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Structural aspects and physico-chemical properties of some aromatic polar nitro compounds in solvent benzene at different temperatures under Giga Hertz electric field

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Abstract : An interesting method based on complex orientational susceptibilities χ_{ij}^* to study the dielectric relaxation mechanism of some standard polar nitro compounds in nonpolar solvent benzene has been prescribed and applied successfully to arrive at their structural and physico-chemical properties. The dielectric orientational susceptibilities χ_{ij}' , the real and χ_{ij}'' , the imaginary part of χ_{ij}^* are involved with the measured relative permittivities ϵ_{ij}' and ϵ_{ij}'' of ϵ_{ij}^* of Pant *et al.* to measure the relaxation time τ_j of all the polar solutes from the ratio of the linear coefficients of individual variations of χ_{ij}'' and χ_{ij}' with weight fraction w_j 's of the respective solute. They are further compared with τ_j 's obtained from the direct slope of the linear variations of χ_{ij}'' and χ_{ij}' and Gopala Krishna's method measured by Pant *et al.* The temperature variation of τ_j 's from the former method helps one get the thermodynamic energy parameters i.e. enthalpy of activation ΔH_τ , entropy of activation ΔS_τ , and free energy of activation ΔF_τ of dielectric relaxation by using the rate process equation of Eyring *et al.*, to throw much light on their structural and physico-chemical properties. The dimensionless parameter δ ($= \Delta H_\tau / \Delta H \eta_\tau$) which is the slope of the linear equation of $\ln \tau_j T = \ln a + \delta \ln \eta_i$, where η_i is the coefficient of viscosity of the solvent, is used to get Debye and Kalman factors. They reflect the associative nature along with the applicability of Debye-Smyth model of dielectric relaxation for such polar nitro molecules. The estimated dipole moments μ_j 's in terms of linear coefficient β 's of χ_{ij}' vs w_j like $\chi_{ij}' = \alpha + \beta w_j + \gamma w_j^2$ curves and dimensionless parameters b 's involved with measured τ_j 's are finally compared with theoretical dipole moments μ_{theo} 's, obtained from available bond angles and bond moments of the substituent polar groups of the molecules as well as with μ_j 's of Gopala Krishna's method used by Pant *et al.* to shed more light on the conformations of the molecules, in addition to inductive, mesomeric and electromeric effects.

Keywords : Structural aspects, nitro compounds, Giga Hertz electric field.

The dielectric relaxation mechanism of polar liquid molecules in nonpolar solvents is of much importance as it provides an useful and essential tool to study their structural aspects and physico-chemical properties. The method is involved with estimation of several dielectric relaxation parameters such as relaxation time τ_j , dipole moments μ_j , μ_{theo} and thermodynamic energy parameters. There exists several methods^{1,2} for estimation of relaxation parameters, but all these methods are not so simple like our present one based on susceptibility measurement. Their method^{1,2} consist of placing ϵ_{ij}'' against ϵ_{ij}' measured at different frequencies of GHz range to get semicircular plot which cuts ϵ' -axis in the lower and higher points giving rise ϵ_{oi} and ϵ_{oi} respectively. Migahed *et al.*³ and Nandi *et al.*⁴ used the method of thermally stimulated depolarisation current density (TSDC) in terms of *hf* relative permittivities to study

the relaxation mechanism of some polar liquids and the physico-chemical properties of some proteins, polymers, micelles etc. Although several workers^{3,4} studied the relaxation mechanism of polar liquid molecules in nonpolar solvent in terms of measured relative permittivities of ϵ_{ij}^* , the real part and ϵ_{ij}'' , the imaginary part of high frequency (*hf*) complex permittivity ϵ_{ij}^* , but no such investigation on polar nitro compounds by susceptibility measurement has yet been made. The method includes the estimation of real χ_{ij}' ($= \epsilon_{ij}' - \epsilon_{\text{oi}}$) and imaginary χ_{ij}'' ($= \epsilon_{ij}''$) parts of high frequency (*hf*) complex dimensionless dielectric orientational susceptibility χ_{ij}^* at different experimental temperatures in °C under a Giga Hertz electric field from the measured permittivities of ϵ_{ij}' and ϵ_{ij}'' of Pant *et al.*⁵. χ_{ij}^* 's are involved only with the molecular orientational polarisation and the evaluation of accurate relaxation parameters are made pos-

Table 1. Measured τ_j 's from ratio of slopes of individual variations of χ_{ij} and χ_{ij}'' with w_j , relaxation time τ_j from Murthy *et al.*, reported τ_j all are in pico second, correlation coefficient and % of error of $\chi_{ij} - w_j$ and $\chi_{ij}'' - w_j$ curves of Figs. 2 and 3, of aromatic polar nitro compounds in nonpolar solvent C_6H_6 at different experimental temperatures in $^{\circ}C$ under 9.58 GHz electric field frequency

Sl. no.	Systems	Temp. ($^{\circ}C$)	Individual slope of variation		Slope of χ_{ij}'' vs χ_{ij}' (eq. (4))	Ratio of slope of ind. variation	Correlation coeff. (<i>r</i>) of $\chi_{ij} - w_j$ and $\chi_{ij}'' - w_j$ curves	% of errors of $\chi_{ij} - w_j$ and $\chi_{ij}'' - w_j$ curves	τ_j in psec (eq. (4))	τ_j in psec (eq. (5))	Reported τ_j in psec of Pant <i>et al.</i> ⁵
			Slope of χ_{ij}' vs w_j at $w_j \rightarrow 0$	Slope of χ_{ij}'' vs w_j at $w_j \rightarrow 0$							
1.	2,5-Dichloro-nitrobenzene	20	24.73	16.36	0.66	0.68	0.98	1.04	10.98	10.98	10.01
		30	77.03	45.93	0.60	0.60	0.92	4.81	9.90	9.90	9.43
		40	78.54	46.01	0.59	0.59	0.90	5.76	9.72	9.72	6.64
2.	3,5-Dichloro-nitrobenzene	20	27.35	21.10	0.77	0.77	0.96	2.55	12.81	12.81	11.95
		30	131.44	88.76	0.68	0.68	0.91	5.05	11.21	11.21	8.20
		40	39.69	20.04	0.50	0.50	0.99	0.71	8.38	8.38	7.48
3.	2,5-Dibromo-nitrobenzene	20	91.74	135.29	1.47	1.47	0.96	2.13	24.48	24.48	21.50
		30	3.40	4.63	1.36	1.36	0.99	0.87	22.62	22.62	19.63
		40	29.92	39.28	1.31	1.31	0.98	1.15	21.79	21.79	19.19
4.	2,4-Dinitro-chlorobenzene	20	5.23	5.36	1.02	1.02	0.98	1.48	17.00	17.00	15.24
		30	25.42	23.24	0.91	0.91	0.89	6.45	15.18	15.17	14.32
		40	20.00	14.47	0.72	0.72	0.94	3.56	12.01	12.01	11.21
5.	3,4-Dinitro-chlorobenzene	20	1.29	1.37	1.06	1.06	0.97	1.78	17.60	17.60	15.83
		30	9.59	8.24	0.86	0.86	0.96	2.44	14.25	14.25	13.01
		40	0.23	0.16	0.71	0.71	0.96	2.52	11.82	11.82	10.12

Table 2. The coefficients of α , β , γ of $\chi_{ij} - w_j$ curves of Fig. 3, dimensionless parameters b 's with τ_j of eq. (8), measured dipole moment μ_j , reported dipole moment μ_j (Gopala Krishna), theoretical dipole moments μ_j in coulomb metre (C.m.) of some aromatic polar liquids in benzene at various experimental temperatures in $^{\circ}C$ under 9.58 GHz electric field frequency

Sl. no.	Systems (Molecular weight, M_j)	Temp. ($^{\circ}C$)	$\chi_{ij} = \alpha + \beta w_j + \gamma w_j^2$			Dimensionless parameter $b = 1/(1 + \omega^2 \tau_j^2)$	Measured $\mu_j \times 10^{30}$ (C.m.)	$\mu_j \times 10^{30}$ in C.m. (Pant <i>et al.</i>)	μ_j (theo.) $\times 10^{30}$ in C.m. from bond moments
			α	β	γ				
1.	2,5-Dichloro-nitrobenzene ($M_j = 0.1920$ kg)	20	-284.43	24.727	-0.35	0.696	26.18	15.19	
		30	-1223.1	77.025	-1.06	0.738	45.99	15.44	14.17
		40	-1262.6	78.537	-1.07	0.745	47.33	14.82	
2.	3,5-Dichloro-nitrobenzene ($M_j = 0.1920$ kg)	20	-404.56	27.352	-0.36	0.627	29.01	8.87	
		30	-1978.7	131.44	-1.94	0.687	62.27	16.41	14.17
		40	-448.35	39.688	-0.69	0.797	32.52	17.06	
3.	2,5-Dibromo-nitrobenzene ($M_j = 0.2810$ kg)	20	-1456.2	91.74	-1.3	0.315	90.66	34.33	
		30	203.44	3.3988	-0.13	0.350	16.97	30.99	14.17
		40	-323.28	29.92	-0.46	0.367	50.33	30.81	
4.	2,4-Dinitro-chlorobenzene ($M_j = 0.2025$ kg)	20	37.556	5.2318	-0.15	0.488	14.77	17.74	
		30	-264.67	25.42	-0.47	0.545	31.58	12.37	12.36
		40	-186.98	20.003	-0.36	0.656	26.12	12.59	
5.	3,4-Dinitro-chlorobenzene ($M_j = 0.2025$ kg)	20	191.45	1.2885	0.019	0.471	7.46	17.76	
		30	-147.89	9.5948	-0.01	0.576	18.87	12.37	25.18
		40	199.23	0.2286	0.068	0.663	2.78	14.69	

sible. It is evident from Fig. 1 that the variation of χ_{ij}'' with χ_{ij}' is strictly linear, the slope of which presented in Table 1, is used to get τ_j 's of the polar solutes. Murthy *et al.*⁶, however, showed earlier that a similar linear relationship exists between hf imaginary part $K_{ij}''(w_j)$ and real part $K_{ij}'(w_j)$ of complex conductivity $K_{ij}^*(w_j)$ from which τ_j for polar molecules could be estimated. But for associative liq-

uids in the higher concentration the variation of χ_{ij}'' and χ_{ij}' is not always linear⁷, the ratio of the linear coefficients of individual polynomial variation of both χ_{ij}' and χ_{ij}'' with weight fractions w_j 's like $\chi_{ij}' = \alpha + \beta w_j + \gamma w_j^2$ of solutions⁸ as displayed in Figs. 2 and 3, may be a better choice⁹ to estimate τ_j 's of polar liquid compounds τ_j 's so estimated, are presented in Table 1 for comparison with τ_j 's (11th col-

Table 3. The thermodynamic energy parameters : enthalpy of activation ΔH_{τ} , entropy of activation ΔS_{τ} and free energy of activation ΔF_{τ} , measured by our method (a) and measured by Pant *et al.* (b), value of δ from equation $\ln \tau_j T = \ln a + \delta \ln \eta_j$, enthalpy of activation ΔH_{η_j} due to viscous flow of solvent, Debye factor and Kalman factor of some aromatic polar liquids in benzene at various experimental temperatures in °C under 9.58 GHz electric field frequency

Sl. no.	System	Temp. (°C)	ΔH_{τ} (kJ mol ⁻¹)		ΔS_{τ} (J mol ⁻¹)		ΔF_{τ} (kJ mol ⁻¹)		Value of δ	$\Delta H_{\eta_j} = (\Delta H_{\tau}/\delta)$ (kJ mol ⁻¹)	Debye factor $(\tau_j T/\eta_j) \times 10^6$	Kalman factor $(\tau_j T/\eta_j^{\delta})$
			a	b	a	b	a	b				
			1.	2,5-Dichloro-nitrobenzene	20	2.16	13.00	-0.0277				
		30	2.16	13.00	-0.0274	0.0088	10.45	10.33	0.04	5.99	5.35	4.45×10^{-8}
		40	2.16	13.00	-0.0277	0.0101	10.83	9.84	0.36	5.99	5.82	4.63×10^{-8}
2.	3,5-Dichloro-nitrobenzene	20	13.58	15.44	0.0100	0.0169	10.65	10.49	2.10	6.46	6.08	2.09×10^{-2}
		30	13.58	15.44	0.0093	0.0181	10.77	9.97	2.10	6.46	6.05	2.30×10^{-2}
		40	13.58	15.44	0.0100	0.0169	10.45	10.15	2.10	6.46	5.02	2.07×10^{-2}
3.	2,5-Dibromo-nitrobenzene	20	1.93	1.86	-0.0352	-0.0343	12.24	11.92	0.31	6.15	11.62	7.26×10^{-8}
		30	1.93	1.86	-0.0350	-0.0341	12.54	12.18	0.31	6.15	12.22	7.15×10^{-8}
		40	1.93	1.86	-0.0352	-0.0344	12.94	12.61	0.31	6.15	13.04	7.27×10^{-8}
4.	2,4-Dinitro-chorobenzene	20	10.69	9.12	-0.0023	-0.0067	11.35	11.08	1.65	6.46	8.07	1.02×10^{-3}
		30	10.69	9.12	-0.0028	-0.0075	11.53	11.38	1.65	6.46	8.20	1.10×10^{-3}
		40	10.69	9.12	-0.0022	-0.0067	11.39	11.21	1.65	6.46	7.19	1.01×10^{-3}
5.	3,4-Dinitro-chorobenzene	20	12.67	14.50	0.0042	0.0114	11.43	11.17	2.00	6.33	8.36	1.37×10^{-2}
		30	12.67	14.50	0.0043	0.0111	11.37	11.14	2.00	6.33	7.69	1.39×10^{-2}
		40	12.67	14.50	0.0042	0.0114	11.34	10.94	2.00	6.33	7.07	1.37×10^{-2}

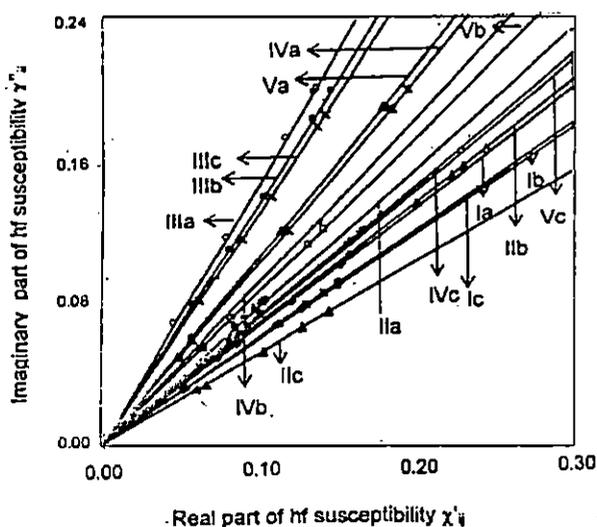


Fig. 1. Variation of imaginary part χ''_{ij} of hf orientational susceptibility against real part χ'_{ij} of hf orientation susceptibility of some polar nitro compounds in nonpolar solvent benzene at different temperatures in °C under 9.5846 GHz electric field frequency of 2,5-dichloronitrobenzene [Ia at 20 °C (◇), Ib at 30 °C (◆), Ic at 40 °C (□)], 3,5-dichloronitrobenzene [IIa at 20 °C (■), IIb at 30 °C (Δ), IIc at 40 °C (▲)], 2,5-dibromonitrobenzene [IIIa at 20 °C (○), IIIb at 30 °C (●), IIIc at 40 °C (×)], 2,4-dinitrochlorobenzene [IVa at 20 °C (*), IVb at 30 °C (-), IVc at 40 °C (+)], 3,4-dinitrochlorobenzene [Va at 20 °C (Δ), Vb at 30 °C (□), Vc at 40 °C (○)].

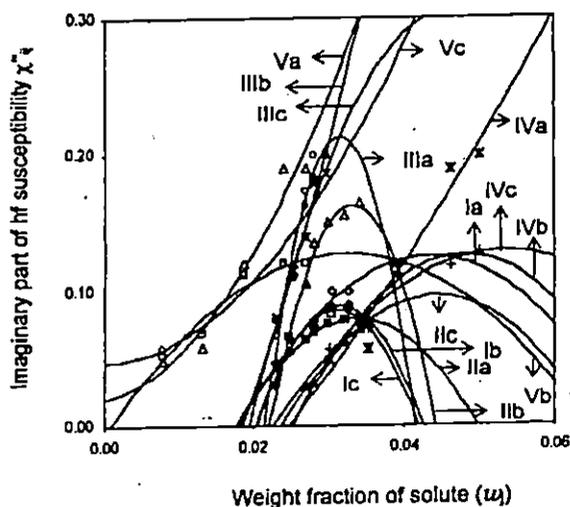


Fig. 2. Variation of imaginary part χ''_{ij} of hf orientational susceptibility against weight fraction w_j of some polar nitro compounds in nonpolar solvent benzene at different temperatures in °C under 9.5846 GHz electric field frequency of 2,5-dichloronitrobenzene [Ia at 20 °C (◇), Ib at 30 °C (◆), Ic at 40 °C (□)], 3,5-dichloronitrobenzene [IIa at 20 °C (■), IIb at 30 °C (Δ), IIc at 40 °C (▲)], 2,5-dibromonitrobenzene [IIIa at 20 °C (○), IIIb at 30 °C (●), IIIc at 40 °C (×)], 2,4-dinitrochlorobenzene [IVa at 20 °C (*), IVb at 30 °C (-), IVc at 40 °C (+)], 3,4-dinitrochlorobenzene [Va at 20 °C (Δ), Vb at 30 °C (□), Vc at 40 °C (○)].

umn) calculated by Pant *et al.*⁵ by using Gopala Krishna's method¹⁰. The excellent agreement of τ_j 's by both of

prescribed methods in case of polar nitro compounds which includes the names of 2,5-dichloronitrobenzene, 3,5-dichloronitrobenzene, 2,5-dibromonitrobenzene, 2,4-dinitro-

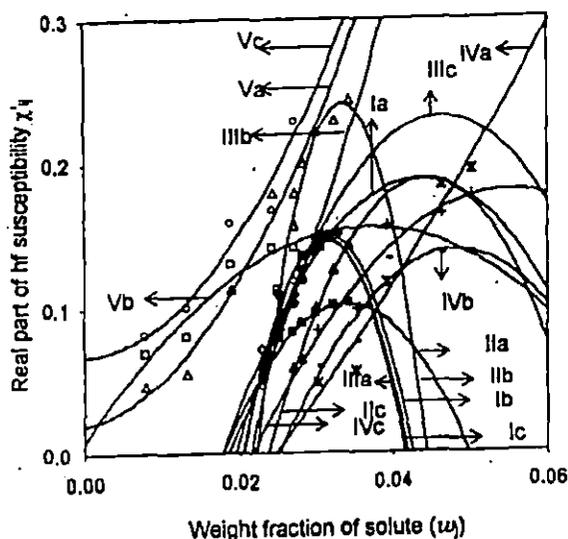


Fig. 3. Variation of real part χ'_{ij} of *hf* orientational susceptibility against weight fraction w_j of some polar nitro compounds in nonpolar solvent benzene at different temperatures in °C under 9.5846 GHz electric field frequency of 2,5-dichloronitrobenzene [Ia at 20 °C (○), Ib at 30 °C (◊), Ic at 40 °C (◻)], 3,5-dichloronitrobenzene [IIa at 20 °C (■), IIb at 30 °C (Δ), IIc at 40 °C (▲)], 2,5-dibromonitrobenzene [IIIa at 20 °C (○), IIIb at 30 °C (◊), IIIc at 40 °C (×)], 2,4-dinitrochlorobenzene [IVa at 20 °C (*), IVb at 30 °C (-), IVc at 40 °C (+)], 3,4-dinitrochlorobenzene [Va at 20 °C (Δ), Vb at 30 °C (◻), Vc at 40 °C (○)].

chlorobenzene. 3,4-dinitrochlorobenzene indicates that the data of $\chi''_{ij}(w_j)$ and $\chi'_{ij}(w_j)$ are of low weight fractions w_j 's so that the polar-polar interactions are almost eliminated. The estimated τ_j 's involved with dimensionless parameter b 's are now used to obtain *hf* dipole moment μ_j in terms of linear coefficients β 's of curves of $\chi'_{ij} - w_j$ of Fig. 2 using Debye's relation¹¹. The dimensionless parameter b 's, linear coefficients β 's and estimated μ_j 's are placed in Table 2 to compare with μ_j 's by Gopala Krishna's method¹⁰ measured by Pant *et al.*⁵ and theoretical dipole moments μ_{theo} 's of Fig. 4, evaluated by vector addition of available bond moments of the substituent polar groups of the nitro compounds as seen in Table 2. The disagreement between estimated μ_j and μ_{theo} shows the probable existence of inductive, mesomeric and electromeric effects¹² suffered by the polar groups under the electric field of GHz frequency. μ_j 's thus measured when plotted against t °C shows convex and concave shapes as seen in Fig. 5, which reflects the stability or instability of the polar-nonpolar liquid mixtures observed elsewhere¹³. The eq. (10) is a linear equation in $\tau_j T$ against $1/T$ of Fig. 6. The slope and intercept are used to measure the required thermodynamic energy parameters. ΔH_τ , ΔS_τ and ΔF_τ as placed in Table 3. The parameters so estimated provides a deep insight into the physico-chemical properties¹⁴ of the solute molecules in solvent benzene under GHz electric field. The Debye and Kalman factors as seen in Table 3 shows Debye relaxation mechanism obeyed by the molecules.

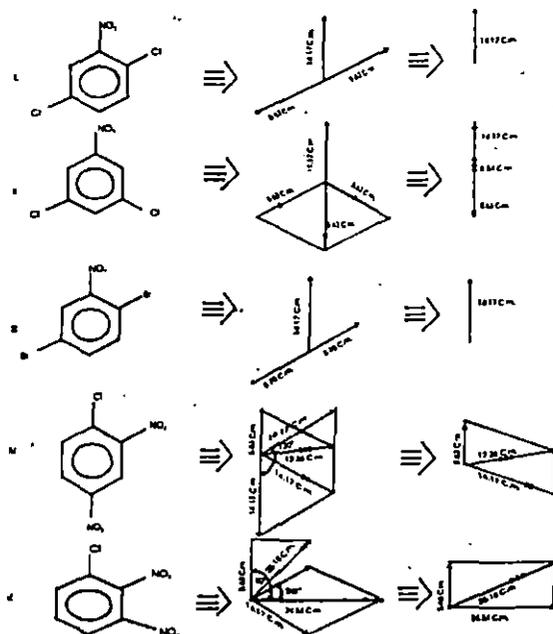


Fig. 4. Theoretical dipole moment μ_{theo} ($\times 10^{30}$) in coulomb metre (C.m.) from available bond angle and bond moments of (I) 2,5-dichloronitrobenzene, (II) 3,5-dichloronitrobenzene, (III) 2,5-dibromonitrobenzene, (IV) 2,4-dinitrochlorobenzene, (V) 3,4-dinitrochlorobenzene.

