w_j curves can be used to test the accuracies of the measurements of all the relative permittivities. The X_{ij}s are involved with the low and infinitely hf ε_{0ij} and $\varepsilon_{\infty ij}$ permittivities of a given polar–non-polar liquid mixture. The computation of τ_j, μ_j and μ_s from σ_{ij} and X_{ij} measurement of a polar unit in a given solvent appears to be more simple, straightforward and topical one to locate the accuracy of τ_j, μ_j and μ_s, which are claimed to be accurate within 10% and 5% respectively. The calculated results of μ_j, τ_j and μ_s appear to be of more archival values to reveal some interest in the area of dielectric relaxation. Both μ_j and μ_s agree with μ_1 only to support that a part of the molecule is rotating under GHz electric field. μ_s/μ_{theo}s are almost constant for all the molecules under study revealing the material property of the systems. The reduction in bond moments of the substituent polar groups by the factor μ_s/μ_{theo} exhibits the presence of mesomeric, inductive and electromeric moments in them under static and hf electric fields.

References

[1] H D Purohit and H S Sharma, *Indian J. Pure Appl. Phys.* **11**, 664 (1973)
[2] H D Purohit, H S Sharma and A D Vyas, *Indian J. Pure Appl. Phys.* **12**, 273 (1974)
[3] S K Srivastava and S L Srivastava, *Indian J. Pure Appl. Phys.* **13**, 179 (1975)
[4] M B R Murthy, R L Patil and D K Deshpande, *Indian J. Phys.* **B63**, 491 (1989)
[5] K Dutta, R C Basak, S K Sit and S Acharyya, *J. Mol. Liq.* **88**, 241 (2000)
[6] A Sharma and D R Sharma, *J. Phys. Soc. Jpn.* **61**, 1049 (1992)
[7] A K Sharma, D R Sharma, K C Sharma and D S Gill, *Z. Phys. Chem. Neue Folge Bd.* **S141**, 15 (1984)
[8] F Alvarez, A Alegria and J Colmenero, *J. Chem. Phys.* **103(2)** 798 (1995)
[9] A K Jonscher, *Physics of dielectric solids*, Invited papers edited by CHL Goodman, 1980
[10] R C Basak, S K Sit, N Nandi and S Acharyya, *Indian J. Phys.* **B70**, 37 (1996)
[11] K Dutta, S K Sit and S Acharyya, *Pramana – J. Phys.* **57**, 775 (2001)
[12] S K Sit and S Acharyya, *Indian J. Pure Appl. Phys.* **34**, 255 (1996)
[13] R C Basak, A Karmakar, S K Sit and S Acharyya, *Indian J. Pure Appl. Phys.* **37**, 224 (1999)
[14] K V Gopalakrishna, *Trans. Faraday Soc.* **53**, 767 (1957)
[15] A K Chatterjee, U Saha, N Nandi, R C Basak and S Acharyya, *Indian J. Phys.* **B66**, 291 (1992)
[16] K Dutta, S K Sit and S Acharyya, *J. Mol. Liq.* **92**, 263 (2001)