Theoretical formulations :

If ϵ_{oij} be subtracted from ϵ'_{ij} , the susceptibility contains only the orientational polarisation¹⁵ and thus the fast polarisation is avoided unlike the ϵ_{ij}^* . In absence of reliable measured values of infinitely *hf* and low frequency (*lf*) permittivities ϵ_{oij} and ϵ_{oij} , the following Debye-Pallate's equations¹⁶ may safely be used from the measured values of the real ϵ'_{ij} and imaginary ϵ''_{ij} parts of the *hf* complex ϵ_{ij}^* of Pant *et al.*⁵

$$\epsilon'_{ij} = \epsilon_{oij} + \frac{\epsilon_{oij} - \epsilon_{\alpha ij}}{1 + \omega^2 \tau_j^2} \quad (1)$$

and

$$\epsilon''_{ij} = \frac{\epsilon_{oij} - \epsilon_{\alpha ij}}{1 + \omega^2 \tau_j^2} \omega \tau_j \quad (2)$$

χ''_{ij} and χ'_{ij} 's of functions of w_j 's are well displayed in Figs. 3 and 2 respectively. Both ϵ'_{ij} and ϵ''_{ij} parts of ϵ_{ij}^* are related by¹¹

$$\epsilon'_{ij} = \epsilon_{oij} + \frac{1}{\omega \tau_j} \epsilon''_{ij} \quad (3)$$

In terms of real χ'_{ij} and imaginary χ''_{ij} parts of *hf* complex susceptibility χ_{ij}^* , one obtains

$$\chi''_{ij} = (\omega \tau_j) \chi'_{ij} \text{ or } d\chi''_{ij} / d\chi'_{ij} = \omega \tau_j \quad (4)$$

Murthy *et al.*⁶ showed earlier that a similar linear relationship exists between *hf* conductivity $K''_{ij}(w_j)$ and $K'_{ij}(w_j)$ from

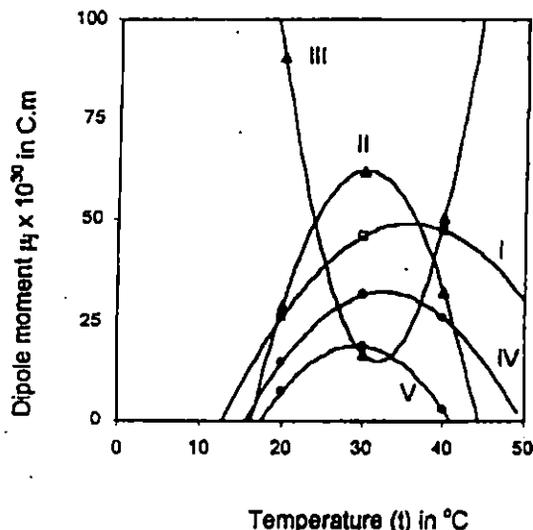


Fig. 5. Variation of dipole moment μ_j against temperature t in $^{\circ}\text{C}$ of some polar nitro compounds in nonpolar solvent benzene under 9.5846 GHz electric field frequency of (I) 2,5-dichloronitrobenzene (\square), (II) 3,5-dichloronitrobenzene (Δ), (III) 2,5-dibromonitrobenzene (\blacktriangle), (IV) 2,4-dinitrochlorobenzene (\circ), (V) 3,4-dinitrochlorobenzene (\bullet).

which they estimated the relaxation time for polar molecules. The eqs. (4) is a straight line between χ''_{ij} and χ'_{ij} observed graphically in Fig. 1, the slope of which is used to get τ_j of a polar solute⁶ as seen in Table 1. But for most of the associative liquids, the variation of χ''_{ij} against χ'_{ij} is not strictly linear⁹. For such associative polar-nonpolar liquid mixture χ'_{ij} is related with w_j by $\chi'_{ij} = \alpha + \beta w_j + \gamma w_j^2$ the slope of eq. (4) can be represented by :

$$\frac{(d\chi''_{ij}/dw_j)_{w_j \rightarrow 0}}{(d\chi'_{ij}/dw_j)_{w_j \rightarrow 0}} = \omega\tau_j \quad (5)$$

The eq. (5) represents the ratio of linear coefficients of individual variation of both χ''_{ij} and χ'_{ij} with w_j of a polar solute displayed graphically in Figs. 2 and 3 respectively, τ_j 's estimated from eq. (5) are placed in Table 1 in order to compare them with τ_j 's obtained by direct slope $\chi''_{ij} - \chi'_{ij}$ of Fig. 1 and those of Gopala Krishna's method¹⁰ measured by Pant *et al.*⁵.

The imaginary part χ''_{ij} of $hf \chi_{ij}^*$ is related to w_j of polar solute by¹¹

$$\chi''_{ij} = \frac{N\rho_{ij}\mu_j^2}{27\epsilon_0 M_j k_B T} \left(\frac{\omega\tau_j}{1 + \omega^2\tau_j^2} \right) (\epsilon_{ij} + 2)^2 w_j \quad (6)$$

which on differentiation with respect to w_j and in the limit of $w_j = 0$ yields that

$$\left(\frac{d\chi''_{ij}}{dw_j} \right)_{w_j=0} = \frac{N\rho_{ij}\mu_j^2}{27\epsilon_0 M_j k_B T} \left(\frac{\omega\tau_j}{1 + \omega^2\tau_j^2} \right) (\epsilon_{ij} + 2)^2 \quad (7)$$

From eqs. (5) and (7) one obtains $hf \mu_j$ by

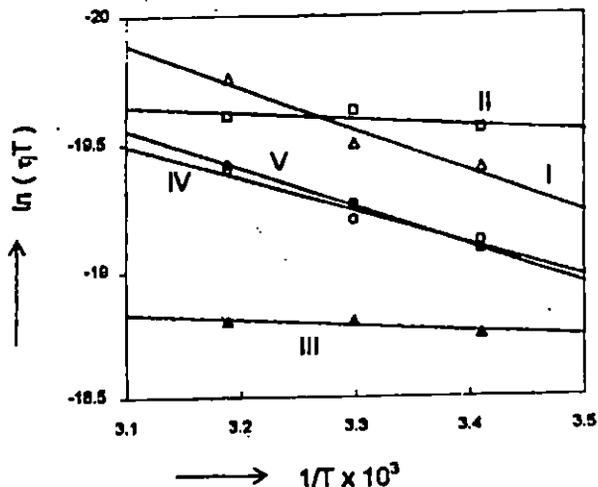


Fig. 6. Variation of $\ln(\tau_j T)$ against $1/T$ of some polar nitro compounds in nonpolar solvent benzene under 9.5846 GHz electric field frequency of (I) 2,5-dichloronitrobenzene (\square), (II) 3,5-dichloronitrobenzene (Δ), (III) 2,5-dibromonitrobenzene (\blacktriangle), (IV) 2,4-dinitrochlorobenzene (\circ), (V) 3,4-dinitrochlorobenzene (\bullet).

$$\mu_j = \left[\frac{27\epsilon_0 M_j k_B T \beta}{N\rho_{ij} (\epsilon_{ij} + 2)^2 b} \right]^{1/2} \quad (8)$$

M_j = Molecular weight of j -th liquid in Kilogram, ϵ_0 = permittivity of free space = 8.854×10^{-12} Farad metre⁻¹, k_B = Boltzmann constant = 1.38×10^{-23} J mol⁻¹ K⁻¹, T = temperature in absolute scale, $\beta = (d\chi''_{ij}/dw_j)_{w_j \rightarrow 0}$ = linear coefficient of $\chi''_{ij} - w_j$ curves of Fig. 3 at $w_j \rightarrow 0$, N = Avogadro's number = 6.023×10^{23} , ρ_{ij} = density of solvent C_6H_6 , ϵ_{ij} = dielectric relative permittivity of solvent C_6H_6 , $b = 1/(1 + \omega^2\tau_j^2)$, a dimensionless parameter involved with the estimated τ_j of eq. (5).

Dielectric relaxation is a process of rotation of the polar molecules under hf electric field and it requires an activation energy ΔF_{τ} , known as free energy of activation to overcome the energy barrier between two equilibrium positions. ΔF_{τ} is, however, related with estimated τ_j of eq. (5) by the relation¹⁴.

$$\tau_j = \frac{A}{T} \exp(\Delta F_{\tau}/RT) \quad (9)$$

As $\Delta F_{\tau} = \Delta H_{\tau} - T\Delta S_{\tau}$, so we have

$$\text{or, } \ln(\tau_j T) = \ln A' + \frac{\Delta H_{\tau}}{R} \frac{1}{T} \quad (10)$$

$$\text{where } A' = A e^{(-\Delta S_{\tau}/R)} \quad (11)$$

The eq. (10) is a linear equation of $\ln \tau_j T$ against $1/T$ of Fig. 6. The slope and intercept are used to measure the required thermodynamic energy parameters of the molecules as presented in Table 3 in agreement with those of Pant *et al.*⁵.

Results and discussion

The τ_j 's of aromatic polar nitro compounds in solvent C_6H_6 at different experimental temperatures in $^{\circ}C$ under 9.58 Giga Hertz electric field are worked out from the slope of the fitted linear eq. (4) between the variables χ_{ij}'' and χ_{ij}' displayed graphically in Fig. 1 with the symbols showing the experimental points. τ_j 's so obtained are compared with τ_j 's estimated from the ratio of linear coefficients of individual variations of both χ_{ij}'' and χ_{ij}' with w_j 's shown graphically in Figs. 2 and 3. τ_j 's estimated by both the method are presented in Table 1. The excellent agreement of τ_j 's by both the methods at once indicates the data χ_{ij}'' and χ_{ij}' are of low concentrations such that the polar-polar interactions are almost eliminated⁹ at $w_j \rightarrow 0$. The τ_j 's by the latter method²¹ are more reliable. Gopala Krishna's method¹⁰ was employed by Pant *et al.*⁵ to get τ_j 's. They are presented in Table 1. The close agreement between τ_j 's of Pant *et al.*⁵ and estimated τ_j 's of eqs. (4) and (5) at once reflects the basic soundness of our method to get τ_j in the limit $w_j = 0$. The correlation coefficient and % of error of both $\chi_{ij}'' - w_j$ and $\chi_{ij}' - w_j$ curves of Figs. 2 and 3 are given in Table 1 only to show how far they are correlated with w_j 's. It is evident from Table 1 that τ_j 's decrease with temperature. This can be explained on the basis of the fact that at constant temperature, the relaxation time depends upon the energy difference between the activated and normal states. At higher temperature thermal agitation causes an increase in energy loss due to large number of collisions and thereby decreasing the relaxation time^{9,16}. Dipole moments μ_j 's of the polar solutes as estimated from eq. (8) are placed in Table 2 together with linear coefficients β 's of $\chi_{ij}' - w_j$ curves of Fig. 2 and dimensionless parameter b 's involved with τ_j of eq. (5) as seen in Table 2 respectively. They are, however, compared with μ_j 's of Pant *et al.*⁵ and theoretical μ_{theo} 's obtained from vector addition of bond moments¹⁷ of the substituted polar groups of the compounds, as seen in the Table 2. The theoretical dipole moment and its orientation as a consequence of known structure of the pertinent nitro-compound is displayed in Fig. 4. The resonance effect thus obtained by solvent benzene compound into an inductive effect-operated by the substituent polar groups in the ring is expected to play a prominent role¹⁸ in the measured $hf\mu_j$'s. The disagreement between $hf\mu_j$'s and μ_{theo} 's is explained by the influence of hf electric field coupled with inductive and mesomeric moments on the flexible polar groups. μ_{theo} 's with reference to Fig. 4 gives a deep insight into the structures of the molecules concerned.

The symmetry and asymmetry of the molecules being a physico-chemical property can well be explained on the basis of $\mu_j - t$ curves of Fig. 5. It is seen that unlike system III all the systems show convex $\mu_j - t$ curves having minimum μ_j 's at lower and higher temperatures due to strong symmetry attained⁸ at those temperatures. The system III shows maximum μ_j 's at lower and higher temperature due to asymmetric shape of the molecule. Physico-chemical properties of the systems can also be explained from the stand point of thermodynamics by estimating the energy parameters ΔH_{τ} , ΔS_{τ} and ΔF_{τ} from the intercept and slope of a fitted linear equation of $\ln \tau_j T$ against $1/T$ shown graphically in Fig. 6 with the experimental points placed on them. They are placed in Table 3 together with those estimated by Pant *et al.*⁵ by using Gopala Krishna's method¹⁰. It is seen that except the first one the other systems are close to each other. Unlike systems II and V all the systems possess negative ΔS_{τ} 's which suggests that configuration involved in dipolar rotation has an activated state which is more ordered than the normal state^{8,19} while the reverse is true for the rest two systems. ΔF_{τ} 's for all the systems are nearly same in magnitude, as the activation is accomplished by the rupture of bond of dipolar groups in the same degrees of freedom^{7,19}. Unlike 2,5-dichloronitrobenzene and 2,5-dibromonitrobenzene all the systems possess $\delta > 0.50$ as seen in Table 3 indicating solvent environment around the solute molecules¹⁵. Moreover, they show higher ΔH_{η_i} 's than that ΔH_{τ} 's as seen in Table 3. It is due to the fact that ΔH_{η_i} is involved with both transitional and rotational motion of the molecules. Other systems possess lower values than that of ΔH_{τ} for high value of δ for those systems. Debye factor $\tau_j T / \eta$ and Kalman factor $\tau_j T / \eta^6$, being proportional to volume of the rotating unit are carefully estimated and are placed in Table 3. Debye factors are all of the order of 10^6 and Kalman factors although of different orders but found to have constant values for all systems at each temperature, indicating at once the validity of Debye model of dielectric relaxation mechanism for such aromatic polar nitro compounds in C_6H_6 under GHz electric field^{9,13}.

Conclusion :

Our group²¹ have developed a new method based on the complex susceptibility χ_{ij}^* in the limit $w_j=0$ to study the structural aspects and physico-chemical properties of the polar nitro liquid compounds 2,5-dichloronitrobenzene, 3,5-dichloronitrobenzene, 2,5-dibromonitrobenzene, 2,4-dinitrochlorobenzene and 3,4-dinitrochlorobenzene in C_6H_6 under GHz electric field at different experimental temperatures. The excellent agreement of τ_j 's estimated by our methods of eqs. (4) and (5) at once establishes the ap-

plicability of the method suggested to get τ_j 's at $w_j \rightarrow 0$ as it eliminates polar-polar interaction²¹ in a given solution. The correlation coefficients r 's and % of errors obtained by careful regression analysis between variables of curves of Figs. 2 and 3 show how far the variables χ''_{ij} and χ'_{ij} are correlated with w_j 's to establish the statistical validity¹⁵ of eq. (5). The thermodynamic energy parameters such as ΔH_τ , ΔS_τ and $\Delta f'_\tau$ worked out in terms of temperature variation of τ_j 's are useful and important tools to comment on the physico-chemical properties of dipolar liquid molecules. The theoretical dipole moment μ_{theo} 's and its comparison with measured $hf \mu_j$'s of the eq. (8) explore new concept regarding structures of the molecules in addition to inductive, mesomeric and electromeric effects present in them. Almost the constant values of Debye and Kalman factors and the curves satisfied by experimental points in all the figures reflect the validity of the theoretical formulations within the framework of Debye-Smyth model of dielectric relaxation. The significant contribution to study the structural aspects and physico-chemical properties of the polar liquid molecules as sketched in Fig. 4 in nonpolar solvent under nearly 10 GHz electric field are thus found to be important to enhance scientific content of the existing knowledge of dielectric relaxation processes.

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Dielectric relaxation phenomena of some aprotic polar liquids under giga hertz electric field

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The two relaxation times τ_1 and τ_2 due to rotations of the flexible parts and the whole molecules of some aprotic polar liquids (j) like N, N-dimethyl sulphoxide (DMSO); N, N-dimethyl formamide (DMF), N, N-dimethyl acetamide (DMA) and N, N-diethyl formamide (DEF) in benzene (i) are estimated from the measured real χ_{ij}' and imaginary χ_{ij}'' part of *hf* complex dielectric orientational susceptibility χ_{ij}^* and low frequency susceptibility χ_{oij} at different weight fractions w_j 's of solute at various experimental temperatures [Saha *et al.*, *J Phys. D: Appl Phys*, 27 (1994) 596]. The relative contributions c_1 and c_2 due to τ_1 and τ_2 are calculated from Fröhlich's equations and graphical technique. All the c 's are positive from Fröhlich's equations while some c_2 's are negative from graphical method. The dipole moments μ_2 and μ_1 in Coulomb-metre (C.m) measured from the slope β 's of $\chi_{ij}'-w_j$ curves are compared with those of conductivity σ_{ij} measurements using τ 's from the ratio of individual slope of $(d\chi_{ij}''/dw_j)_{w_j \rightarrow 0}$ and $(d\chi_{ij}'/dw_j)_{w_j \rightarrow 0}$, linear slope of $\chi_{ij}^*-\chi_{ij}'$ along with Gopalakrishna's method [Trans Faraday Soc, 53 (1957) 767]. The estimated μ_1 's agree with the measured and reported μ 's to indicate that the flexible part of the molecule is rotating under GHz electric field. The theoretical dipole moment μ_{theo} 's are obtained in terms of available bond moments of the substituent polar groups attached to the parent molecules acting as pusher or puller of electrons due to inductive, mesomeric and electromeric effects in them under *hf* electric field. The variation of μ_1 with temperature suggests the elongation of bond moments. The energy parameters such as enthalpy of activation ΔH_a , free energy of activation ΔF_a and entropy of activation ΔS_a 's are obtained for DMSO only assuming dielectric relaxation as a rate process to know the molecular dynamics. The variation of $\ln(\tau_1 T)$ against $1/T$ of DMSO reveals that it obeys Eyring rate theory unlike $\ln(\tau_2 T)$ against $1/T$ curve.

Keywords: Dielectric relaxation, Aprotic polar liquids, Dipole moment

IPC Code: G01R27/26

1 Introduction

The relaxation behaviour of polar-nonpolar liquid mixtures under high frequency (*hf*) electric field is of much importance to study the molecular shapes, sizes as well as associational behaviour¹⁻³ in them. Researchers in this field usually analyse the experimental data obtained through relaxation mechanisms involved on the basis of various models⁴⁻⁶ applicable to polar liquids. Dhull *et al.*⁷ and Sharma and Sharma⁸ had, however, measured the real ϵ_{ijk}' , ϵ_{ij}' or ϵ_{ik}' and imaginary ϵ_{ijk}'' , ϵ_{ij}'' or ϵ_{ik}'' parts of relative complex permittivities ϵ_{ijk}^* , ϵ_{ij}^* or ϵ_{ik}^* of some interesting binary or single polar liquids (jk, j or k) in a non-polar solvent under X-band electric field at different or fixed temperatures. The purpose of the work was to detect monomer (solute-solvent) or dimer (solute-solute) molecular associations and molecular dynamics of the systems in terms of estimated relaxation time τ_j and dipole moment μ_j .

The measured⁹ values of the relative permittivities ϵ_{ij} 's of some aprotic polar liquids like N, N-dimethyl sulphoxide (DMSO); N, N-dimethyl formamide (DMF); N, N-dimethyl acetamide (DMA) and N, N-diethyl formamide (DEF) in benzene under the most effective dispersive region of nearly 10 GHz electric field at 25, 30, 35 and 40°C for DMSO; 25°C for DMA and DMF and 30°C for DEF respectively. DMSO is a aprotic dipolar liquid of high penetrating power and wide applications in medicine and industry. It acts as good constituent of binary mixtures because of its associative¹⁰ nature. Amides, on the other hand, are the building blocks of proteins and enzymes and have wide biological applications. The liquids usually show two relaxation times τ_2 and τ_1 , for the rotation of the whole molecules and the flexible parts attached to the parent molecules from the single frequency measurement technique^{11,12}.

All these facts inspired us to study τ_2 and τ_1 and dipole moments μ_2 and μ_1 of these liquids in terms of real $\chi_{ij}' (= \epsilon_{ij}' - \epsilon_{\infty ij})$ and imaginary $\chi_{ij}'' (= \epsilon_{ij}'')$ parts of complex orientational susceptibility $\chi_{ij}^* (= \epsilon_{ij}' - \epsilon_{\infty ij})$ in benzene at different temperatures. The low frequency susceptibility $\chi_{oij} (= \epsilon_{oij} - \epsilon_{\infty ij})$ is, however, real. χ_{ij}' can be obtained by subtracting either 1 or $\epsilon_{\infty ij}$ from the measured ϵ_{ij}' 's. If 1 is subtracted from the relative permittivity ϵ_{ij}' and ϵ_{oij} one gets χ_{ij}' and χ_{oij} containing all types of polarisation processes including fast polarisations. When high frequency relative permittivity or the optical permittivity $\epsilon_{\infty ij}$ be subtracted from ϵ_{ij}' and ϵ_{oij} of the solution at a certain weight fraction w_j 's of the solute the susceptibility χ_{ij}' , χ_{ij}'' and χ_{oij} result due to orientational polarisation only. Our earlier study⁹ was to calculate τ 's and μ 's in terms of either relative permittivities ϵ_{ij}' 's or hf conductivities σ_{ij}' 's. ϵ_{ij}' 's are involved with all types of polarisations while σ_{ij}' 's are related only to bound molecular charges of polar liquids. Now-a-days relaxation mechanisms are studied in terms¹³ of χ_{ij}' 's because measurements of μ 's in terms of ϵ_{ij}' 's or σ_{ij}' 's include contributions due to all types of polarisations and bound molecular charges, respectively. Moreover, relaxation processes are highly thermally activated to yield τ within the framework of Debye-Smith model of polar-nonpolar liquid mixture.

The purpose of the present work is to assess the contribution of fast polarisation and bound molecular charges in the measurement of μ 's when compared with μ 's from χ_{ij} and σ_{ij} measurements. The variation of μ 's with temperature provides knowledge of the state of the system through the measured energy parameters.

The detailed experimental technique involved in the measurement of dielectric relaxation parameters of solution has been described elsewhere¹⁴. A Hewlett Packard Impedance Analyser (HP-4192A) measured the capacitance and conductance of the cell containing polar-nonpolar liquid mixtures at different frequencies and temperatures for a fixed w_j of solute. The real and imaginary parts of relative permittivities ϵ_{ij}' or susceptibility χ_{ij}' are obtained from complex impedances of the cell measured within the range of frequencies from 5 Hz to 13 MHz. The measured ϵ_{ij}' 's are then plotted in a Cole-Cole semicircular arc to get the values of ϵ_{ij}' , ϵ_{ij}'' , ϵ_{oij} and $\epsilon_{\infty ij}$ at nearly 10 GHz electric field (Table 1). Again ϵ_{oij} is measured at 1 kHz whereas high frequency permittivity $\epsilon_{\infty ij} (= n_{Dij}^2)$ is

measured by Abbe's refractometer to compare the values obtained from Cole-Cole plot. The cell containing experimental liquid mixture is then kept in Mettler Hot Stage FP-52 chamber to regulate temperature. Multiply distilled C_6H_6 is used as a solvent in measurement after several times fractional distillation to get the purest quality of sample. The measured data ϵ_{ij}' or χ_{ij}' 's are accurate within $\pm 5\%$.

Bergmann *et al.*¹⁵, however, proposed a graphical technique to get τ_1 , τ_2 and c_1 , c_2 for a pure polar liquid at different frequencies of the microwave electric field. In order to avoid clumsiness of algebra and fast polarisation processes, the molecular orientational polarisations in terms of established symbols of χ_{ij}' 's can be written as⁵

$$\frac{\chi_{ij}'}{\chi_{oij}} = \frac{c_1}{1 + \omega^2 \tau_1^2} + \frac{c_2}{1 + \omega^2 \tau_2^2} \quad \dots (1)$$

$$\frac{\chi_{ij}''}{\chi_{oij}} = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \quad \dots (2)$$

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

Saha *et al.*¹¹ and Sit *et al.*¹² put forward an analytical technique to measure τ_1 , τ_2 and c_1 , c_2 of a polar-nonpolar liquid mixture in terms of measured χ_{ij}' , χ_{ij}'' , χ_{oij} at different w_j 's of solute under a single frequency electric field and temperature. Eqs (1) and (2) are solved to get:

$$\frac{\chi_{oij} - \chi_{ij}'}{\chi_{ij}'} = \omega (\tau_1 + \tau_2) \frac{\chi_{ij}''}{\chi_{ij}'} - \omega^2 \tau_1 \tau_2 \quad \dots (3)$$

Eq. (3) gives a straight line when $(\chi_{oij} - \chi_{ij}')/\chi_{ij}'$ is plotted against χ_{ij}''/χ_{ij}' for different w_j 's of solute for a given angular frequency $\omega (= 2\pi f)$, f being the frequency of the applied electric field. The slope $\omega(\tau_1 + \tau_2)$ and intercept $-\omega^2 \tau_1 \tau_2$ of straight line of Eq. (3) are obtained through linear regression analysis as shown in Fig. 1. Relaxation times τ_2 and τ_1 are calculated from the slopes and intercepts of Eq. (3) of Fig. 1 in terms of measured data of Table 1. They are then compared with measured τ_j 's from the linear slope of the χ_{ij}'' against χ_{ij}' curve of Fig. 2 at different w_j 's of the form:

$$\frac{d\chi_{ij}''}{d\chi_{ij}'} = \omega \tau \quad \dots (4)$$

Both χ_{ij}'' and χ_{ij}' are functions of w_j 's of solute. It is better to use the individual slopes $\chi_{ij}''-w_j$ and $\chi_{ij}'-w_j$

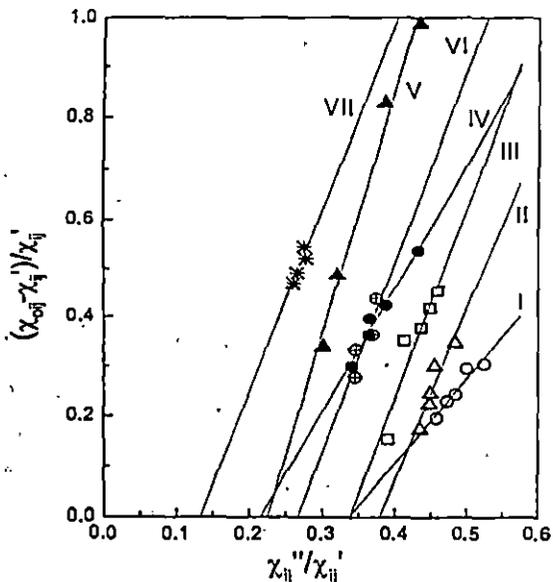


Fig. 1—Linear plot of $(\chi'_{oij}-\chi'_{ij})/\chi'_{oij}$ against χ''_{ij}/χ'_{ij} for different w_j 's of DMSO, DEF, DMF and DMA in benzene (I) DMSO at 25°C (-o-), (II) DMSO at 30°C (-Δ-), (III) DMSO at 35°C (-□-), (IV) DMSO at 40°C (-●-), (V) DEF at 30°C (-▲-), (VI) DMF at 25°C (-⊕-) and (VII) DMA at 25°C (-*-)

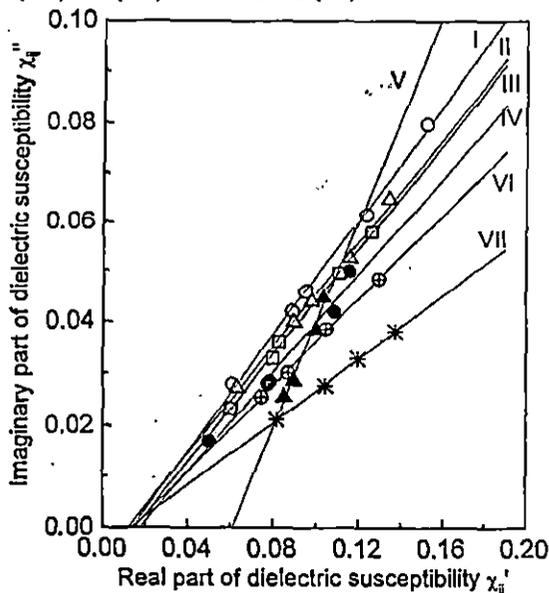


Fig. 2—Linear variation of imaginary part of dielectric susceptibility χ''_{ij} against real part of dielectric susceptibility χ'_{ij} for different w_j 's of DMSO, DEF, DMF and DMA in benzene (I) DMSO at 25°C (-o-), (II) DMSO at 30°C (-Δ-), (III) DMSO at 35°C (-□-), (IV) DMSO at 40°C (-●-), (V) DEF at 30°C (-▲-), (VI) DMF at 25°C (-⊕-) and (VII) DMA at 25°C (-*-)

curves in Figs 3 and 4 at $w_j \rightarrow 0$ to measure τ using the following equation:

$$\frac{(d\chi''_{ij}/dw_j)_{w_j \rightarrow 0}}{(d\chi'_{ij}/dw_j)_{w_j \rightarrow 0}} = \omega\tau \quad \dots (5)$$

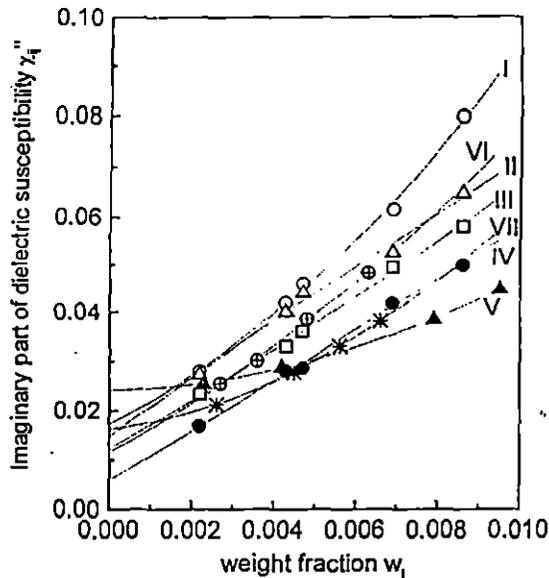


Fig. 3—Plot of imaginary part of dielectric susceptibility χ''_{ij} with weight fraction w_j of DMSO, DEF, DMF and DMA in benzene (I) DMSO at 25°C (-o-), (II) DMSO at 30°C (-Δ-), (III) DMSO at 35°C (-□-), (IV) DMSO at 40°C (-●-), (V) DEF at 30°C (-▲-), (VI) DMF at 25°C (-⊕-) and (VII) DMA at 25°C (-*-)

τ 's from both the methods along with τ 's from conductivity measurement technique using Eqs (25) and (26) are placed in Table 2 in order to compare with τ measured by Gopalakrishna's method¹⁶.

Eqs (1) and (2) are solved for c_1 and c_2 to get:

$$c_1 = \frac{(\chi'_{ij}\alpha_2 - \chi''_{ij})(1 + \alpha_1^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad \dots (6)$$

$$c_2 = \frac{(\chi''_{ij} - \chi'_{ij}\alpha_1)(1 + \alpha_2^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad \dots (7)$$

where $\alpha_1 = \omega\tau_1$ and $\alpha_2 = \omega\tau_2$, such that $\alpha_2 > \alpha_1$. The values of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} are also obtained from following Fröhlich's equations¹⁷:

$$\frac{\chi'_{ij}}{\chi_{oij}} = 1 - \frac{1}{2A} \ln \left(\frac{1 + \omega^2\tau_2^2}{1 + \omega^2\tau_1^2} \right) \quad \dots (8)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = \frac{1}{A} \left[\tan^{-1}(\omega\tau_2) - \tan^{-1}(\omega\tau_1) \right] \quad \dots (9)$$

where $A = \text{Fröhlich parameter} = \ln(\tau_2/\tau_1)$. The theoretical values of relative contributions c_1 and c_2 towards dielectric relaxation processes for τ_1 and τ_2 are computed from Eqs (8) and (9). They are presented in Table 3. The graphical plots of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} curves as a function of w_j are shown in Figs 5 and 6, respectively. The experimental values of c_1 and c_2 are

Table 1—Real χ_{ij}' and imaginary χ_{ij}'' , parts of the complex dielectric orientation susceptibility χ_{ij}^* and static dielectric susceptibility χ_{oij} which are real for various weight fractions w_j 's of some aprotic polar liquids in benzenes at different temperatures under hf electric field

System	Temp. °C	Weight fraction w_j	χ_{ij}'	χ_{ij}''	χ_{oij}
I. DMSO	25	0.0022	0.0611	0.0280	0.0731
		0.0043	0.0890	0.0420	0.1094
		0.0047	0.0950	0.0460	0.1181
		0.0069	0.1231	0.0616	0.1594
		0.0086	0.1520	0.0798	0.1982
II. DMSO	30	0.0022	0.0630	0.0274	0.074
		0.0043	0.0915	0.0400	0.1095
		0.0047	0.0980	0.0440	0.1220
		0.0069	0.1155	0.0526	0.1500
		0.0086	0.1340	0.0648	0.1802
III. DMSO	35	0.0022	0.0600	0.0234	0.0693
		0.0043	0.0800	0.0330	0.108
		0.0047	0.0825	0.0360	0.1135
		0.0069	0.1104	0.0496	0.1564
		0.0086	0.1260	0.0580	0.1830
IV. DMSO	40	0.0022	0.0499	0.0170	0.0648
		0.0043	0.0774	0.0282	0.1054
		0.0047	0.0784	0.0286	0.1094
		0.0069	0.1083	0.0420	0.1541
		0.0086	0.1155	0.0500	0.1775
V. DEF	30	0.0023	0.0850	0.0256	0.1137
		0.0042	0.0899	0.0288	0.1335
		0.0079	0.0997	0.0384	0.1822
		0.0095	0.1033	0.0448	0.2053
VI. DMF	25	0.0027	0.0742	0.0256	0.0948
		0.0036	0.0872	0.0302	0.1162
		0.0048	0.1045	0.0386	0.1423
		0.0063	0.1291	0.0484	0.1855
VII. DMA	25	0.0026	0.0818	0.0213	0.1201
		0.0045	0.1046	0.0278	0.1559
		0.0056	0.1198	0.0330	0.1851
		0.0066	0.1370	0.0381	0.2083

also estimated from Eqs (1) and (2) with the measured values of $(\chi_{ij}'/\chi_{oij})_{w_j \rightarrow 0}$ and $(\chi_{ij}''/\chi_{oij})_{w_j \rightarrow 0}$ of Figs 5 and 6. These c_1 and c_2 are finally compared with theoretical ones in Table 3.

The symmetric and asymmetric distribution parameters γ and δ of the molecules under study are calculated and placed in the last columns of the Table 3 along with all the c_1 and c_2 's in order to see that the relaxation mechanism for such liquids are symmetric. The dipole moments μ_2 and μ_1 due to rotation of the whole molecule as well as the flexible parts of the molecules are determined from the slope β_1 of $\chi_{ij}'-w_j$ curve of Fig. 4 at $w_j \rightarrow 0$ in terms of estimated τ_1 and τ_2 of Eq. (3) as placed in Table 4. μ_2 's are again calculated from the τ 's of Eqs (4) and (25) of Murthy *et*

*al.*¹⁸ and the ratio of the individual slopes of Eqs (5) and (26) from susceptibility and conductivity measurements using slope β_1 of $\chi_{ij}'-w_j$ of Fig. 4 and β_2 of $\sigma_{ij}-w_j$ curve of Fig. 7. μ 's from both the measurements are entered in Table 4 along with estimated μ 's from Gopalakrishna's method¹⁶ quoted as reported ones in the Table 4.

The variations of measured μ_2 and μ_1 for DMSO in benzene with temperature in °C are given by the equations:

$$\begin{aligned} \mu_2 &= -231.61 + 15.597 t - 0.2272 t^2 \\ \mu_1 &= 19.825 - 0.626 t + 0.0108 t^2 \end{aligned} \quad \dots (10)$$

μ_2 of the parent molecule attains a maximum value of 36 C.m at 34.32°C with zero dipole moments at 21.72

Table 2—Relaxation times τ_2 and τ_1 from the slope and intercept of straight line Eq. (3), measured τ_j from different methods of susceptibility and conductivity measurement technique, reported τ , symmetric and characteristic relaxation times τ_s and τ_{cs} for different aprotic polar liquids under effective dispersive region of nearly 10 GHz electric field

System	Temp °C	Estimated τ_1 and τ_2 , ps		τ_j^a ps	τ_j^b ps	τ_j^c ps	τ_j^d ps	Rept [*] τ_j ps	τ_s ps	τ_{cs} ps
		τ_1	τ_2							
I. DMSO	25	8.09	21.07	9.91	6.79	8.77	6.01	5.37	4.88	3.69
II. DMSO	30	7.51	52.02	9.07	6.34	8.04	5.86	4.96	4.82	3.05
III. DMSO	35	6.50	59.68	9.08	9.03	7.47	8.95	4.70	4.21	—
IV. DMSO	40	4.51	39.00	8.38	4.90	7.09	4.46	4.33	3.74	22.20
V. DEF	30	3.89	76.41	16.86	1.06	6.64	0.58	2.42	4.16	15.66
VI. DMF	25	4.60	56.24	6.73	6.69	5.87	5.58	5.09	3.02	8.47
VII. DMA	25	2.20	56.61	3.05	6.53	4.96	3.11	6.53	3.90	81.95

τ_j^a = relaxation time from direct slope of Eq. (4); τ_j^b = relaxation time from ratio of individual slope of Eq. (5); τ_j^c = relaxation time from direct slope of Eq. (25); τ_j^d = relaxation time from ratio of individual slope of Eq. (26) and reported τ_j by using Gopalakrishna's¹⁶ method

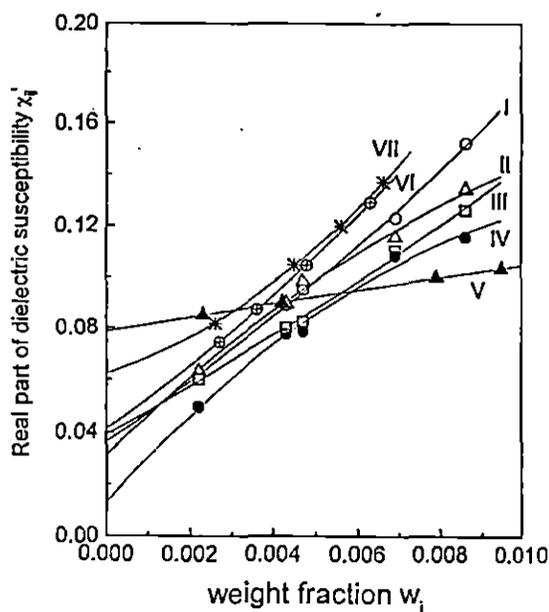


Fig. 4—Plot of real part of dielectric susceptibility χ'_{ij} with weight fraction w_j of DMSO, DEF, DMF and DMA in benzene (I) DMSO at 25°C (-o-), (II) DMSO at 30°C (-Δ-), (III) DMSO at 35°C (-□-), (IV) DMSO at 40°C (-●-), (V) DEF at 30°C (-▲-), (VI) DMF at 25°C (-⊕-) and (VII) DMA at 25°C (-*-)

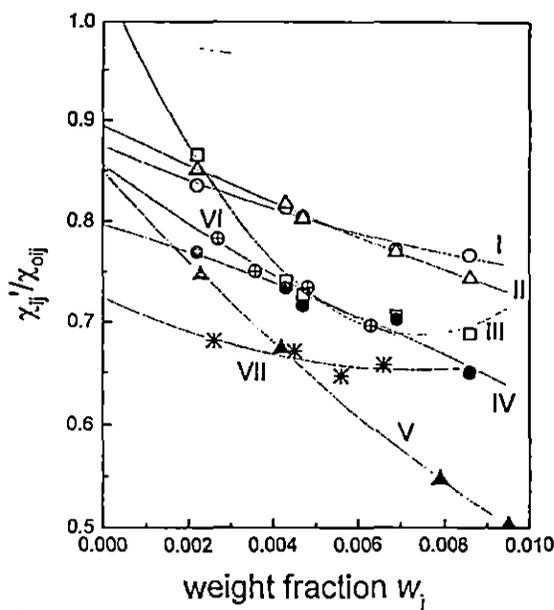


Fig. 5—Variation of χ'_{ij}/χ_{oij} with w_j 's of DMSO, DEF, DMF and DMA in benzene (I) DMSO at 25°C (-o-), (II) DMSO at 30°C (-Δ-), (III) DMSO at 35°C (-□-), (IV) DMSO at 40°C (-●-), (V) DEF at 30°C (-▲-), (VI) DMF at 25°C (-⊕-) and (VII) DMA at 25°C (-*-)

and 46.92°C, respectively due to monomer formation with C_6H_6 ring.

The theoretical dipole moment μ_{theo} 's of the molecules are calculated from the available infrared spectroscopic data of bond moments assuming the molecules are planar as sketched in Fig. 8. They are found to vary with the measured μ_j 's. The difference, how-

ever, indicates that the effect of inductive, mesomeric and electromeric moments of the substituent polar groups within the molecules along with temperature in the hf electric field is to be considered to have the conformation of the molecules under interest.

The thermodynamic energy parameters like enthalpy of activation ΔH_τ , free energy of activation ΔF_τ

Table 3—Fröhlich's parameter A [$=\ln(\tau_2/\tau_1)$], theoretical and experimental values of χ_{ij}'/χ_{oij} and χ_{ij}''/χ_{oij} of Fröhlich Eqs (8) and (9) and from fitting equations of Figs 5 and 6 at $\omega_j \rightarrow 0$, respectively, theoretical and experimental relative contributions c_1 and c_2 towards dielectric dispersion due to τ_1 and τ_2 , symmetric and asymmetric distribution parameters γ and δ for polar-nonpolar liquid mixtures of some aprotic polar liquids under effective dispersion region of nearly 10 GHz electric field

System	Temp °C	A	Theoretical values of χ_{ij}'/χ_{oij} and χ_{ij}''/χ_{oij} from Eqs (8) and (9)		Theoretical values of c_1 and c_2		Experimental values of χ_{ij}'/χ_{oij} and χ_{ij}''/χ_{oij} at $\omega_j \rightarrow 0$ of Figs 5 and 6		Experimental values of c_1 and c_2		Estimated values of γ and δ	
			χ_{ij}'/χ_{oij}	χ_{ij}''/χ_{oij}	c_1	c_2	χ_{ij}'/χ_{oij}	χ_{ij}''/χ_{oij}	c_1	c_2	γ	δ
I. DMSO	25	0.957	0.629	0.466	0.485	0.571	0.874	0.380	1.095	-0.061	-0.07	2.00
II. DMSO	30	1.935	0.449	0.434	0.423	0.933	0.894	0.389	1.049	0.022	-0.08	2.37
III. DMSO	35	2.217	0.454	0.419	0.425	1.043	1.039	0.371	1.192	-0.076	-0.29	--
IV. DMSO	40	2.241	0.611	0.409	0.507	0.794	0.797	0.266	0.803	0.228	0.21	0.36
V. DEF	30	2.978	0.476	0.378	0.443	1.380	0.849	0.247	0.890	0.210	0.17	0.36
VI. DMF	25	2.505	0.497	0.405	0.451	1.086	0.855	0.262	0.921	0.065	0.13	0.61
VII. DMA	25	3.248	0.601	0.357	0.531	1.093	0.724	0.185	0.713	0.338	0.47	0.18

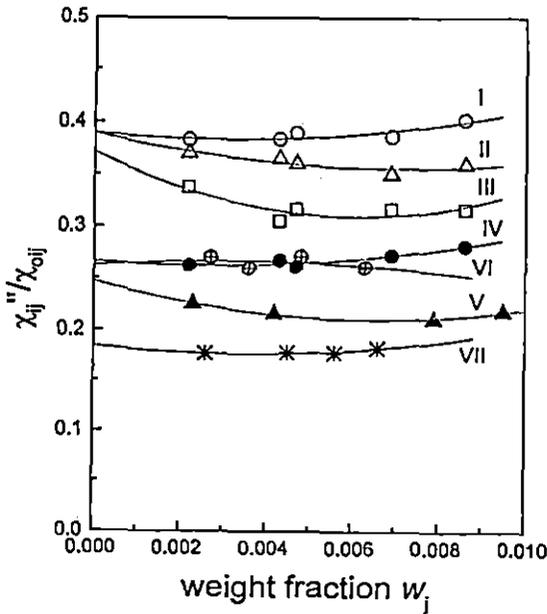


Fig. 6—Variation of χ_{ij}''/χ_{oij} with w_j 's of DMSO, DEF, DMF and DMA in benzene (I) DMSO at 25°C (-o-), (II) DMSO at 30°C (-Δ-), (III) DMSO at 35°C (-□-), (IV) DMSO at 40°C (-●-), (V) DEF at 30°C (-▲-), (VI) DMF at 25°C (-⊕-) and (VII) DMA at 25°C (-*-))

and entropy of activation ΔS_τ were obtained from the slope and intercept of linear equation of $\ln(\tau_1 T)$ against $1/T$ for DMSO as given by the equation:
 $\ln(\tau_2 T) = -4.8353 - 4.088 \times 10^3(1/T)$
 $\ln(\tau_1 T) = -30.568 + 3.216 \times 10^3(1/T)$... (11)

The variation of $\ln(\tau_1 T)$ or $\ln(\tau_2 T)$ against $1/T$ indicates that τ_1 obeys the Eyring rate process whereas τ_2 does not.

2 Symmetric and Asymmetric Distribution Parameters γ and δ

The polar-nonpolar liquid mixtures under study are non-rigid in nature exhibiting two relaxation times τ_2 and τ_1 at a single frequency electric field¹⁹. The measured values of χ_{ij}''/χ_{oij} when plotted against χ_{ij}'/χ_{oij} at $\omega_j \rightarrow 0$ for different frequency ω at a fixed experimental temperature for DMSO may either show Cole-Cole semicircular arc or Cole-Davidson skewed arc having symmetric and asymmetric distribution of relaxation behaviour according to following equations:

$$\frac{\chi_{ij}'}{\chi_{oij}} = \frac{1}{1 + (j\omega\tau_s)^{1-\gamma}} \quad \dots (12)$$

$$\frac{\chi_{ij}''}{\chi_{oij}} = \frac{1}{(1 + j\omega\tau_{cs})^\delta} \quad \dots (13)$$

where τ_s and τ_{cs} are symmetric and characteristics relaxation times related to symmetric and asymmetric distribution parameters γ and δ , respectively. On separation, the real and imaginary parts of Eq. (12), one gets:

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[\left(1 - \frac{\chi_{ij}'}{\chi_{oij}} \right) \frac{\chi_{ij}'/\chi_{oij}}{\chi_{ij}''/\chi_{oij}} - \frac{\chi_{ij}''}{\chi_{oij}} \right] \quad \dots (14)$$

$$\tau_s = \frac{1}{\omega} \left[\frac{1}{\left(\frac{\chi_{ij}'/\chi_{oij}}{\chi_{ij}''/\chi_{oij}} \cos \frac{\gamma\pi}{2} - \sin \frac{\gamma\pi}{2} \right)^{1-\gamma}} \right] \quad \dots (15)$$

Table 4—Slope β_1 of χ'_{ij} versus w_j and β_2 of σ_{ij} versus w_j curves, measured dipole moments μ_2 and μ_1 from susceptibility measurement technique, μ_j^a 's from Eqs (22) and (29), respectively, reported dipole moment, theoretical dipole moment μ_{theo} from available bond angles and bond moments expressed in Coulomb metre (C.m) and the values of μ_1/μ_{theo} for some aprotic polar liquids in benzene under effective dispersion region of nearly 10 GHz electric field

System mol wt	Slope of χ'_{ij} - w_j and σ_{ij} - w_j curves		Dipole moments μ_j ($\times 10^{-30}$) in Coulomb metre							μ_1/μ_{theo}	
	β_1	β_2	From Eq (22)		μ_j^a	μ_j^b	μ_j^c	μ_j^d	μ_j^e		μ_{theo}
			μ_2	μ_1							
I.DMSO at 25°C $M_j=0.078$ kg	10.943	6.280	14.69	10.30	10.75	10.03	11.10	10.48	12.65	15.18	0.67
II.DMSO at 30°C $M_j=0.078$ kg	16.440	9.096	36.69	12.64	13.09	12.35	13.31	12.75	12.79	15.18	0.83
III.DMSO at 35°C $M_j=0.078$ kg	8.950	4.621	31.09	9.27	9.79	9.78	9.50	9.82	13.49	15.18	0.61
IV.DMSO at 40°C $M_j=0.078$ kg	17.646	9.894	30.37	12.69	13.70	12.82	13.94	13.32	13.73	15.18	0.83
V.DEF at 30°C $M_j=0.101$ kg	2.870	2.922	26.62	5.67	7.91	5.53	8.18	7.58	12.96	13.30	0.42
VI.DMF at 25°C $M_j=0.073$ kg	10.938	7.282	33.21	9.37	9.81	9.80	10.54	10.48	12.09	12.73	0.74
VII.DMA at 25°C $M_j=0.087$ kg	5.147	2.792	24.97	6.83	7.07	6.89	7.00	6.81	11.26	13.37	0.51

μ_j^a = dipole moment by using τ from the direct slope of Eq. (4); μ_j^b = dipole moment by using τ from the ratio of individual slopes of Eq. (5); μ_j^c = dipole moment by using τ from the direct slope of Eq. (25); μ_j^d = dipole moment by using τ from the ratio of individual slopes of Eq. (26); μ_j^e = reported dipole moment using Gopalakrishna's¹⁶ τ and μ_{theo} = theoretical dipole moment from the available bond moments.

On simplification of Eq. (13) further, one gets :

$$\frac{1}{\phi} \log(\cos \phi) = \frac{\log \left[\left(\chi'_{ij} / \chi_{oij} \right) / \cos(\phi\delta) \right]}{\phi\delta} \quad \dots (16)$$

$$\tan(\phi\delta) = \frac{\left(\chi''_{ij} / \chi_{oij} \right)_{w_j \rightarrow 0}}{\left(\chi'_{ij} / \chi_{oij} \right)_{w_j \rightarrow 0}} \quad \dots (17)$$

where $\tan \phi = \omega\tau_{cs}$

A theoretical curve of $(1/\phi) \log(\cos \phi)$ with ϕ in degrees was drawn⁵ to get the known values of ϕ and δ in terms of measured parameter of $[\log \{ (\chi'_{ij} / \chi_{oij}) / \cos(\phi\delta) \}] / (\phi\delta)$ of Eqs (16) and (17). All the τ_s , τ_{cs} and δ ϕ are given in Tables 2 and 3, respectively.

3 Dipole Moment μ_j from Susceptibility Measurement

Debye equation²⁰ of relative permittivities of a polar solute (j) dissolved in a non-polar solvent (i) in terms of complex dielectric orientational susceptibility χ^*_{ij} of solution can be written as:

$$\frac{\chi^*_{ij}}{\chi_{oij}} = \frac{1}{1 + j\omega\tau} \quad \dots (18)$$

where χ'_{ij} ($=\epsilon_{ij}' - \epsilon_{\infty ij}$) and χ''_{ij} ($=\epsilon_{ij}''$) are the real and imaginary parts of $\chi^*_{ij} = \chi'_{ij} - j\chi''_{ij}$. $j = \sqrt{-1}$ is a complex number χ_{oij} ($=\epsilon_{oij} - \epsilon_{\infty ij}$) is the low frequency susceptibility which is real.

Again, the imaginary part of dielectric orientational susceptibility χ''_{ij} as a function of w_j can be written according to Smith²¹ as:

$$\chi''_{ij} = \frac{N\rho_{ij}\mu_j^2}{27\epsilon_o k_B T M_j} \frac{\omega\tau}{1 + \omega^2\tau^2} (\epsilon_{ij} + 2)^2 w_j \quad \dots (19)$$

On differentiation of Eq. (19) w.r. to w_j at $w_j \rightarrow 0$, one gets:

$$\left(\frac{d\chi''_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_{ij}\mu_j^2}{27\epsilon_o k_B T M_j} \frac{\omega\tau}{1 + \omega^2\tau^2} (\epsilon_i + 2)^2 \quad \dots (20)$$

where k_B is the Boltzmann constant, N the Avogadro's Number ϵ_i the relative permittivity of the solute and ϵ_o

is the absolute permittivity of free space = $8.854 \times 10^{-12} \text{ F.m}^{-1}$, all expressed in SI units. Comparing Eqs (4) and (20), one gets:

$$\left(\frac{d\chi_{ij}'}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_i \mu_j^2}{27\epsilon_0 k_B T M_j} \frac{1}{1 + \omega^2 \tau^2} (\epsilon_i + 2)^2 = \beta_1 \quad \dots (21)$$

where β_1 is the slope of $\chi_{ij}' - w_j$ curves at $w_j \rightarrow 0$.

From Eq. (21), one gets the dipole moment μ_j as:

$$\mu_j = \left(\frac{27\epsilon_0 k_B T M_j \beta_1}{N\rho_i (\epsilon_i + 2)^2 b} \right)^{\frac{1}{2}} \quad \dots (22)$$

where $b = 1/(1 + \omega^2 \tau^2)$ is the dimensionless parameter involved with measured τ_j of Table 2. All the μ_j 's are placed in Table 4.

4 Dipole Moment μ_j from hf Conductivity Measurement

The hf complex conductivity σ_{ij}^* of a polar-non-polar liquid mixture is given by:

$$\sigma_{ij}^* = \sigma_{ij}' + j\sigma_{ij}'' = \omega\epsilon_0 (\epsilon_{ij}' + j\epsilon_{ij}'') \quad \dots (23)$$

the real σ_{ij}' and imaginary σ_{ij}'' parts of σ_{ij}^* are related by:

$$\sigma_{ij}'' = \sigma_{\infty ij} + \frac{1}{\omega\tau_j} \sigma_{ij}' \quad \dots (24)$$

where $\sigma_{\infty ij}$ is the constant conductivity at infinite dilution i.e. at $w_j \rightarrow 0$. The Eq. (24) on differentiation w.r.t. σ_{ij}' yields:

$$\frac{d\sigma_{ij}''}{d\sigma_{ij}'} = \frac{1}{\omega\tau_j} \quad \dots (25)$$

which provides a convenient method to obtain τ_j of a polar molecule. It is, however, better to use the ratio of the slopes of variation of σ_{ij}'' and σ_{ij}' with w_j in order to avoid polar-polar interactions at $w_j \rightarrow 0$ in a given solvent to get τ_j from:

$$\frac{(d\sigma_{ij}''/dw_j)_{w_j \rightarrow 0}}{(d\sigma_{ij}'/dw_j)_{w_j \rightarrow 0}} = \frac{1}{\omega\tau_j} \quad \dots (26)$$

In hf region of GHz range, it is generally observed that $\sigma_{ij}'' \cong \sigma_{ij}$ the total hf conductivity²² of the solution. Therefore, the Eq. (24) can be written as:

$$\sigma_{ij} = \sigma_{\infty ij} + \frac{1}{\omega\tau_j} \sigma_{ij}' \quad \dots (27)$$

$$\beta_2 = \frac{1}{\omega\tau_j} \left(\frac{d\sigma_{ij}'}{dw_j} \right)_{w_j \rightarrow 0}$$

where β_2 is the slope of $(d\sigma_{ij}'/dw_j)_{w_j \rightarrow 0}$. The real part σ_{ij}' of a polar-nonpolar liquid mixture is given by⁵:

$$\sigma_{ij}' = \frac{N\rho_{ij} \mu_j^2}{27k_B T M_j} \frac{\omega^2 \tau_j}{1 + \omega^2 \tau_j^2} (\epsilon_{ij} + 2)^2 w_j$$

$$\left(\frac{d\sigma_{ij}'}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_{ij} \mu_j^2}{27k_B T M_j} \frac{\omega^2 \tau_j}{1 + \omega^2 \tau_j^2} (\epsilon_i + 2)^2 \quad \dots (28)$$

Now comparing Eqs (27) and (28), one gets hf μ_j from:

$$\mu_j = \left(\frac{27k_B T M_j \beta_2}{N\rho_{ij} (\epsilon_i + 2)^2 \omega b} \right)^{\frac{1}{2}} \quad \dots (29)$$

where $b = 1/(1 + \omega^2 \tau^2)$ is involved with τ_j 's from Eqs (25) and (26). μ_j 's thus obtained from Eq. (29) are placed in Table 4 along with Gopalakrishna's μ_j and μ_{theo} 's.

5 Results and Discussion

The relaxation parameters in terms of real χ_{ij}' ($=\epsilon_{ij}' - \epsilon_{\infty ij}$), imaginary χ_{ij}'' ($=\epsilon_{ij}''$) and low frequency susceptibility χ_{oij} ($=\epsilon_{oij} - \epsilon_{\infty ij}$), which are real and extracted from the measured relative permittivities ϵ_{ij} 's for different w_j 's of solute at 25, 30, 35 and 40°C for DMSO, 25°C for DMA and DMF and 30°C for DEF under nearly 10 GHz electric field as shown in Table 1. The curves of $(\chi_{oij} - \chi_{ij}')/\chi_{ij}'$ against χ_{ij}''/χ_{ij}' at different w_j 's of solute are plotted from the measured data in Fig. 1. All the curves show two relaxation times τ_2 and τ_1 due to rotation of the whole molecule and the flexible part attached to the parent ones as evident from Table 2. It indicates that the molecules are of non-rigid nature. Unlike τ_2 's, τ_1 's of DMSO at 25, 30, 35 and 40°C decrease gradually (Table 2). This indicates that τ_1 's obey the Debye relaxation mechanism. It is also evident from Table 2 and Fig. 1 that the graphs of $(\chi_{oij} - \chi_{ij}')/\chi_{ij}'$ against χ_{ij}''/χ_{ij}' for different w_j 's of DMSO shift towards the origin with the increase of temperature. τ_2 's of all the liquids are much larger in magnitude than τ_1 . The parent mole-

cule takes larger time to lag with the electric field frequency for its inertia in comparison to its flexible parts which are supported by the two relaxation model of polar unit under nearly 10 GHz electric field²³. τ_j 's are estimated and placed in Table 2 from Eqs (4) and (5) using linear slope of χ_{ij}'' against χ_{ij}' at different w_j 's and the ratio of individual slopes of $\chi_{ij}''-w_j$ and $\chi_{ij}'-w_j$ curves at $w_j \rightarrow 0$ of Figs 3 and 4, respectively. The values of τ_j from Eq. (4) are larger than from Eq. (5). Reported τ 's and τ_j 's calculated from both the Gopalakrishna's method¹⁶ as well as conductivity measurement technique using Eqs (25) and (26), respectively. The agreement is better from the τ_j 's due to ratio of the individual slopes of $\chi_{ij}''-w_j$ and $\chi_{ij}'-w_j$ curves at $w_j \rightarrow 0$ of Figs 3 and 4 because the polar-polar interactions are almost avoided. They are then compared with the reported τ_s and τ_{cs} of the molecules assuming symmetric and asymmetric distribution of relaxation processes only to show that the molecules obey symmetric distribution. The curves χ_{ij}'' against χ_{ij}' of Fig. 2 of the molecules are found to meet at a point in the region of $0 < w_j < 0.02$ except DEF the data was measured at 30°C. The experimental curves of $\chi_{ij}''-w_j$ and $\chi_{ij}'-w_j$ are not linear as shown in Figs 3 and 4, respectively. Like $\chi_{ij}'-w_j$ curves all the curves of $\chi_{ij}''-w_j$ of Fig. 3 are parabolic in nature and increase with the w_j 's of solute. The magnitude of χ_{ij}'' is, however, maximum in lower temperature region and decrease with the rise of temperature. This indicates the absorption of electric energy in the polar-non-polar mixture in the lower temperature region.

The relative contributions c_1 and c_2 due to τ_1 and τ_2 could, however, be estimated from the χ_{ij}''/χ_{oij} and χ_{ij}'/χ_{oij} of Fröhlich's Eqs (8) and (9) and placed in Table 3 assuming a continuous distribution of τ between limiting values of τ_1 and τ_2 . c_1 and c_2 are also calculated in terms of fixed values of $(\chi_{ij}''/\chi_{oij})_{w_j \rightarrow 0}$ and $(\chi_{ij}'/\chi_{oij})_{w_j \rightarrow 0}$ of the graphical plots of $(\chi_{ij}''/\chi_{oij})-w_j$ and $(\chi_{ij}'/\chi_{oij})-w_j$ curves of Figs 5 and 6 respectively. All the curves are extrapolated to get the fixed values of (χ_{ij}''/χ_{oij}) and (χ_{ij}'/χ_{oij}) at $w_j \rightarrow 0$. They are substituted in the Bergmann's Eqs (6) and (7) to get c_1 and c_2 for the fixed values of τ_1 and τ_2 , respectively. All the c 's are placed in Table 3 for comparison with Fröhlich's method. Both c_1 and c_2 from Fröhlich's¹⁵ equations are all +ve for all the liquids. But c_2 for DMSO at 25 and 35°C are -ve from the graphical method. The -ve value of c_2 is physically

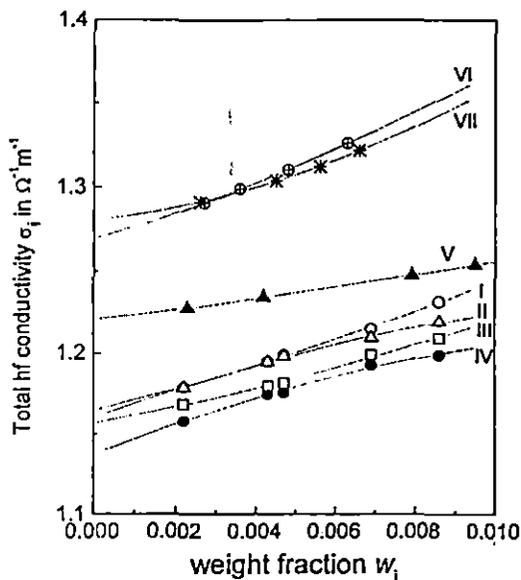


Fig. 7—Variation of total hf conductivity σ_{ij} with w_j 's of DMSO, DEF, DMF and DMA in benzene (I) DMSO at 25°C (-o-), (II) DMSO at 30°C (-Δ-), (III) DMSO at 35°C (-□-), (IV) DMSO at 40°C (-●-), (V) DEF at 30°C (-▲-), (VI) DMF at 25°C (-⊕-) and (VII) DMA at 25°C (-*-)

meaningless as they are considered to be the relative contributions towards dielectric relaxation processes. This may indicate that the rotation of whole molecule under hf electric field is not in accord with the flexible part probably due to inertia as observed elsewhere^{10,11}. The variation of χ_{ij}''/χ_{oij} and χ_{ij}'/χ_{oij} with w_j as shown in Figs 5 and 6 are expected to be concave and convex^{10,11} respectively. All the curves of Figs 5 and 6 are, however, concave except systems VI (-⊕-) of Fig. 6. This type of anomalous behaviour in the variation of χ_{ij}''/χ_{oij} and χ_{ij}'/χ_{oij} with w_j invariably demands careful measurement of data in low concentration region.

The dipole moments μ_1 and μ_2 are also calculated from the slope β_1 of $\chi_{ij}'-w_j$ curve of Fig. 4 and estimated τ_1 and τ_2 as shown in Table 4. They are compared with μ_j 's from τ_j 's of Eqs (4) and (5), respectively. μ_j 's from Gopalakrishna's method¹⁶ and conductivity measurement technique⁹ are also reported and placed in Table 4 for comparison among them. The total hf conductivity σ_{ij} is plotted against w_j 's of the polar-nonpolar liquid mixture as seen in Fig. 7 only to show that all the curves are parabolic in nature exhibiting maximum conductivity at lower temperature and higher concentration for DMSO. At $w_j \rightarrow 0$, the curves are found to yield different value of σ_{ij} probably due to the term $1/(M_j T)$ in the Eq. (28) as seen in Fig. 7. The difference in estimated μ_2 and μ_1 from conductivity and susceptibility measurements

suggests the involvement of bound molecular charges towards μ 's of polar liquid. It is evident from Table 4 that μ_1 's of the polar liquids are found to be in excellent agreement with the reported μ 's. It, thus, reveals that a part of the molecule is rotating under 10 GHz electric field as observed earlier²⁴. The variation of μ_1 and μ_2 with temperature for DMSO is given by Eq. (10). The convex nature of μ_1 - t equation reveals the fact that the molecule DMSO attains higher asymmetry of larger μ_1 at a certain temperature. It also shows zero dipole moments at two different temperatures indicating the symmetric nature of the molecule. The variation of μ_1 with temperature may occur due to elongation of bond moments. This further invites the extensive study of the relaxation phenomena of highly non-spherical dipolar molecules at different experimental temperatures and in different solvents.

The theoretical dipole moment μ_{theo} 's of the polar molecules are calculated assuming the planar structure from the available bond moments of 7.83×10^{-30} C.m., 5.17×10^{-30} C.m. for polar groups $S \leftarrow \text{CH}_3$, $\text{O} \leftarrow \text{S}$ in DMSO 2.13×10^{-30} C.m., 2.60×10^{-30} C.m., 1.23×10^{-30} C.m. of $\text{N} \leftarrow \text{CH}_3$, $\text{N} \leftarrow \text{C}_2\text{H}_5$, $\text{CH}_3 \leftarrow \text{C}$ in DMF, DEF and DMA respectively. The other bond moments are 1×10^{-30} C.m., 1.5×10^{-30} C.m., 10.33×10^{-30} C.m. for $\text{C} \leftarrow \text{H}$, $\text{C} \leftarrow \text{N}$ and $\text{C} \leftarrow \text{O}$ in them. The bond moments are, however, reduced by a factor μ_1/μ_{theo} to yield exact μ 's as sketched in Fig. 8. The reduction or elongation in bond moments of the substituent polar groups may occur due to inductive, mesomeric and electromeric effects which in turn subsequently act as pusher or puller of electrons in them. The solvent C_6H_6 is a cyclic and planar compound and has three double bonds and six p-electrons on six C-atoms. The dipolar liquid molecules are aliphatic and planar ones. Hence, π - π interaction or resonance effect combined with inductive effect commonly known as mesomeric effect in excited state called the electromeric effect may play the vital role in the estimation of μ_{theo} 's of Fig. 8.

The thermodynamic energy parameters like enthalpy of activation ΔH_τ entropy of activation ΔS_τ and free energy of activation ΔF_τ of DMSO were calculated from the slope and intercept of $\ln(\tau_1 T)$ against $(1/T)$ of Eq. (11) on the basis of Eyrings theory considering the rotation of the polar molecule as a rate process. Unlike $\ln(\tau_2 T)$ against $(1/T)$; $\ln(\tau_1 T)$ against $(1/T)$ of DMSO is in accord with the Eyring's rate

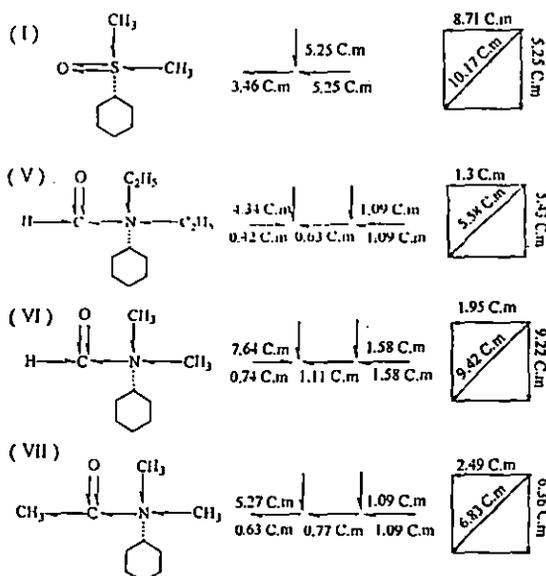


Fig. 8—Conformational structures of aprotic polar liquids in terms of reduced bond length due to mesomeric and inductive moments in Coulomb metre (Cm) $\times 10^{30}$ of the substituent polar groups: (I) DMSO (II) DEF (III) DMF (IV) DMA

theory²⁰. The value of ΔH_τ for DMSO is 6.85 in KJ mole⁻¹ ΔS_τ are -8.21 , -8.15 , -11.65 , -11.48 in J mole⁻¹ K⁻¹ and ΔF_τ are 9.30, 9.32, 10.43 and 10.45. at 25, 30, 35 and 40°C, respectively in KJ. mole⁻¹. It is observed that ΔS_τ are $-ve$ indicating the activated states are more ordered than the normal states especially for DMSO.

6 Conclusions

The study of relaxation phenomena of aprotic polar liquids of amides in C_6H_6 in terms of the modern established symbols of dielectric terminologies and parameters of orientational susceptibilities χ_{ij} 's measured under a single frequency electric field is very encouraging and interesting. It seems to be more topical, significant and useful contribution to predict the conformational structures and various molecular associations of the molecules at any given temperatures. The intercept and slope of derived linear Eq. (3) on the measured data of χ_{ij} of different w_j 's are used to get τ_2 and τ_1 . The prescribed methodology in SI units is superior because of the unified, coherent and rationalised nature because χ_{ij} 's are directly linked only with orientational polarisation of the molecules. The significant Eqs (4) and (5) to obtain values of τ_j and hence, values of μ_j from Eq. (22) help the future researchers to shed more light on the relaxation phenomena of complicated non-spherical polar liquids and liquid crystals. The present method to obtain val-

ues of τ_j from Eq. (5) with the use of the ratio of the individual slopes of χ_{ij}'' versus w_j and χ_{ij}' versus w_j curves at $w_j \rightarrow 0$ is a significant improvement over the existing ones, as it eliminates polar-polar interaction almost completely in τ_j 's and μ_j 's, respectively.

The values of τ_j and μ_j are usually claimed to be accurate within 10 and 5%, respectively. The tested correlation coefficients r 's and % of errors of Eq. (3) demand that τ and μ are more than accurate. The DMSO, DMF, DMA and DEF molecules absorb electric energy much more strongly under nearly 10 GHz electric field, at which the variation of χ_{ij}'' against frequency ω seem to be large. This at once indicates the attention to get the double relaxation phenomena from Eq. (3). The sum of the experimental and theoretical values of weighted contributions c_1 and c_2 towards dielectric dispersions due to estimated τ_2 and τ_1 differ significantly to indicate more than two Debye type relaxations in such molecules because of their complexity. It can, further, be observed that only a part of the molecule is rotating under nearly 10 GHz electric field since $\ln(\tau_1 T)$ against $1/T$ obeys the Eyring's rate theory. The values of μ_2 and μ_1 due to τ_2 and τ_1 are expected to be smaller when they are measured from susceptibility measurement technique rather than the hf conductivity and permittivity methods, where approximation of $\sigma_{ij} \approx \sigma'_{ij}$ is usually made. The measurement of μ 's from hf conductivities σ_{ij} 's and hf permittivities ϵ_{ij} 's is involved with the contributions of the bound molecular charges and all types of polarisations including the fast one. The difference of μ_1 and μ_j from μ_{theo} may arise, either by elongation or reduction of the bond moments of the substituted polar groups by factor μ_1/μ_{theo} in agreement with the measured μ 's to take into account of the inductive, mesomeric and electromeric effects of the substituted polar groups in the molecules under investigation. Thus, the correlation between the conformational structures with the observed results enhances the scientific content to add a new horizon of understanding the existing knowledge of dielectric relaxation phenomena.

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The physico-chemical aspects of some long straight chain alcohols from susceptibility measurement under a 24 GHz electric field at 25 °C

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Abstract

The straight line equation $(\chi_{oij} - \chi_{ij}')/\chi_{ij}' = \omega(\tau_1 + \tau_2)(\chi_{ij}''/\chi_{ij}') - \omega^2\tau_1\tau_2$ for different weight fractions w_j 's of some dipolar long straight chain alcohols (j) in *n*-heptane (i) is derived from the available relative permittivities ϵ_{ij}' , ϵ_{ij}'' , ϵ_{oij} and ϵ_{oij} at 25 °C under 24 GHz electric field. The intercepts and slopes of the above equation are used to get relaxation times τ_1 and τ_2 of the rotation of the flexible part and the whole molecule itself. $\chi_{ij}' (= \epsilon_{ij}' - \epsilon_{oij})$ and $\chi_{ij}'' (= \epsilon_{ij}'' - \epsilon_{oij})$ are the real and imaginary parts of hf dimensionless complex dielectric orientational susceptibility χ_{ij}^* and χ_{oij} ($= \epsilon_{oij} - \epsilon_{oij}$) is the low frequency dielectric susceptibility which is real. τ_j 's of such alcohols are also measured from the ratio of the slopes of the individual variations of χ_{ij}' and χ_{ij}'' with w_j at $w_j \rightarrow 0$ and the direct slope of χ_{ij}'' versus χ_{ij}' equations of Murthy et al. [M.B.R. Murthy, R.L. Patil and D.K. Deshpande, Indian J. Phys 63B (1989) 491]. These τ_j 's are finally compared with the reported τ_j 's of Gopalakrishna [K.V. Gopalakrishna, Trans Faraday Soc. 53 (1957) 767] and τ_1 , τ_2 by double relaxation method to see that the flexible part of the molecule is only rotating under the most effective dispersive region of the 24 GHz electric field. The weighted contributions c_1 and c_2 towards dielectric relaxations for estimated τ_1 , τ_2 are, however, obtained from Fföhlich's theoretical formulations of χ_{ij}'/χ_{oij} and χ_{ij}''/χ_{oij} to compare them with those of graphical ones of $(\chi_{ij}'/\chi_{oij})_{w_j \rightarrow 0}$ and $(\chi_{ij}''/\chi_{oij})_{w_j \rightarrow 0}$. The latter ones are used to get the symmetric distribution parameter γ to have the symmetric relaxation times τ_s . The arbitrary curve of $(1/\phi) \log \cos \phi$ against ϕ in degree together with $(\chi_{ij}'/\chi_{oij})_{w_j \rightarrow 0}$ and $(\chi_{ij}''/\chi_{oij})_{w_j \rightarrow 0}$ experimentally obtained gives the asymmetric distribution parameter δ to get the characteristic relaxation time τ_{cs} . All these findings finally establish the symmetric relaxation behaviour for such compounds. The dipole moments μ_1 and μ_2 for the flexible part and the whole molecule are determined from τ_1 and τ_2 and the linear coefficient β of χ_{ij}' versus w_j 's curves. All the measured μ_j 's are compared with the reported μ_j 's and μ_{theo} 's derived from the bond angles and bond moments of the substituted polar groups of the compounds to arrive at the physico-chemical properties by the conformations sketched in the paper. The slight disagreement of estimated μ_j 's and μ_{theo} 's is, however, explained with the consideration of inductive and mesomeric moments in addition to strong hydrogen bonding of the flexible polar groups attached to the parent molecule.

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1. Introduction

The relaxation process of dipolar liquid or solid material (DRL or DRS) is very encouraging in the study of the physico-chemical molecular behaviour and structures through the different experimental techniques [1,2]. The methods consist of the measurements of high frequency (hf) conductivity [3], hf susceptibility [4], thermally stimulated depolarization current density (TSDC) [5], isothermal frequency domain of AC spectroscopy (IFDS) [6], etc. Although the latter two methods are very important as they provide one with the necessary information of dielectric relaxations, these methods are very lengthy and often needs a tedious computer simulation work in

comparison to the former methods. The hf conductivity or susceptibility measurement techniques are much simpler, straightforward and unique one within the framework of the Debye model [7] to give the firm answer to the problem with which the present research group is usually dealing with.

Straight chain alcohols behave almost like polymers in dispersion regions. The strong dipole of the -OH group rotates about the C=O bond without disturbing -CH₃ and -CH₂ groups. They thus have the possibility to exhibit intramolecular as well as intermolecular rotations. Glasser et al. [8] and Crossley et al. [9], however, measured the real ϵ_{ij}' , imaginary ϵ_{ij}'' , parts of hf complex relative permittivity ϵ_{ij}^* along with the static ϵ_{oij} and optical ϵ_{oij} of relative permittivities of alcohols at 25 °C under different gigahertz electric field frequencies. As evident from Table 1, the

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Table 1
Measured relative permittivities ϵ'_{ij} , ϵ''_{ij} , ϵ_{oij} , $\epsilon_{a ij}$, real χ'_{ij} , imaginary χ''_{ij} parts of hf complex susceptibility χ^*_{ij} and low frequency susceptibility χ_{oij} of some dipolar alcohols at 25 °C for different weight fractions w_j of solutes under 24 GHz electric field in solvent *n*-heptane

Systems with mol. wt. (M_j) in kg (in <i>n</i> -heptane)	Weight fraction w_j of solute	ϵ'_{ij}	ϵ''_{ij}	ϵ_{oij}	$\epsilon_{a ij}$	χ'_{ij} (= $\epsilon'_{ij} - \epsilon_{a ij}$)	χ''_{ij} (= ϵ''_{ij})	χ_{oij} (= $\epsilon_{oij} - \epsilon_{a ij}$)
I. 1-butanol ($M_j=0.074$)	0.0291	1.9570	0.0079	1.9710	1.9280	0.0290	0.0079	0.0430
	0.0451	1.9810	0.0147	2.0000	1.9450	0.0360	0.0147	0.0550
	0.0697	2.0110	0.0236	2.0500	1.9580	0.0530	0.0236	0.0920
	0.1163	2.0600	0.0425	2.1750	1.9780	0.0820	0.0425	0.1970
	0.1652	2.1050	0.0644	2.3810	2.0000	0.1050	0.0644	0.3810
	0.2072	2.1440	0.0818	2.6210	2.0200	0.1240	0.0818	0.6010
II. 1-hexanol ($M_j=0.102$)	0.0458	1.9680	0.0131	1.9880	1.9440	0.0240	0.0131	0.0440
	0.0703	1.9840	0.0190	2.0150	1.9520	0.0320	0.0190	0.0630
	0.1028	2.0010	0.0296	2.0640	1.9700	0.0310	0.0296	0.0940
	0.1687	2.0370	0.0425	2.1960	1.9890	0.0480	0.0425	0.2070
	0.2335	2.0880	0.0569	2.3600	2.0020	0.0860	0.0569	0.3580
	0.2901	2.1340	0.0748	2.5800	2.0180	0.1160	0.0748	0.5620
III. 1-heptanol ($M_j=0.116$)	0.0564	1.9680	0.0147	1.9850	1.9320	0.0360	0.0147	0.0530
	0.0735	1.9750	0.0182	2.0080	1.9450	0.0300	0.0182	0.0630
	0.1175	2.0070	0.0265	2.0660	1.9570	0.0500	0.0265	0.1090
	0.1909	2.0760	0.0482	2.1950	1.9890	0.0870	0.0482	0.2060
	0.2465	2.0970	0.0567	2.3150	2.0020	0.0950	0.0567	0.3130
	0.2970	2.1260	0.0693	2.4640	2.0080	0.1180	0.0693	0.4560
IV. 1-decanol ($M_j=0.158$)	0.0572	1.9650	0.0120	1.9760	1.9400	0.0250	0.0120	0.0360
	0.0857	1.9790	0.0223	2.0030	1.9520	0.0270	0.0223	0.0510
	0.1351	2.0030	0.0273	2.0500	1.9640	0.0390	0.0273	0.0860
	0.2140	2.0360	0.0449	2.1470	1.9900	0.0460	0.0449	0.1570
	0.2640	2.0640	0.0513	2.2200	2.0080	0.0560	0.0513	0.2120
	0.3353	2.0970	0.0637	2.3460	2.0300	0.0670	0.0637	0.3160
V. 2-methyl 3-heptanol ($M_j=0.130$)	0.0437	1.9600	0.0156	1.9710	1.9300	0.0300	0.0156	0.0410
	0.1299	2.0220	0.0361	2.0590	1.9660	0.0560	0.0361	0.0930
	0.2522	2.0950	0.0565	2.1720	2.0070	0.0880	0.0565	0.1650
	0.4081	2.1690	0.0809	2.3300	2.0540	0.1150	0.0809	0.2760
VI. 3-methyl-3-heptanol ($M_j=0.130$)	0.0450	1.9650	0.0137	1.9740	1.9340	0.0310	0.0137	0.0400
	0.1334	2.0280	0.0393	2.0690	1.9660	0.0620	0.0393	0.1030
	0.2538	2.1030	0.0674	2.1800	2.0040	0.0990	0.0674	0.1760
	0.4085	2.1680	0.0928	2.3340	2.0570	0.1110	0.0928	0.2770
VII. 4-methyl-3-heptanol ($M_j=0.130$)	0.0466	1.9640	0.0146	1.9760	1.9360	0.0280	0.0146	0.0400
	0.1326	2.0250	0.0375	2.0650	1.9690	0.0560	0.0375	0.0960
	0.2590	2.1040	0.0616	2.1850	2.0110	0.0930	0.0616	0.1740
	0.4124	2.1800	0.0849	2.3520	2.0650	0.1150	0.0849	0.2870
VIII. 5-methyl-3-heptanol ($M_j=0.130$)	0.1228	2.0080	0.0296	2.0480	1.9560	0.0520	0.0296	0.0920
	0.2489	2.0750	0.0511	2.1680	2.0040	0.0710	0.0511	0.1640
	0.3898	2.1480	0.0676	2.3150	2.0400	0.1080	0.0676	0.2750
IX. 4-octanol ($M_j=0.130$)	0.1201	2.0000	0.0265	2.0400	1.9480	0.0520	0.0265	0.0920
	0.2445	2.0670	0.0449	2.1480	1.9970	0.0700	0.0449	0.1510
	0.3838	2.1400	0.0659	2.2820	2.0310	0.1090	0.0659	0.2510
	0.1236	2.0010	0.0245	2.0490	1.9540	0.0470	0.0245	0.0950
X. 2-octanol ($M_j=0.130$)	0.2479	2.0680	0.0513	2.1950	1.9960	0.0720	0.0513	0.1990
	0.3844	2.1410	0.0680	2.4100	2.0360	0.1050	0.0680	0.3740

available relative permittivities ϵ''_{ij} 's, if plotted against frequency ' f ', will show the sharp peak [10] at 24 GHz electric field frequency. At this resonance frequency, the alcohol molecules in the solvent *n*-heptane absorb electric energy much more to give exact and reliable values of relative permittivities. This at once suggests that the 24 GHz electric field frequency is the most effective dispersive region of such normal and octyl alcohols and prompted the present workers to study the physico-chemical aspects of long straight chain alcohols in terms of the hf susceptibilities χ'_{ij} , χ''_{ij} and χ_{oij} as the data are available only at 25 °C. The data are, however, collected in Table 1 upto four decimal places. The hf dielectric susceptibilities could, on the other hand, be

obtained by the subtraction of either 1 or the hf permittivity $\epsilon_{a ij}$ from the real part ϵ'_{ij} and static ϵ_{oij} relative permittivities. If 1 is subtracted, the susceptibilities due to all operating polarization processes result, while if $\epsilon_{a ij}$ is subtracted [11], the susceptibility due to only orientational polarization results. The imaginary part χ''_{ij} is numerically equal to ϵ''_{ij} as shown in Table 1.

The commercially available alcohols were dried over anhydrous calcium sulphate and fractionally distilled. The portions were collected with their known boiling points before use. The solvent *n*-heptane was dried over sodium wire prior to its use to make solution. The real ϵ'_{ij} and the imaginary ϵ''_{ij} parts of the hf complex relative permittivity ϵ^*_{ij} of the solutions were

measured by an apparatus as described elsewhere [9,11] with a Boonton RX meter corrected by a heterodyne beat method. The refractive index n_{Dij} (where $n_{Dij}^2 = \epsilon_{oij}$) of the solutions was measured by a Pulfrich refractometer using the sodium D line [11]. This may introduce some errors in the desired results. The weight fractions w_j 's are given by

$$w_j = \frac{f_j M_j}{f_i M_i + f_j M_j} \quad (1)$$

in terms of mole fractions f_j 's of all the alcohols are defined [12] as the weight of the solute per unit weight of the solution up to four decimal places in Table 1.

All the alcohols may be supposed to possess three relaxation times. They may be attributed to the rotation of –OH group, the orientational motion of the molecular species while the 3rd one is associated with the hydrogen bonded structures. All these long straight chain hydrogen bonded polymer type dipolar alcohol molecules have wide applications in the fields of biological research, medicine and industry. Moreover, they can be used as good solvents to clean the desired parts of the instruments, in lubrication chemistry, viscosity modifiers, in the preparation of emulsifying agents, waxes etc.

Bergmann et al. [13] proposed a graphical method to obtain τ_1 and τ_2 for a pure polar liquid. The respective weighted contributions c_1 and c_2 towards dielectric relaxations for τ_1 and τ_2 were also estimated. The single frequency measurement to get the double relaxation times is not a reliable one. Bhattacharyya et al. [14] subsequently attempted to get τ_1 , τ_2 and c_1 , c_2 for a polar liquid from the relative permittivity measurements at least at two different frequencies in the GHz range. The graphical analysis made by Higasi et al. [15] on polar–nonpolar liquid mixtures suffers from a crude approximation.

Saha et al. [16] and Sit et al. [17], however, advanced an analytical treatment to study the single frequency measurements of the double relaxation times τ_1 and τ_2 from the measured relative permittivities. The object of the present paper is to detect τ_1 and τ_2 and hence to measure μ_1 and μ_2 using χ_{ij} 's. The aspect of molecular orientational polarization is, however, achieved by χ_{ij} 's because ϵ_{oij} includes the fast polarization and it frequently appears as a subtracted term in Bergmann's equations [15]. Thus to avoid the clumsiness of algebra and to exclude the fast polarization, Bergmann's equations [13] are simplified by the established symbols of χ'_{ij} , χ''_{ij} and χ_{oij} of Table 1 in S.I. units, into the following forms:

$$\frac{\chi'_{ij}}{\chi_{oij}} = \frac{c_1}{1 + \omega^2 \tau_1^2} + \frac{c_2}{1 + \omega^2 \tau_2^2} \quad (2)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \quad (3)$$

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

The Eqs. (2) and (3) are then solved to get:

$$\frac{\chi_{oij} - \chi'_{ij}}{\chi'_{ij}} = \omega(\tau_1 + \tau_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \omega^2 \tau_1 \tau_2 \quad (4)$$

which is a linear equation between the variables $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ and χ''_{ij}/χ'_{ij} having the intercept $-\omega^2 \tau_1 \tau_2$ and the slope $\omega(\tau_1 + \tau_2)$ as illustrated in Fig. 1 for all the alcohols.

The intercepts and slopes of all the alcohols were then used to get τ_1 and τ_2 for the flexible part and the whole molecular species with known $\omega (=2\pi f)$, where f being the frequency of the applied electric field, as presented in Table 2.

The real ϵ'_{ij} and imaginary ϵ''_{ij} parts of hf complex relative permittivity are related by

$$\epsilon'_{ij} = \epsilon_{oij} + \frac{1}{\omega \tau_j} \epsilon''_{ij} \quad (5)$$

as $\epsilon'_{ij} - \epsilon_{oij}$ and ϵ''_{ij} are numerically equal to real and imaginary parts of hf complex dimensionless di-electric orientational susceptibility χ_{ij}^* , respectively. So we get

$$\chi_{ij}'' = (\omega \tau_j) \chi_{ij}' \quad (6)$$

which is clearly a straight line [18] between χ_{ij}'' and χ_{ij}' ; the slope $\omega \tau_j$ can be used to get τ_j of a polar unit. But for associative liquids like normal and octyl alcohols under investigation the nature of variation of χ_{ij}'' with χ_{ij}' is not strictly linear as seen in Fig. 2. Non-linear variation of both χ_{ij}' and χ_{ij}'' with weight fractions, w_j 's, of the solute are

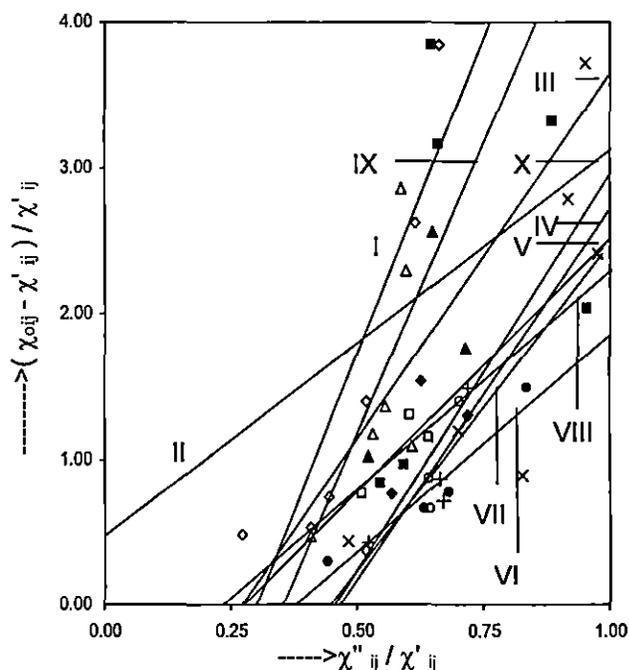


Fig. 1. Linear variation of $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ with χ''_{ij}/χ'_{ij} for different long straight chain dipolar alcohols in *n*-heptane at 25 °C under 24 GHz electric field frequency: I. 1-butanol (-○-), II. 1-hexanol (-■-), III. 1-heptanol (-Δ-), IV. 1-decanol (-x-), V. 2-methyl-3-heptanol (-○-), VI. 3-methyl-3-heptanol (-●-), VII. 4-methyl-3-heptanol (-+-), VIII. 5-methyl-3-heptanol (-◆-), IX. 4-octanol (-□-), X. 2-octanol (-▲-).

Table 2
The relaxation times τ_1 and τ_2 , from the slope and intercept of the straightline Eq. (4), correlation coefficient r 's and % of error in regression technique, measured τ_j from the slope of χ''_{ij} vs χ'_{ij} of Eq. (7) and the ratio of the individual slopes of χ''_{ij} vs. w_j and χ'_{ij} vs. w_j at $w_j \rightarrow 0$ of Eq. (7), reported τ_s , symmetric and characteristic relaxation times τ_{cs} and τ_{cs} for different straight chain aliphatic alcohols in *n*-heptane under effective dispersive region of 24 GHz electric field at 25 °C

System with Sl. No.	Slope and intercept of Eq. (4)		Estimated τ_1 and τ_2 in ps		Correlation coefficient	% of error	τ_j from (Murthy et al.) and (ratio of individual slope)		Reported τ_s in ps	τ_{cs} in ps	τ_{cs} in ps
	Slope	Intercept	τ_1	τ_2							
I. 1-butanol ($M_j=0.074$)	8.66	2.60	2.04	54.56	0.90	5.17	4.95	3.42	2.47	0.98	15.41
II. 1-hexanol ($M_j=0.102$)	2.64	-0.47	-1.10	18.37	0.34	24.28	4.05	3.78	2.25	2.09	6.77
III. 1-heptanol ($M_j=0.116$)	7.99	2.83	2.46	50.49	0.68	14.98	4.12	4.23	2.07	1.97	10.46
IV. 1-decanol ($M_j=0.158$)	5.43	2.48	3.29	32.22	0.82	9.23	7.63	10.20	2.39	1.91	0.50
V. 2-methyl 3-heptanol ($M_j=0.130$)	5.05	2.37	3.42	29.61	0.90	6.34	4.92	4.34	1.86	2.11	4.58
VI. 3-methyl 3-heptanol ($M_j=0.130$)	3.00	1.14	2.91	16.68	0.96	2.33	6.06	4.30	2.26	1.65	5.29
VII. 4-methyl 3-heptanol ($M_j=0.130$)	4.39	1.97	3.31	25.38	0.89	7.30	5.12	4.38	1.95	2.19	8.07
VIII. 5-methyl 3-heptanol ($M_j=0.130$)	2.98	0.69	1.66	17.81	0.57	26.36	4.23	7.59	1.63	1.59	8.37
IX. 4-octanol ($M_j=0.130$)	3.48	0.96	1.97	20.75	0.86	10.34	4.36	4.33	1.68	1.62	15.40
X. 2-octanol ($M_j=0.130$)	5.02	1.37	1.89	30.94	0.63	23.30	4.82	15.91	1.93	2.33	37.08

presented graphically in Figs. 3 and 4, respectively. In such cases

$$\frac{(d\chi''_{ij}/dw_j)_{w_j \rightarrow 0}}{(d\chi'_{ij}/dw_j)_{w_j \rightarrow 0}} = \omega\tau_j \quad (7)$$

is a better representation [19] of the slope of Eq. (6) to get τ_j as it eliminates polar-polar interactions [20,21] in a given solution. τ_j 's from both Eqs. (6) and (7) are placed in Table 2 to compare them with those obtained by the freshly calculated Gopalakrishna's [22] method.

The weighted contributions c_1 and c_2 towards dielectric relaxation in terms of estimated τ_1 and τ_2 are, however, worked

out from Ffóhlich's [23] theoretical equations and given in Table 3 in order to compare them with the experimental ones obtained in terms of the intercepts of the variations of χ''_{ij}/χ_{oij} and χ'_{ij}/χ_{oij} with w_j 's of Figs. 5 and 6. Both χ''_{ij}/χ_{oij} and χ'_{ij}/χ_{oij} at $w_j=0$ together with the curve of $(1/\phi) \log \cos \phi$ against ϕ^0 as seen in Fig. 7 are used to get symmetric and asymmetric distribution parameters γ and δ and hence symmetric and characteristic relaxation times τ_s and τ_{cs} . Both τ_s and τ_{cs} are given in Table 2 and γ , δ are presented in Table 3.

The dipole moments μ_1 and μ_2 by hf susceptibility measurement technique are, however, estimated from linear coefficient β 's of χ''_{ij} vs. w_j curves of Fig. 3 along with the dimensionless parameters b_1 and b_2 involved with estimated τ_1

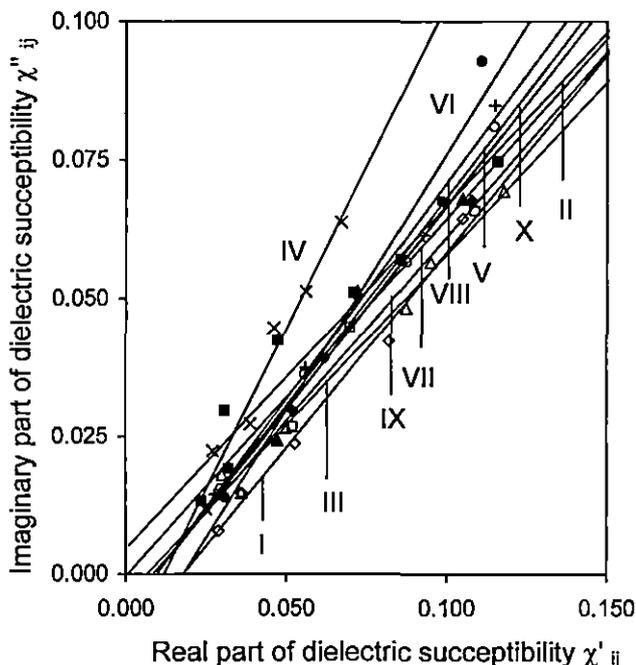


Fig. 2. Linear variation of imaginary part χ''_{ij} of hf dielectric susceptibility against real part χ'_{ij} for different long straight chain dipolar alcohols in *n*-heptane at 25 °C under 24 GHz electric field frequency: I. 1-butanol (\circ), II. 1-hexanol (\blacksquare), III. 1-heptanol (\triangle), IV. 1-decanol (\times), V. 2-methyl-3-heptanol (\circ), VI. 3-methyl-3-heptanol (\bullet), VII. 4-methyl-3-heptanol (+), VIII. 5-methyl-3-heptanol (\blacklozenge), IX. 4-octanol (\square), X. 2-octanol (\blacktriangle).

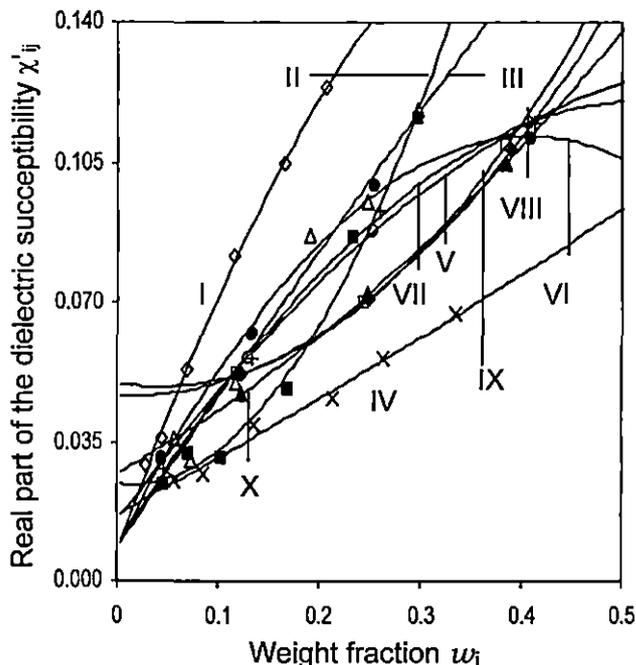


Fig. 3. Variation of real part χ'_{ij} of hf dielectric susceptibility with weight fraction w_j of some dipolar long straight chain alcohols in *n*-heptane at 25 °C under 24 GHz electric field frequency: I. 1-butanol (\circ), II. 1-hexanol (\blacksquare), III. 1-heptanol (\triangle), IV. 1-decanol (\times), V. 2-methyl-3-heptanol (\circ), VI. 3-methyl-3-heptanol (\bullet), VII. 4-methyl-3-heptanol (+), VIII. 5-methyl-3-heptanol (\blacklozenge), IX. 4-octanol (\square), X. 2-octanol (\blacktriangle).

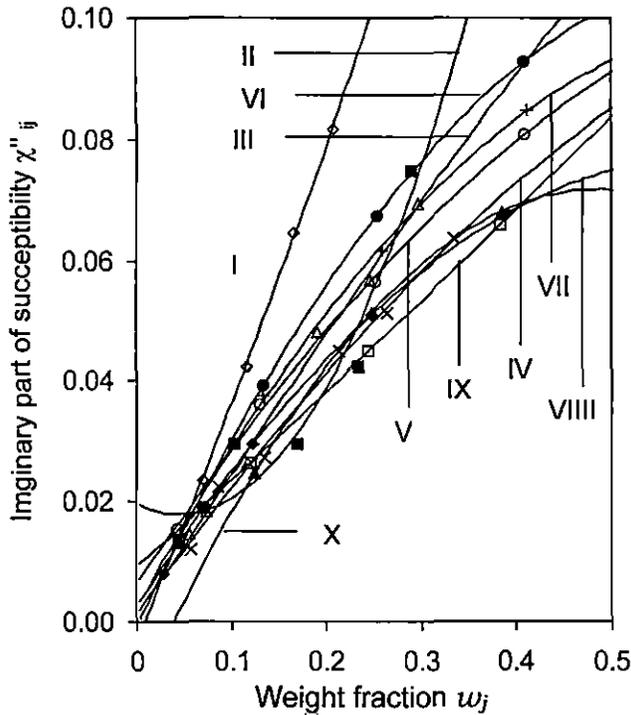


Fig. 4. Variation of imaginary part χ''_{ij} of hf dielectric susceptibility with weight fraction w_j of some dipolar long straight chain alcohols in *n*-heptane at 25 °C under 24 GHz electric field frequency: I. 1-butanol (-◇-), II. 1-hexanol (-■-), III. 1-heptanol (-△-), IV. 1-decanol (-×-), V. 2-methyl-3-heptanol (-○-), VI. 3-methyl-3-heptanol (-●-), VII. 4-methyl-3-heptanol (-+-), VIII. 5-methyl-3-heptanol (-◆-), IX. 4-octanol (-□-), X. 2-octanol (-▲-).

and τ_2 of Table 2. The dipole moments μ_1 and μ_2 due to rotation of the flexible polar groups and end over end rotations of the whole molecule respectively are placed in Table 4 along with μ_{theo} 's and reported μ 's (Gopalakrishna) for comparison.

2. Weighted contributions c_1 and c_2 for estimated τ_1 and τ_2

Taking $\omega\tau_1 = \alpha_1$ and $\omega\tau_2 = \alpha_2$ and solving Eqs. (2) and (3) yields

$$c_1 = \frac{(\chi''_{ij}\alpha_2 - \chi''_{ij}) (1 + \alpha_1^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad (8)$$

Table 3
Fröhlich's parameter A , theoretical and experimental values of χ'_i/χ_{oij} and χ''_i/χ_{oij} of Fröhlich Eqs. ((10) and (11)) and from fitting curves of Figs. 5 and 6 at $w_j \rightarrow 0$, respectively, theoretical and experimental relative contributions c_1 and c_2 towards dielectric dispersion due to τ_1 and τ_2 symmetric and asymmetric distribution parameters γ and δ for some straight chain aliphatic alcohols in solvent *n*-heptane under effective dispersive region of 24 GHz electric field at 25 °C

Systems with Sl. No.	$A = \ln(\tau_2/\tau_1)$	Theoretical values of χ'_i/χ_{oij} and χ''_i/χ_{oij} from Eqs. (10) and (11)		Theoretical values of c_1 and c_2		Experimental values of χ'_i/χ_{oij} and χ''_i/χ_{oij} at $w_j \rightarrow 0$ of Figs. 5 and 6		Experimental values of c_1 and c_2		Estimated values of γ and δ	
		χ'_i/χ_{oij}	χ''_i/χ_{oij}	c_1	c_2	χ'_i/χ_{oij}	χ''_i/χ_{oij}	c_1	c_2	γ	δ
I. 1-butanol	3.286	0.366	0.350	0.370	2.069	0.799	0.195	0.884	-0.474	0.357	0.21
II. 1-hexanol	-	-	-	-	-	0.740	0.348	0.598	1.412	0.128	0.55
III. 1-heptanol	3.023	0.347	0.359	0.358	1.878	0.721	0.298	0.816	0.247	0.230	0.39
IV. 1-decanol	2.281	0.341	0.396	0.364	1.283	0.870	0.404	1.100	-0.193	-0.079	2.49
V. 2-methyl 3-heptanol	2.157	0.345	0.404	0.369	1.198	0.776	0.386	0.995	-0.107	0.041	0.76
VI. 3-methyl 3-heptanol	1.746	0.474	0.446	0.435	0.837	0.814	0.319	1.000	-0.157	0.099	0.55
VII. 4-methyl 3-heptanol	2.036	0.374	0.417	0.386	1.084	0.729	0.358	0.920	-0.051	0.121	0.51
VIII. 5-methyl 3-heptanol	2.371	0.564	0.409	0.486	0.906	0.782	0.287	0.794	0.302	0.189	0.39
IX. 4-octanol	2.353	0.508	0.413	0.455	1.003	0.731	0.243	0.789	0.086	0.328	0.27
X. 2-octanol	2.797	0.451	0.387	0.426	1.351	0.683	0.193	0.741	-0.023	0.477	0.20

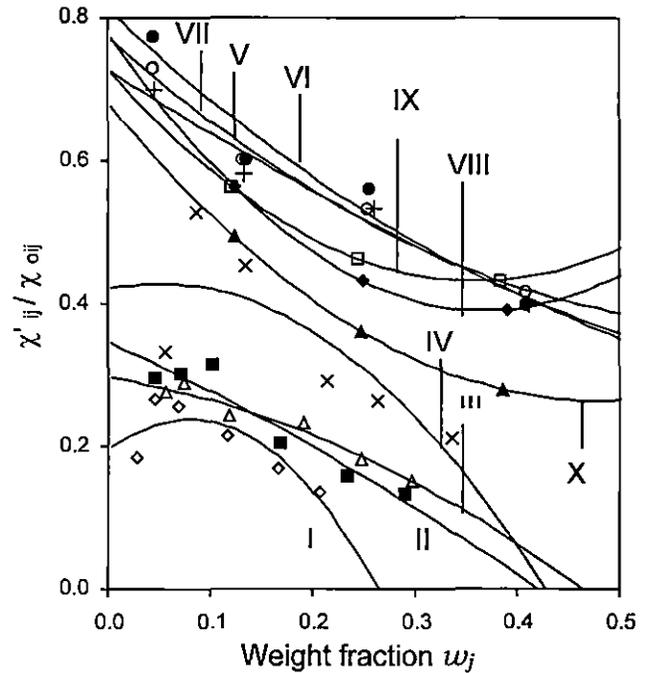


Fig. 5. Plot of χ'_i/χ_{oij} against weight fraction w_j of some dipolar long straight chain alcohols in *n*-heptane at 25 °C under 24 GHz electric field frequency: I. 1-butanol (-◇-), II. 1-hexanol (-■-), III. 1-heptanol (-△-), IV. 1-decanol (-×-), V. 2-methyl-3-heptanol (-○-), VI. 3-methyl-3-heptanol (-●-), VII. 4-methyl-3-heptanol (-+-), VIII. 5-methyl-3-heptanol (-◆-), IX. 4-octanol (-□-), X. 2-octanol (-▲-).

and

$$c_2 = \frac{(\chi''_{ij} - \chi''_{ij}\alpha_1) (1 + \alpha_2^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad (9)$$

provided that $\alpha_2 > \alpha_1$. c_1 and c_2 are estimated from known τ_1 and τ_2 by the double relaxation method. c_1 and c_2 can also be obtained with the known values of χ'_i/χ_{oij} and χ''_i/χ_{oij} from Fröhlich's following theoretical equations [23] with known τ_1 and τ_2 from Eqs. (2) and (3).

$$\frac{\chi'_i}{\chi_{oij}} = 1 - \frac{1}{2A} \ln \left[\frac{1 + \omega^2\tau_2^2}{1 + \omega^2\tau_1^2} \right] \quad (10)$$

$$\frac{\chi''_i}{\chi_{oij}} = \frac{1}{A} [\tan^{-1}(\omega\tau_2) - \tan^{-1}(\omega\tau_1)] \quad (11)$$

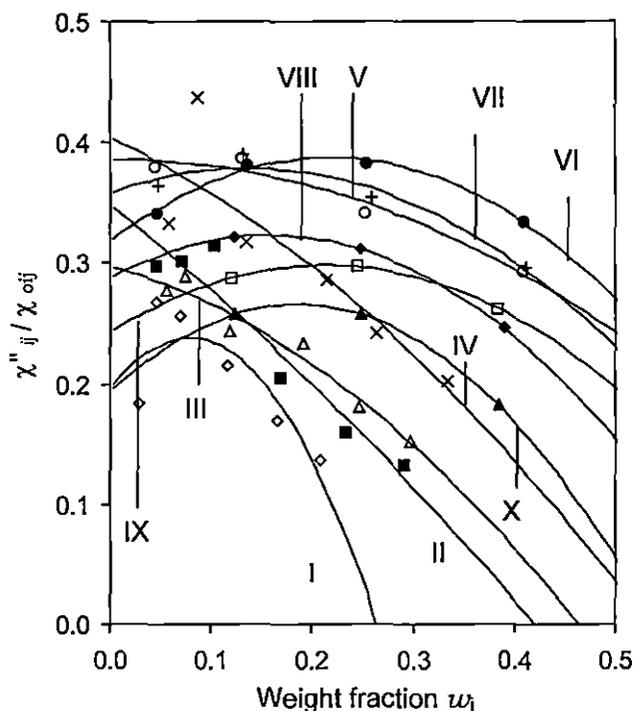


Fig. 6. Plot of χ''_{ij}/χ_{oij} against weight fraction w_j of some dipolar long straight chain alcohols in *n*-heptane at 25 °C under 24 GHz electric field frequency: I. 1-butanol (\diamond), II. 1-hexanol (\blacksquare), III. 1-heptanol (\triangle), IV. 1-decanol (\times), V. 2-methyl-3-heptanol (\circ), VI. 3-methyl-3-heptanol (\bullet), VII. 4-methyl-3-heptanol (\dagger), VIII. 5-methyl-3-heptanol (\blacklozenge), IX. 4-octanol (\square), X. 2-octanol (\blacktriangle).

c_1 and c_2 thus estimated are placed in Table 3 for comparison with those worked out from the intercept of the fitted polynomial plots of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} against w_j curves of Figs. 5 and 6. Fäöhlich's parameter A for each system is also placed in the same table.

3. Formulations for symmetric and characteristic relaxation times and also symmetric and asymmetric distribution parameter

The molecules under investigation appear to behave like nonrigid ones under 24 GHz electric field frequency having either symmetric or asymmetric relaxation behaviour characterized by either symmetric τ_s and characteristic τ_{cs} relaxation times involved with the following equations:

$$\frac{\chi_{ij}^*}{\chi_{oij}} = \frac{1}{1 + (j\omega\tau_s)^{1-\gamma}} \quad (12)$$

$$\frac{\chi_{ij}^*}{\chi_{oij}} = \frac{1}{(1 + j\omega\tau_{cs})^\delta} \quad (13)$$

separating the real and imaginary parts of the above equations and rearranging them in terms of intercepts viz. $(d\chi'_{ij}/dw_j)_{w_j=0}$ and $(d\chi''_{ij}/dw_j)_{w_j=0}$ of the graphically fitted plots of Figs. 5 and 6 one gets γ and τ_s as:

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[\left(1 - \frac{\chi'_{ij}}{\chi_{oij}} \right) \frac{\chi'_{ij}/\chi_{oij}}{\chi''_{ij}/\chi_{oij}} - \frac{\chi''_{ij}}{\chi_{oij}} \right] \quad (14)$$

$$\tau_s = \frac{1}{\omega} \left[\frac{1}{\left\{ \left(\chi'_{ij}/\chi_{oij} \right) / \left(\chi''_{ij}/\chi_{oij} \right) \cos(\gamma\pi/2) - \sin(\gamma\pi/2) \right\}^{1/\gamma}} \right] \quad (15)$$

Similarly, δ and τ_{cs} can be evaluated from Eq. (13):

$$\tan(\phi\delta) = \frac{\left(\chi''_{ij}/\chi_{oij} \right)_{w_j=0}}{\left(\chi'_{ij}/\chi_{oij} \right)_{w_j=0}} \quad (16)$$

and

$$\tan\phi = \omega\tau_{cs} \quad (17)$$

since ϕ can not be estimated directly, a theoretical curve between $(1/\phi) \log \cos\phi$ against ϕ in degrees has been drawn in Fig. 7. The value of $(1/\phi) \log \cos\phi$ can be estimated from the following relation

$$(1/\phi) \log \cos\phi = \log \left[\frac{\chi'_{ij}/\chi_{oij}}{\cos\phi\delta} \right] / \phi\delta. \quad (18)$$

The known value of $(1/\phi) \log \cos\phi$ is used to get ϕ from the curve. With the known ϕ , Eqs. (16) and (17) were used to obtain δ and τ_{cs} . Estimated τ_s and τ_{cs} are placed in Table 2 to compare with τ_j 's obtained by ratio of slopes of individual variations of χ'_{ij} and χ''_{ij} with w_j , τ_j 's by the method of Murthy et al. [18], reported τ_j (Gopalakrishna) and τ_1 and τ_2 by the double relaxation method. Also γ and δ are shown in Table 3.

4. Theoretical formulations to obtain hf dipole moment μ_j

The imaginary part χ''_{ij} of hf complex χ_{ij}^* is [4,20,24]

$$\chi''_{ij} = \frac{N\rho_{ij}\mu_j^2}{27\varepsilon_0 M_j k_B T} \frac{\omega\tau_j}{(1 + \omega^2\tau_j^2)} (\varepsilon_{ij} + 2)^2 w_j \quad (19)$$

which on differentiation with respect to w_j and at $w_j=0$ yields that

$$\left(\frac{d\chi''_{ij}}{dw_j} \right)_{w_j=0} = \frac{N\rho_{ij}\mu_j^2}{27\varepsilon_0 M_j k_B T} \frac{\omega\tau_j}{(1 + \omega^2\tau_j^2)} (\varepsilon_{ij} + 2)^2 w_j \quad (20)$$

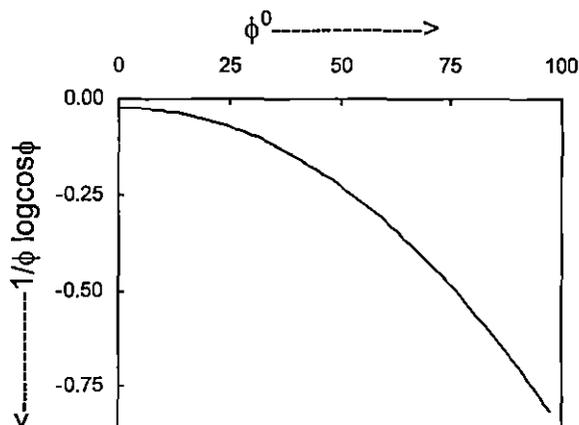


Fig. 7. Variation of $(1/\phi) \log(\cos\phi)$ against ϕ^0 .

Table 4

Linear coefficient β of χ'_{ij} vs. w_j curves of Fig. 3, dimensionless parameters b_1, b_2 from τ_1 and τ_2 of Eq. (4), correlation coefficient and % of error of $\chi'_{ij}-w_j$ estimated dipole moment μ_1, μ_2 from Eq. (22), computed dipole moment μ_j from τ_j of Eq. (7), reported dipole moment (Gopalakrishna's method), all are expressed in C m for different straight chain alcohols in solvent *n*-heptane at 25 °C under 24 GHz electric field

Systems with Sl. No. and mol. wt. M_j in kg mol ⁻¹ (in <i>n</i> -heptane)	Linear coefficients of χ'_{ij} vs. w_j curves of Fig. 3 β	Dimensionless parameters		Correlation coefficients of $\chi'_{ij}-w_j$	% of errors	Estimated dipole moments $\mu \times 10^{30}$ in C m			Reported $\mu \times 10^{30}$ in C m Gopalakrishna's method	$\mu_{theo}^a \times 10^{30}$ in C m
		b_1	b_2			μ_1	μ_2	μ_j		
I. 1-butanol ($M_j=0.074$)	0.719	0.911	0.014	0.997	0.00003	3.02	24.25	3.26	3.58	3.74
II. 1-hexanol ($M_j=0.102$)	0.371	0.973	0.112	0.969	0.00037	2.47	7.25	2.81	3.35	3.49
III. 1-heptanol ($M_j=0.116$)	0.392	0.879	0.017	0.987	0.00015	2.84	20.49	3.16	3.59	3.73
IV. 1-decanol ($M_j=0.158$)	0.142	0.798	0.040	0.994	0.00007	2.10	9.43	3.47	3.55	3.68
V. 2-methyl 3-heptanol ($M_j=0.130$)	0.359	0.785	0.047	0.998	0.00003	3.05	12.53	3.24	1.33	1.86
VI. 3-methyl 3-heptanol ($M_j=0.130$)	0.508	0.835	0.133	0.985	0.00023	3.52	8.81	3.85	1.18	2.11
VII. 4-methyl 3-heptanol ($M_j=0.130$)	0.429	0.796	0.062	0.996	0.00006	3.31	11.83	3.55	3.42	1.95
VIII. 5-methyl 3-heptanol ($M_j=0.130$)	0.211	0.939	0.119	0.967	0.00056	2.14	6.01	3.17	3.54	1.39
IX. 4-octanol ($M_j=0.130$)	0.217	0.917	0.090	0.985	0.00025	2.20	7.00	2.52	3.48	1.11
X. 2-octanol ($M_j=0.130$)	0.143	0.923	0.043	0.977	0.00038	1.78	8.25	4.49	3.24	1.45

^a Ghosh et al. [10].

From Eqs. (7) and (19) one obtains

$$\omega\tau_j(d\chi'_{ij}/dw_j)_{w_j \rightarrow 0} = \frac{N\rho_i\mu_j^2}{27\varepsilon_0M_jk_B T} \frac{\omega\tau_j}{(1+\omega^2\tau_j^2)}(\varepsilon_i+2)^2 \quad (21)$$

or

$$\omega\tau_j\beta = \frac{N\rho_i\mu_j^2}{27\varepsilon_0M_jk_B T} \frac{\omega\tau_j}{(1+\omega^2\tau_j^2)}(\varepsilon_i+2)^2$$

or

$$\mu_j = \left[\frac{27\varepsilon_0M_jk_B T\beta}{N\rho_i(\varepsilon_i+2)^2b} \right]^{1/2} \quad (22)$$

where

- ε_0 =Permittivity of free space= 8.854×10^{-12} F m⁻¹
- M_j =Molecular weight of solute in kg mol⁻¹
- k_B =Boltzmann constant= 1.38×10^{-23} J k⁻¹
- T =Temperature in K
- $\beta=(d\chi'_{ij}/dw_j)_{w_j \rightarrow 0}$ =Linear coefficient of $\chi'_{ij}-w_j$ curve of Fig. 5 at $w_j \rightarrow 0$
- N =Avogadro's number= 6.023×10^{23} mol⁻¹
- ρ_i =Density of solvent *n*-heptane= 680.15 kg m⁻³
- ε_i =Dielectric relative permittivity of the solvent= 1.917
- $b=1/(1+\omega^2\tau_j^2)$ =a dimensionless parameter involved with estimated τ_j .

When $j=1$ and 2 the dipole moments μ_1 and μ_2 associated with rotation of flexible polar groups and rotation of the whole molecules are evaluated in terms of b_1 and b_2 involved with τ_1 and τ_2 and are placed in Table 4 to compare them with μ_{theo} 's and reported μ 's (Gopalakrishna).

5. Results and discussion

The least squares fitted straight line equations: $(\chi_{oij}-\chi'_{ij})/\chi'_{ij}=\omega(\tau_1+\tau_2)\chi''_{ij}/\chi'_{ij}-\omega^2\tau_1\tau_2$ have been shown graphically in Fig. 1 for some normal and octyl alcohols with the symbols showing the experimental points in the solvent *n*-heptane at 25 °C under 24 GHz electric field frequency. The real χ'_{ij} and imaginary parts χ''_{ij} of hf complex dimensionless dielectric orientational susceptibility χ_{ij}^* and static or low frequency real dielectric susceptibility χ_{oij} have been derived from the measured relative permittivities [8,9] $\varepsilon'_{ij}, \varepsilon''_{ij}, \varepsilon_{oij}$ and ε_{oij} . They are carefully collected in Table 1. The slopes and intercepts of Eq. (4) used to get τ_1 and τ_2 are placed in the 2nd and 3rd columns of Table 2 along with the estimated τ_1 and τ_2 in the 4th and 5th columns. Correlation coefficients (r) and % of errors of curves of Fig. 1 have been calculated and are placed in the 6th and 7th columns of Table 2 only to show how far the variables $(\chi_{oij}-\chi'_{ij})/\chi'_{ij}$ and χ''_{ij}/χ'_{ij} are correlated with each other. It is seen that ' r ' is very low and corresponding % of errors is very high for 5-methyl 3-heptanol and 2-octanol, which may be probably due to errors introduced in their permittivity ε_{ij} measurements. This fact is further confirmed by remarkable deviations of experimental points from the fitted linear curves as seen in Fig. 1.

In absence of reliable τ_j values, the slopes of the linear curves [18] of Fig. 2 of the variables χ''_{ij} and χ'_{ij} are utilized to get τ_j . But for associative liquids like normal and octyl alcohols, the variation of χ''_{ij} against χ'_{ij} is not strictly linear as seen in Fig. 2. Under such context, the ratio of the slopes of individual variations of both χ'_{ij} and χ''_{ij} with w_j 's is a better representation [20,21] of the method of Murthy et al. [18] as it eliminates polar-polar interactions in a given solution [4]. τ_j 's estimated so far by this method are entered in the 9th column of

Table 2 along with τ_j 's due to the method of Murthy et al. and reported ones as seen in the 8th and 10th columns. Nonlinear variation of both χ_{ij}^I and χ_{ij}^{II} against w_j 's as seen in Figs. 3 and 4 arises due to solute–solvent and solute–solute molecular associations which is supposed to be a physico-chemical property [21] of the solutes under consideration. Symmetric and characteristic relaxation times τ_s and τ_{cs} estimated from Eqs. (15) and (17), respectively, in terms of γ and δ are seen in the 11th and 12th column of Table 2. It is observed that in comparison to τ_{cs} , τ_s is the same order of magnitude of τ_j 's from Eq. (7) and reported (Gopalakrishna) ones. This fact at once establishes the very basic soundness of our method [20,21] employed to get hf τ_j and also the symmetric relaxation behaviour [19] obeyed by the molecules. Larger τ_2 values arise for bigger size of rotating units $\tau_j T / \eta \gamma$ due to solute–solvent and solute–solute molecular associations, supposed to be

physico-chemical property of the solutes which is further supported by non linear variations of both χ_{ij}^I and χ_{ij}^{II} with w_j 's as seen in Figs. 3 and 4.

The theoretical weighted contributions c_1 and c_2 towards dielectric relaxations from Eqs. (8) and (9) are, however, worked out with χ_{ij}^I/χ_{oij} and $\chi_{ij}^{II}/\chi_{oij}$ values of Eqs. (10) and (11) and also with estimated τ_1 and τ_2 of Table 2. They are placed in the 5th and 6th columns of Table 3 in order to compare them with the experimental c_1 and c_2 estimated in terms of $(\chi_{ij}^I/\chi_{oij})_{w_j=0}$ and $(\chi_{ij}^{II}/\chi_{oij})_{w_j=0}$ of the graphically fitted plots of Figs. 5 and 6 and are placed in the 9th and 10th columns. Theoretical c 's for 1 hexanol could not be estimated as τ_1 is found to be negative probably due to errors [19] in the measurement of ϵ_{ij}^I , ϵ_{ij}^{II} , ϵ_{oij} and ϵ_{oij} . Both theoretical and experimental c_1 and c_2 shows that $c_1 + c_2 \approx 1$, which confirms the validity of Eq. (4) to get τ_1 and τ_2 . It is seen that for some systems experimental c_2 is

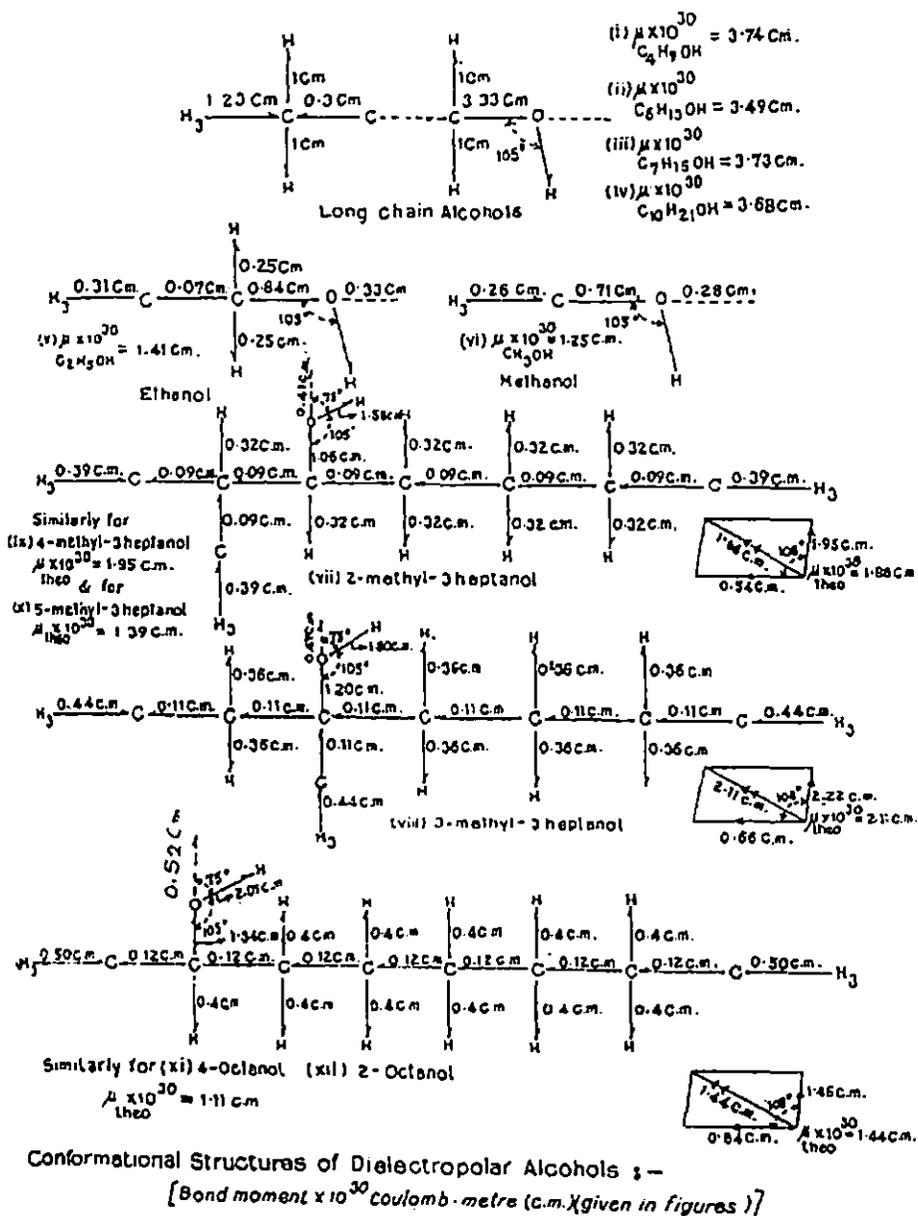


Fig. 8. Conformational structures of dielectropolar alcohols (theoretical dipole moments μ_{theo} from bond angles and reduced bond moments).

negative. This can, however, be explained on the basis of the fact that internal hydrogen bonding among –OH groups in dipolar alcohol molecules gives rise to inertia [25] of the flexible polar groups with respect to the whole molecule. Solute–solvent and solute–solute molecular interaction being a physicochemical aspect is also supported by slight deviations of experimental points from the curves of Figs. 5 and 6.

The dipole moments μ_1 and μ_2 of the flexible polar groups and the whole molecules were estimated in terms of dimensionless parameters b_1 and b_2 involved with estimated τ_1 and τ_2 and linear coefficient β of $\chi'_{ij}-w_j$ curves of Fig. 3. They are entered in the 5th and 6th columns of Table 4 to compare them with μ_j 's estimated with τ_j 's of Eq. (7), reported μ 's due to Gopalakrishna [22] and theoretical μ 's obtained with available bond angles and bond moments of the polar groups assuming the molecules to be planar ones, sketched here. Correlation coefficients r 's and % of errors of $\chi'_{ij}-w_j$ curves of Fig. 3 were made from by careful regression analysis of the measured data, are seen in the 5th and 6th columns of Table 4 only to suggest how far the variables $\chi'_{ij}-w_j$ are correlated with each other. Almost all the $\chi'_{ij}-w_j$ curves show a tendency to be closer within the range $0.00 \leq w_j \leq 0.10$, which is due to equal polarity [4,25] of the molecules in addition to solute–solvent and solute–solute molecular interaction which is assumed to be physico-chemical behaviour [20,21] of the solutes in *n*-heptane. The close agreement of the estimated μ_1 and μ_2 with reported (Gopalakrishna) and theoretical μ 's establishes the very basic soundness of the present method to get hf μ_j 's in addition to the fact that a part of the molecule is rotating under GHz electric field [19]. It is seen that estimated μ_1 and μ_j 's are lower than those of μ_{theo} 's for normal alcohols while the reverse is true in octyl alcohols. It is probably due to the fact that strong hydrogen bonding among –OH groups in normal alcohols (1-butanol, 1-hexanol, 1-heptanol and 1-decanol) offers higher resistance due to –OH groups to rotate under hf electric field to give lower μ_1 and μ_j values. In octyl alcohols hydrogen, on the otherhand, bonding between –OH groups is not so strong giving μ_1 's and μ_j 's higher than that of μ_{theo} 's as they are screened by a large number of –CH₃ and –CH₂ groups. The conformations are presented in Fig. 8 in excellent agreement of the measured values in order to account of the mesomeric and electromeric effects of the substituted polar groups in alcohols by multiplying available bond moments by a factor μ_s/μ_{theo} where μ_s is the low frequency or static dipole moment estimated elsewhere [10].

6. Conclusion

Theoretical formulations developed so far in SI units within the frame work of the Debye-Smyth model appear to be the simpler straightforward and topical ones to get the many interesting equations which are worked out in terms of χ'_{ij} 's. They are useful to explain various physico-chemical aspects of several dipolar alcohol molecules in solvent *n*-heptane at 25 °C under 24 GHz (Q-band microwave) electric field frequency. The derived straight line Eq. (4) has significant contribution in the field of dielectric relaxation

as it gives microscopic τ_1 and macroscopic τ_2 due to both rotations of the flexible polar groups and the whole molecule while Eq. (7) gives microscopic τ only [20,21]. Both theoretical and graphical experimental c_1 and c_2 confirm the validity of Eq. (4). As seen in Table 3 $c_1+c_2 \approx 1$ is due to the fact that under 24 GHz electric field the rotations of the straight chained molecules are influenced by the moment of inertia of the flexible groups attached to the parent ones. $\epsilon_{\alpha ij} \approx 1 - 1.5n_{Dij}^2$. But $\epsilon_{\alpha ij} \approx n_{Dij}^2$ may introduce some errors in getting τ_1 and τ_2 and c_1 and c_2 also. Correlation coefficients r 's and % of errors between several variables involved in the curves of Figs. 1 and 3 are worked out only to establish the statistical validity [20,21] of Eq. (4) and χ'_{ij} vs. w_j equations. The close agreement of estimated relaxation parameters viz. τ 's and μ 's with the reported ones confirms the very basic soundness of the theoretical formulations so far developed. The physico-chemical properties of the systems are, however, inferred in terms of solute–solvent (monomer) and solute–solute (dimer) associations as supported by slight deviations of measured parameters from their reported and standard values and also observed by deviation of experimental points from the fitted polynomial plots of several figures.

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Studies on physico-chemical properties with the relaxation phenomena of some normal aliphatic alcohols in non polar solvent under Giga Hertz electric field at a single temperature

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Abstract : Double relaxations of some normal aliphatic alcohols have been studied to get relaxation times τ_1 and τ_2 due to rotation of flexible part and end over end rotation of the whole molecule from the intercept and slope of a linear equation of $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ against χ''_{ij}/χ'_{ij} for different weight fractions w_j 's of solute in *n*-heptane at 25 °C under electric field frequencies of 24.33, 9.25 and 3.00 GHz. Alcohols like 1-butanol, 1-hexanol, 1-heptanol and 1-decanol are long straight chain hydrogen bonded polymer type molecules having -OH groups which may bend twist or rotate internally about C-C bond under GHz electric field exhibiting characteristic τ . Estimated τ_j obtained from ratio of slopes of individual variation of χ''_{ij} and χ'_{ij} against w_j at $w_j \rightarrow 0$ are compared with those of Murthy *et al.*, Gopalakrishna (reported data) and τ_1, τ_2 by double relaxation method. Relative contributions c_1 and c_2 due to τ_1 and τ_2 towards dielectric relaxations estimated from Fröhlich's equations are compared with the experimental ones obtained by graphical technique. Graphical variations of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} with w_j at $w_j=0$ together with arbitrary curve of $(1/\phi) \log(\cos \phi)$ against ϕ in degree have been utilised to get symmetric γ and asymmetric δ distribution parameters. The symmetric relaxation time τ_s by γ and characteristic relaxation time τ_{cs} by δ and ϕ are computed to suggest symmetric relaxation behaviour of the molecules. Linear coefficient β 's of $\chi'_{ij} - w_j$ curves and dimensionless parameters b_1 and b_2 involved with estimated τ_1 and τ_2 are used to get dipole moments μ_1 and μ_2 due to rotation of flexible part and the whole molecule which are compared with reported μ 's (Gopalakrishna) and μ_{theo} 's. The slight disagreement between μ_j and μ_{theo} obtained from available bond angles and reduced bond moments of substituent polar groups attached to parent molecules arises due to strong internal hydrogen bonds present among the -OH groups of dipolar liquid molecules.

Keywords : Relaxation, aliphatic alcohol, non-polar solvent.

Relaxation mechanism of polar molecules in non polar solvents under high frequency electric field is of special interest as it provides one with useful tool to study structural configuration and molecular associations in the formation of monomer¹ and dimer^{2,3} through measured relaxation parameters like relaxation time τ and dipole moment μ obtained by any conventional method^{4,5}. The technique also gives valuable information regarding stability or unstability⁶ of the systems undergoing relaxation phenomena. Also τ_j obtained from the ratio of slopes of individual variations of $\chi''_{ij} - w_j$ and $\chi'_{ij} - w_j$ are conveniently used to shed more light on structural and associational aspects⁷ in addition to physico-chemical properties of the polar molecules.

Glasser *et al.*⁸ measured the real ϵ'_{ij} and imaginary ϵ''_{ij} parts of complex hf dielectric relative permittivity ϵ^*_{ij} together with static and hf relative permittivity ϵ_{oij}

and ϵ_{oij} of some normal alcohols like 1-butanol, 1-hexanol, 1-heptanol and 1-decanol at various mole fractions under different electric field frequencies in *n*-heptane at 25 °C. The purpose of their study was to observe triple relaxation phenomena in them under different concentrations characterized by relaxation times τ_1, τ_2, τ_3 which arise respectively due to hydrogen bonded structure, orientational motion of the molecules and rotation of -OH groups about C-C bond. The alcohols under study are of special importance for their wide applications in the fields of biological research, medicine and industry.

But the modern trend is to study relaxation phenomena in polar-non polar liquid mixtures in terms of hf complex dimensionless dielectric orientational susceptibility χ^*_{ij} rather than permittivity ϵ^*_{ij} or conductivity σ^*_{ij} . As all types of polarisations are associated with ϵ^*_{ij} , while σ^*_{ij} includes within it transport of bound molecular charges,

so it is more reasonable to work with χ_{ij} 's as it is directly linked with orientational polarisation of the molecules. Moreover, the present study have been carried out in modern concept of intemationally accepted symbols of dielectric terrninology and parameter in SI units because of its unified, coherent and rationalized nature. Under such context we have derived a straight line equation interms of real χ'_{ij} and imaginary χ''_{ij} parts of hf complex susceptibility χ^*_{ij} together with low frequency real dielectric susceptibility χ_{oij} to have τ_1 and τ_2 of alcohol molecules in *n*-heptane at 25 °C under GHz electric field. The frequency 24.33 GHz has been found out to be the most effective dispersive region of the alcohol molecules. When χ''_{ij} of the molecules are plotted against frequency (*f*) they showed peak in the neighbourhood of 24 GHz which is probably due to dielectric reorientation of polar molecules⁹. At this frequency the alcohol molecules absorb electrical energy much more strongly to show reliable τ_1 and τ_2 from intercept and slope of the least squares fitted straight line equation of $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ against χ''_{ij}/χ'_{ij} signifying the material property of the systems.

The validity of straight line equations of Fig. 1 is tested by correlation coefficient (*r*) and % of errors. In absence of reliable τ_j 's of these normal alcohols the ratio of slopes of individual variations of χ''_{ij} and χ'_{ij} with w_j at $w_j \rightarrow 0$ as seen in Figs. 2 and 3 were utilised to get hf τ_j to compare them with those of Murthy *et al.*¹⁰ of Fig. 4 and Gopalakrishna's method¹¹.

The theoretical weighted contributions c_1 and c_2 towards dielectric dispersions interms of measured τ_1 and τ_2 were worked out from Fröhlich's equations¹² to compare them with the experimental ones by graphical variation of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} with w_j at $w_j \rightarrow 0$ of Figs. 5 and 6. The symmetric γ and asymmetric δ distribution parameters were obtained from graphical extrapolation techniques of Figs. 5 and 6 in the limit $w_j=0$ and from variation of $(1/\phi) \log(\cos \phi)$ against ϕ^0 of Fig. 7 respectively. Symmetric relaxation time τ_s from γ and characteristic relaxation time τ_{cs} from δ and ϕ , were however, estimated to conclude about symmetric relaxation behaviour of polar molecules.

The dipole moment's μ_1 and μ_2 interms of b_1 and b_2 involved with estimated τ_1 and τ_2 were worked out to present them in Table 1 to compare with reported μ_j 's (Gopalakrishna) and μ_{theq} obtained from bond angles and reduced bond moments¹³ of substituent polar groups attached to parent molecules. The comparison however suggests that the flexible part of the molecules rotate internally under GHz electric field^{14,15}. The slight

disagreement between experimental and theoretical μ 's estestablishes the very existence of strong internal hydrogen bonding among -OH groups of long straight chain alcohol molecules. Physico-chemical aspects of different solute molecules in non polar solvent can be explained by non linear variation of both τ_2 and μ_2 against frequency (*f*) of the applied electric field as shown in Fig. 8.

Experimental

The dielectric constants ϵ'_{ij} and losses ϵ''_{ij} of the alcohols in *n*-heptane at different mole fractions of solutes were measured⁸ with a Boonton RX meter corrected by a heterodyne beat method. Refractive indices ($n_{Dij} = \sqrt{\epsilon_{ij}}$) of the solution were estimated by a Pulfrich refractometer for sodium D-line. The alcohols 1-butanol, 1-hexanol, 1-heptanol and 1-decanol were obtained from various commercial sources dried for a period over "Drierite" (anhydrous calcium sulphate) and fractionally distilled at atmospheric pressure. Commercial *n*-heptane was dried over sodium wire prior to its use and its relative permittivity ($\epsilon_1 = 1.917$) was checked in agreement with literature value at 25 °C.

Theoretical formulations to estimate double relaxation times τ_1 , τ_2 and c_1 , c_2 :

The hf complex dielectric relative permittivity ϵ^*_{ij} of polar-non polar liquid mixtures is associated with a number of non-interacting Debye type dispersions in accordance with Budo's relation¹⁶

$$\frac{\epsilon^*_{ij} - \epsilon_{\infty ij}}{\epsilon_{oij} - \epsilon_{\infty ij}} = \sum \frac{c_k}{1 + j\omega\tau_k} \quad (1)$$

where $j = \sqrt{-1}$, is a complex number and c_k is the relative contribution for the *k*-th type of relaxation process.

But when ϵ^*_{ij} consists of two Debye type dispersions Budo's relation reduces to Bergmann's equations¹⁷. $\epsilon_{\infty ij}$ includes within it fast polarization and frequently appears as a subtracted term in Bergmann's equations. Thus to avoid the clumsiness of algebra and to use the modern concept of dielectric terminology and parameter one gets

$$\chi'_{ij} = (\epsilon'_{ij} - \epsilon_{\infty ij}), \chi''_{ij} = \epsilon''_{ij}, \chi_{oij} = (\epsilon_{oij} - \epsilon_{\infty ij})$$

The Bergmann's equations thus becomes

$$\frac{\chi'_{ij}}{\chi_{oij}} = c_1 \frac{1}{1 + \omega^2\tau_1^2} + c_2 \frac{1}{1 + \omega^2\tau_2^2} \quad (2)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = c_1 \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + c_2 \frac{\omega\tau_2}{1 + \omega^2\tau_2^2} \quad (3)$$

The relative weighted factors C_1 and C_2 are such that $C_1 + C_2 = 1$. χ'_{ij} and χ''_{ij} are the real and imaginary parts of hf complex dielectric orientational susceptibility χ_{ij}^* and χ_{oij} is low frequency dielectric susceptibility which is real. The introduction of χ 's in Bergmann's equations are then concerned with the molecular orientational polarization alone.

Putting $\omega\tau_1 = \alpha_1$ and $\omega\tau_2 = \alpha_2$ eqs. (2) and (3) are solved to get

$$c_1 = \frac{(\chi'_{ij}\alpha_2 - \chi''_{ij})(1 + \alpha_1^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad (4)$$

and

$$c_2 = \frac{(\chi''_{ij} - \chi'_{ij}\alpha_1)(1 + \alpha_2^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad (5)$$

provided $\alpha_2 - \alpha_1 \neq 0$.

As $c_1 + c_2 = 1$, we have

$$\frac{(\chi'_{ij}\alpha_2 - \chi''_{ij})(1 + \alpha_1^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} + \frac{(\chi''_{ij} - \chi'_{ij}\alpha_1)(1 + \alpha_2^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} = 1$$

$$\text{or, } \chi'_{ij}\alpha_2 + \chi'_{ij}\alpha_2\alpha_1^2 - \chi''_{ij} - \chi''_{ij}\alpha_1^2 + \chi''_{ij} + \chi''_{ij}\alpha_2^2 - \chi'_{ij}\alpha_1 - \chi'_{ij}\alpha_1\alpha_2^2 = \chi_{oij}(\alpha_2 - \alpha_1)$$

$$\text{or, } \chi'_{ij}(\alpha_2 - \alpha_1) - \chi'_{ij}\alpha_1\alpha_2(\alpha_2 - \alpha_1) + \chi''_{ij}(\alpha_2^2 - \alpha_1^2) = \chi_{oij}(\alpha_2 - \alpha_1)$$

$$\text{or, } \chi'_{ij} - \chi'_{ij}\alpha_1\alpha_2 + \chi''_{ij}(\alpha_2 + \alpha_1) = \chi_{oij}$$

$$\text{or, } \chi''_{ij}(\alpha_1 + \alpha_2) - \chi'_{ij}\alpha_1\alpha_2 = \chi_{oij} - \chi'_{ij}$$

$$\text{or, } \frac{\chi_{oij} - \chi'_{ij}}{\chi'_{ij}} = (\alpha_1 + \alpha_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \alpha_1\alpha_2$$

substituting $\alpha_1 = \omega\tau_1$ and $\alpha_2 = \omega\tau_2$ we have

$$\text{or, } \frac{\chi_{oij} - \chi'_{ij}}{\chi'_{ij}} = \omega(\tau_1 + \tau_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \omega^2\tau_1\tau_2 \quad (6)$$

which is a straight line equation between the variables $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ and χ''_{ij}/χ'_{ij} with slope $\omega(\tau_1 + \tau_2)$ and intercept $\omega^2\tau_1\tau_2$, where $\omega = 2\pi f$, f being frequency of the applied electric field in GHz range. The above equation is, however, satisfied by experimental points as seen in Fig. 1 for different weight fractions w_j 's of solute at 25 °C under electric field frequencies of 24.33, 9.25 and 3.00 GHz. The eq. (6) has been used to estimate τ_1 and τ_2 in order to place them in Table 1.

The theoretical weighed contributions c_1 and c_2 were, then obtained from eqs. (4) and (5) with the variables χ''_{ij}/χ_{oij} and χ''_{ij}/χ'_{ij} of Fröhlich's eqs. (7) and (8) in

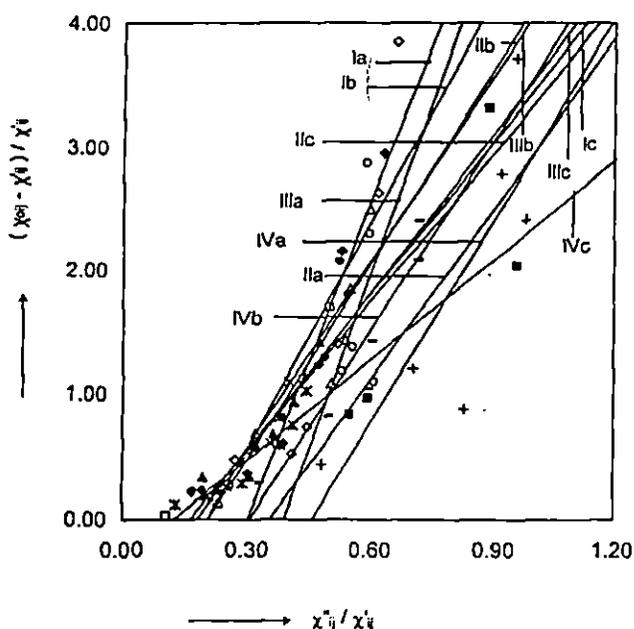


Fig. 1. Linear variation of $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ with χ''_{ij}/χ'_{ij} for alcohols in *n*-heptane at 25 °C of (Ia) 1-butanol (○) at 24.33 GHz, (Ib) 1-butanol (◊) at 9.25 GHz, (Ic) 1-butanol (◻) at 3.00 GHz, (IIa) 1-hexanol (■) at 24.33 GHz, (IIb) 1-hexanol (Δ) at 9.25 GHz, (IIc) 1-hexanol (▲) at 3.00 GHz, (IIIa) 1-heptanol (○) at 24.33 GHz, (IIIb) 1-heptanol (●) at 9.25 GHz, (IIIc) 1-heptanol (×) at 3.00 GHz, (IVa) 1-decanol (+) at 24.33 GHz, (IVb) 1-decanol (-) at 9.25 GHz, (IVc) 1-decanol (*) at 3.00 GHz.

terms of known τ_1 and τ_2 .

$$\frac{\chi'_{ij}}{\chi_{oij}} = 1 - \frac{1}{2A} \ln \left(\frac{1 + \omega^2\tau_2^2}{1 + \omega^2\tau_1^2} \right) \quad (7)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = \frac{1}{A} \left[\tan^{-1}(\omega\tau_2) - \tan^{-1}(\omega\tau_1) \right] \quad (8)$$

Theoretical formulations to estimate symmetric and characteristic relaxation times τ_s and τ_{cs} :

The molecules under present investigation appear to behave like non-rigid ones having symmetric and asymmetric distribution parameters γ and δ involved with eqs. (9) and (10)

$$\frac{\chi_{ij}^*}{\chi_{oij}} = \frac{1}{1 + (j\omega\tau_s)^{1-\gamma}} \quad (9)$$

$$\frac{\chi_{ij}^*}{\chi_{oij}} = \frac{1}{(1 + j\omega\tau_{cs})^\delta} \quad (10)$$

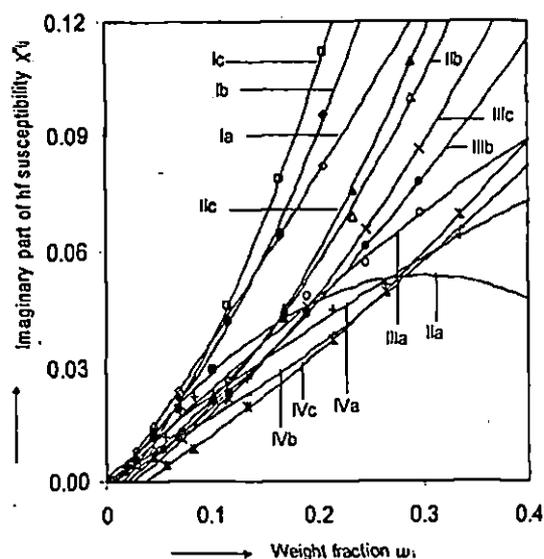


Fig. 2. Variation of imaginary part of hf susceptibility χ''_{ij} with weight fraction w_j for alcohols in *n*-heptane at 25 °C of (Ia) 1-butanol (\diamond) at 24.33 GHz, (Ib) 1-butanol (\blacklozenge) at 9.25 GHz, (Ic) 1-butanol (\square) at 3.00 GHz, (IIa) 1-hexanol (\blacksquare) at 24.33 GHz, (IIb) 1-hexanol (\triangle) at 9.25 GHz, (IIc) 1-hexanol (\blacktriangle) at 3.00 GHz, (IIIa) 1-heptanol (\circ) at 24.33 GHz, (IIIb) 1-heptanol (\bullet) at 9.25 GHz, (IIIc) 1-heptanol (\times) at 3.00 GHz, (IVa) 1-decanol ($+$) at 24.33 GHz, (IVb) 1-decanol ($-$) at 9.25 GHz, (IVc) 1-decanol ($*$) at 3.00 GHz.

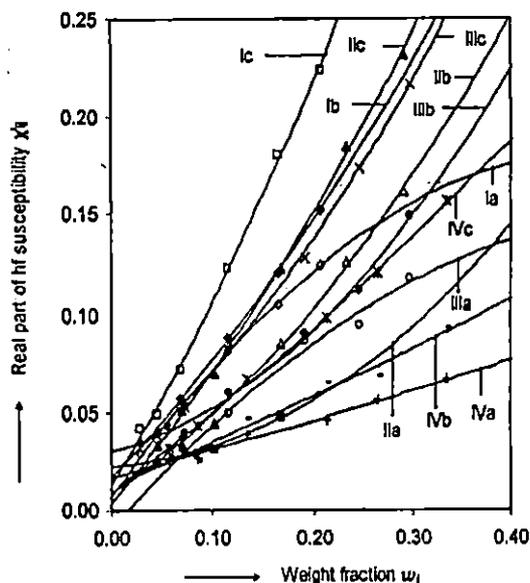


Fig. 3. Variation of real part of hf susceptibility χ'_{ij} with weight fraction w_j for alcohols in *n*-heptane at 25 °C of (Ia) 1-butanol (\diamond) at 24.33 GHz, (Ib) 1-butanol (\blacklozenge) at 9.25 GHz, (Ic) 1-butanol (\square) at 3.00 GHz, (IIa) 1-hexanol (\blacksquare) at 24.33 GHz, (IIb) 1-hexanol (\triangle) at 9.25 GHz, (IIc) 1-hexanol (\blacktriangle) at 3.00 GHz, (IIIa) 1-heptanol (\circ) at 24.33 GHz, (IIIb) 1-heptanol (\bullet) at 9.25 GHz, (IIIc) 1-heptanol (\times) at 3.00 GHz, (IVa) 1-decanol ($+$) at 24.33 GHz, (IVb) 1-decanol ($-$) at 9.25 GHz, (IVc) 1-decanol ($*$) at 3.00 GHz.

The former one is associated with symmetric relaxation time τ_s while the later one with characteristic relaxation times τ_{cs} . On separating the real and imaginary parts of eqs. (9) and (10) and rearranging them in terms of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} at $w_j \rightarrow 0$ as seen in Figs. 5 and 6, the γ and τ_s were obtained as

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[\left(1 - \frac{\chi'_{ij}}{\chi_{oij}} \right) \frac{\chi'_{ij}}{\chi''_{ij}} - \frac{\chi''_{ij}}{\chi_{oij}} \right] \quad (11)$$

and

$$\tau_s = \frac{1}{\omega} \left[\frac{1}{(\chi'_{ij}/\chi''_{ij}) \cos(\gamma\pi/2) - \sin(\gamma\pi/2)} \right]^{1/(1-\gamma)} \quad (12)$$

Similarly δ and τ_{cs} can be had from eq. (10) as

$$\tan(\phi\delta) = \frac{(\chi''_{ij}/\chi_{oij})_{w_j \rightarrow 0}}{(\chi'_{ij}/\chi_{oij})_{w_j \rightarrow 0}} \quad (13)$$

$$\text{and } \tan \phi = \omega\tau_{cs} \quad (14)$$

As ϕ can not be evaluated directly, an arbitrary theoretical curve between $(1/\phi) \log(\cos \phi)$ against ϕ in degree was drawn in Fig. 7 from which

$$(1/\phi) \log(\cos \phi) = \frac{\log \{(\chi'_{ij}/\chi_{oij})/(\cos \phi\delta)\}}{\phi\delta} \quad (15)$$

can be known. The known value of $(1/\phi) \log(\cos \phi)$, is used to know ϕ from Fig. 7. With known ϕ eqs. (13) and (14) can be used to obtain δ and τ_{cs} respectively.

Theoretical formulations to obtain relaxation time τ_j and hf dipole moment μ_j :

The real ϵ'_{ij} and imaginary ϵ''_{ij} parts of hf complex dielectric relative permittivity ϵ^*_{ij} are related by

$$\begin{aligned} \epsilon'_{ij} &= \epsilon_{\infty ij} + (1/\omega\tau)\epsilon''_{ij} \\ \text{or, } (\epsilon'_{ij} - \epsilon_{\infty ij}) &+ (1/\omega\tau)\epsilon''_{ij} \\ \text{or, } \chi''_{ij} &= (1/\omega\tau)\chi''_{ij} \\ \text{or, } (d\chi''_{ij}/d\chi'_{ij}) &= \omega\tau_j \end{aligned} \quad (16)$$

χ''_{ij} 's are found to vary almost linearly¹⁰ with χ'_{ij} as seen in Fig. 4, the slope $\omega\tau_j$ is used to obtain τ_j .

But earlier investigation on some isomers of anisidines and toluidines¹⁵ and the present investigation on normal alcohols shows that variation of χ''_{ij} against χ'_{ij} as seen in Fig. 4 are strictly not linear. The ratio of slopes of

individual variations of χ''_{ij} and χ'_{ij} with w_j 's in Figs. 2 and 3 is a better representation of eq. (16) to get τ_j where polar-polar interactions are almost avoided¹⁵. Thus

$$\frac{(d\chi''_{ij}/dw_j)_{w_j \rightarrow 0}}{(d\chi'_{ij}/dw_j)_{w_j \rightarrow 0}} = \omega\tau_j \quad (17)$$

Imaginary part χ''_{ij} of χ^*_{ij} can be represented^{18,19} as

$$\chi''_{ij} = \frac{N\rho_{ij}\mu_j^2}{27 \epsilon_0 M_j k_B T} \frac{\omega\tau_j}{(1 + \omega^2\tau_j^2)} (\epsilon_{ij} + 2)^2 w_j \quad (18)$$

which on differentiation with respect to w_j and at $w_j \rightarrow 0$ yields that

$$(d\chi''_{ij}/dw_j)_{w_j \rightarrow 0} = \frac{N\rho_{ij}\mu_j^2}{27 \epsilon_0 M_j k_B T} \frac{\omega\tau_j}{(1 + \omega^2\tau_j^2)} (\epsilon_i + 2)^2 \quad (19)$$

Now in comparison to earlier works presented elsewhere^{6,13} the approximation that $\chi_{ij} \approx \chi''_{ij}$ like $\sigma_{ij} \approx \sigma''_{ij}$ is not necessary to obtain μ_j from τ_j where σ''_{ij} is the imaginary part of complex hf conductivity and σ_{ij} is the total hf conductivity of polar-nonpolar liquid mixture. From eqs. (17) and (19) one gets

$$(d\chi''_{ij}/dw_j) = \frac{N\rho_{ij}\mu_j^2}{27 \epsilon_0 M_j k_B T} \frac{\omega\tau_j}{(1 + \omega^2\tau_j^2)} (\epsilon_i + 2)^2$$

$$\text{or, } \omega\tau_j\beta = \frac{N\rho_{ij}\mu_j^2}{27 \epsilon_0 M_j k_B T} \omega\tau_j b (\epsilon_i + 2)^2$$

$$\text{or, } \beta = \frac{N\rho_{ij}\mu_j^2}{27 \epsilon_0 M_j k_B T} b (\epsilon_i + 2)^2$$

$$\text{or, } \mu_j = \left[\frac{27 \epsilon_0 M_j k_B T \beta}{N\rho_{ij}(\epsilon_i + 2)^2 b} \right]^{1/2} \quad (20)$$

which is directly interrelated with the measured τ 's through b , where

ϵ_0 = Permittivity of free space = 8.854×10^{-12} Farad metre⁻¹,

M_j = Molecular weight of solute in kilogramme,

k_B = Boltzmann constant = 1.38×10^{-23} J mol⁻¹ K⁻¹,

T = Temperature in absolute scale,

$\beta = d\chi'_{ij}/dw_j =$ Linear coefficient of $\chi'_{ij} - w_j$ curves of Fig. 3 at $w_j \rightarrow 0$,

Table 1. The relaxation times τ_1 and τ_2 from the slope and intercept of straight line eq. (6), estimated dipole moment μ_1, μ_2 from eq. (20). Computed dipole moment μ_j from τ_j of eq. (17), reported dipole moment (Gopalakrishna's method), all are expressed in Coulomb-metre for different straight chain alcohols in *n*-heptane at 20 °C under different GHz electric field

System with sl. no. and mol. weight in kg	Frequency (f) in GHz	Estimated τ_1 and τ_2 in psec		Estimated dipole moment $\mu \times 10^{30}$ in Coulomb metre (C.m.)			Reported $\mu \times 10^{30}$ in C.m. by Gopalakrishna's method	$\mu_{\text{theo}}^a \times 10^{30}$ in C.m. from reduced bond moments
		τ_1	τ_2	μ_1	μ_2	μ_j		
I. 1-Butanol ($M_j = 0.074$)	24.33	2.04	54.56	3.02	24.25	3.26	3.58	
	9.25	3.72	101.78	2.56	14.99	2.69	3.80	3.74
	3.00	9.09	211.22	3.14	12.72	3.23	4.30	
II. 1-Hexanol ($M_j = 0.102$)	24.33	2.54	27.46	0.79	3.18	8.25	3.35	
	9.25	3.75	85.16	2.35	11.59	2.52	3.87	3.49
	3.00	9.17	204.07	3.16	12.39	3.17	4.27	
III. 1-Heptanol ($M_j = 0.116$)	24.33	2.65	59.09	3.52	29.69	3.60	3.59	
	9.25	3.29	82.96	1.57	7.59	2.86	3.60	3.73
	3.00	10.05	220.31	2.90	12.17	3.06	4.27	
IV. 1-Decanol ($M_j = 0.158$)	24.33	3.29	32.22	2.10	9.43	3.47	3.55	
	9.25	5.60	83.06	2.49	11.67	2.82	3.83	3.68
	3.00	6.88	135.54	3.12	8.50	3.36	4.33	

^aRef. 19.

$N = \text{Avogadro's number} = 6.023 \times 10^{23}$,

$\rho_i = \text{Density of solvent } n\text{-heptane at } 25^\circ\text{C} = 680.15 \text{ kg m}^{-3}$,

$\epsilon_i = \text{Relative permittivity of the solvent } n\text{-heptane} = 1.917$,

$b = 1/(1 + \omega^2\tau^2)$ = a dimensionless parameter involved with estimated τ_1 and τ_2 of eq. (6) and τ_j of eq. (17).

Dipole moments μ_1 and μ_2 obtained with the knowledge of b_1 and b_2 involved with estimated τ_1 and τ_2 by double relaxation method are entered in the 5th and 6th column of Table 1. They are, however, compared to μ_j with τ_j of eq. (17) and reported μ 's (Gopalakrishna) and μ_{theo} as seen in 7th, 8th and 9th columns.

Results and discussion

The least square fitted straight line equation of $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ against χ''_{ij}/χ'_{ij} for different weight fractions w_j 's of solute at 25°C in n -heptane under different GHz electric field frequency are shown graphically in Fig. 1 together with experimental points placed on them. The real χ'_{ij} and imaginary χ''_{ij} parts of hf complex dimensionless dielectric orientational susceptibility χ^*_{ij} and low frequency real dielectric susceptibility χ_{oij} are, however, derived

from measured⁸ permittivities ϵ'_{ij} , ϵ''_{ij} , ϵ_{oij} and $\epsilon_{\infty ij}$. The linearity of all curves of Fig. 1 are confirmed by correlation coefficients r 's and percentage of errors. The relaxation times τ_1 and τ_2 estimated from eq. (6) are placed in the 3rd and 4th columns of Table 1. It is seen that both τ_1 and τ_2 are of low values at 24.33 GHz and tends to increase with the lower frequencies of 9.25 and 3.00 GHz electric fields. It may be explained on the basis of the fact that at higher frequencies the rate of hydrogen bond rupture is maximum in such long chain alcohols to reduce τ for each rotating unit²⁰.

In absence of reliable τ_j of such molecules it was tried to calculate τ_j from the least square fitted straight line equation of χ''_{ij} against χ'_{ij} in Fig. 4 as claimed by Murthy *et al.*¹⁰. But the experimental points are found to deviate from linearity as seen in Fig. 4 which is probably due to various associational aspects of polar molecules in non polar solvent¹³. The individual plots of χ''_{ij} and χ'_{ij} against w_j of normal alcohols are not linear as seen in Figs. 2 and 3 which confirms the probable solute-solute (dimer) and solute-solvent (monomer) molecular associations. The reliability of both $\chi''_{ij} - w_j$ and $\chi'_{ij} - w_j$ variations are confirmed by correlation coefficients r 's and % of errors. This fact at once inspired us to evaluate τ_j from the ratio of slopes of individual variations of χ''_{ij} and χ'_{ij} with w_j at $w_j \rightarrow 0$. τ_j so obtained shows close agreement with τ_1

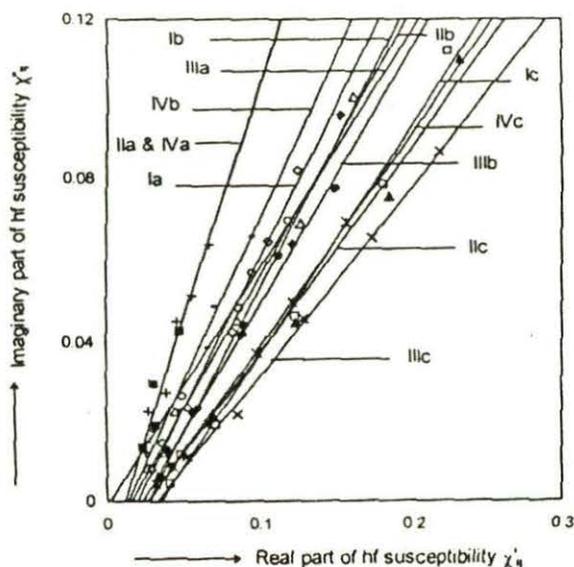


Fig. 4. Variation of imaginary part of hf susceptibility χ''_{ij} with real part of hf susceptibility χ'_{ij} of alcohols in n -heptane at 25°C of (Ia) 1-butanol (\circ) at 24.33 GHz, (Ib) 1-butanol (\blacklozenge) at 9.25 GHz, (Ic) 1-butanol (\square) at 3.00 GHz, (IIa) 1-hexanol (\blacksquare) at 24.33 GHz, (IIb) 1-hexanol (Δ) at 9.25 GHz, (IIc) 1-hexanol (\blacktriangle) at 3.00 GHz, (IIIa) 1-heptanol (\circ) at 24.33 GHz, (IIIb) 1-heptanol (\bullet) at 9.25 GHz, (IIIc) 1-heptanol (\times) at 3.00 GHz, (IVa) 1-decanol ($+$) at 24.33 GHz, (IVb) 1-decanol ($-$) at 9.25 GHz, (IVc) 1-decanol ($*$) at 3.00 GHz.

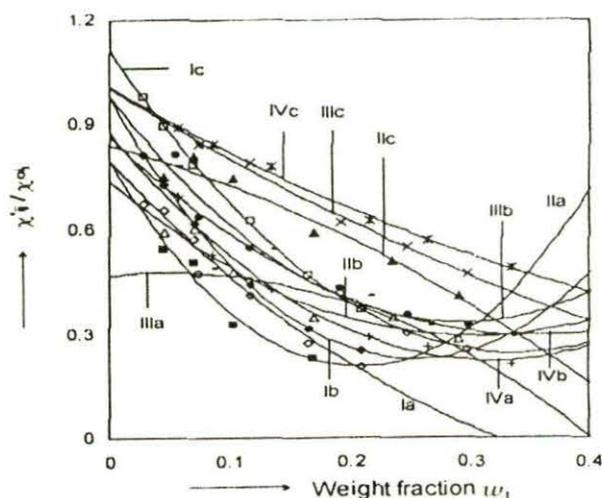


Fig. 5. Variation χ''_{ij}/χ'_{oij} with weight fraction w_j for alcohols in n -heptane at 25°C of (Ia) 1-butanol (\circ) at 24.33 GHz, (Ib) 1-butanol (\blacklozenge) at 9.25 GHz, (Ic) 1-butanol (\square) at 3.00 GHz, (IIa) 1-hexanol (\blacksquare) at 24.33 GHz, (IIb) 1-hexanol (Δ) at 9.25 GHz, (IIc) 1-hexanol (\blacktriangle) at 3.00 GHz, (IIIa) 1-heptanol (\circ) at 24.33 GHz, (IIIb) 1-heptanol (\bullet) at 9.25 GHz, (IIIc) 1-heptanol (\times) at 3.00 GHz, (IVa) 1-decanol ($+$) at 24.33 GHz, (IVb) 1-decanol ($-$) at 9.25 GHz, (IVc) 1-decanol ($*$) at 3.00 GHz.

from double relaxation and Gopalakrishna's method¹¹. This approach further confirms that polar-polar interactions are fully avoided^{6,15} in the later method. Thus hf dielectric susceptibility measurement yields the accurate microscopic τ due to orientational polarisation whereas double relaxation method gives both microscopic τ 's^{15,20}.

Higher values of τ_2 's results in bigger size of rotating unit ($\tau_2 T / \eta$) which is due to solute-solvent (monomer) associations under GHz electric field. Distribution of τ 's between two limiting values τ_1 and τ_2 prompts one to estimate the symmetric and asymmetric distribution parameters γ and δ of such molecules from eqs. (11) and (13) with graphical extrapolation values of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} at $w_j = 0$ of Figs. 5 and 6. Values of γ so obtained is used to evaluate τ_s from eq. (12). The arbitrary curve of $(1/\phi) \log(\cos \phi)$ against ϕ in degree is essential to know ϕ for known value of $(1/\phi) \log(\cos \phi)$ from eq. (15). Known ϕ from Fig. 7 was however used to evaluate δ and τ_{cs} from eqs. (13) and (14). The value of γ establishes the non-rigid behaviour of the molecules signifying the applicability of Debye-Smyth model of dielectric relaxation to some extent in such normal alcohols in *n*-heptane under GHz electric field.

Symmetric relaxation time τ_s obtained from eq. (12) with known γ agrees well with τ_1 's by double relaxation

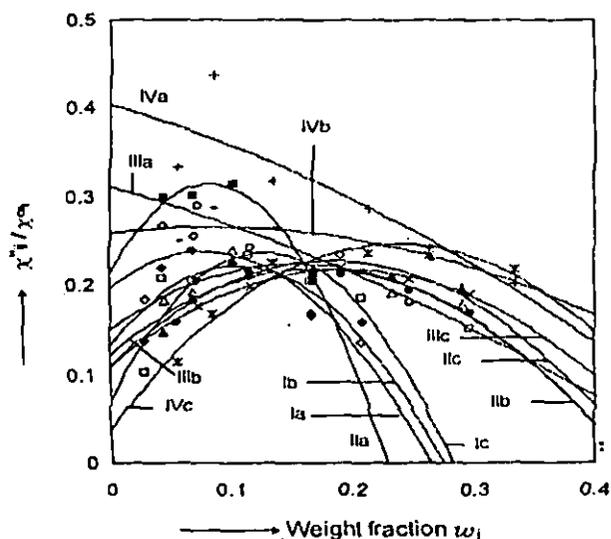


Fig. 6. Variation χ''_{ij}/χ_{oij} with weight fraction w_j for alcohols in *n*-heptane at 25 °C of (Ia) 1-butanol (○) at 24.33 GHz, (Ib) 1-butanol (◊) at 9.25 GHz, (Ic) 1-butanol (◻) at 3.00 GHz, (IIa) 1-hexanol (■) at 24.33 GHz, (IIb) 1-hexanol (Δ) at 9.25 GHz, (IIc) 1-hexanol (▲) at 3.00 GHz, (IIIa) 1-heptanol (○) at 24.33 GHz, (IIIb) 1-heptanol (●) at 9.25 GHz, (IIIc) 1-heptanol (×) at 3.00 GHz, (IVa) 1-decanol (+) at 24.33 GHz, (IVb) 1-decanol (-) at 9.25 GHz, (IVc) 1-decanol (*) at 3.00 GHz.

and τ_1 's by Gopalakrishna's method except at 3.00 GHz electric field frequency. This discrepancy may be explained on the basis of the fact that at lower frequency the rate of hydrogen bond rupture is small resulting in higher value of τ for each rotating unit. High value of τ_{cs} eventually rules out the possibility of occurring asymmetric relaxation behaviour for the alcohols. Fig. 8 represents the plot of both τ_2 and μ_2 against frequency (f) of the applied electric field. It is evident from the plot that τ_2 of the alcohols decreases with frequency. It is due to the fact that at higher frequency the rate of hydrogen bond rupture is maximum, reducing thereby τ_2 for each rotating unit²⁰. For system II and IV the variation of μ_2 against frequency is convex in nature having zero μ_2 values at two frequencies due to strong symmetry attained by the molecules. 1-Butanol (system I) and 1-heptanol (system III) shows minimum μ_2 for their symmetry attained between 3.00 and 9.25 GHz electric field frequency. Beyond 9.25 GHz μ_2 increases with f showing asymmetric nature of the molecules. All types of symmetries and asymmetries arises probably due to various types of molecular associations between solute and solvent molecules which are supposed to be physico-chemical behaviour of the systems¹⁹.

The relative contributions c_1 and c_2 towards dielectric dispersions have been evaluated from eqs. (4) and (5) for fixed τ_1 and τ_2 as predicted from eq. (6) and with estimated χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} from Fröhlich's eqs. (7) and (8). The same are, however, obtained experimentally from the graphical variation of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} with w_j of Figs. 5 and 6 at $w_j = 0$. The Fröhlich's parameter A is the temperature variation of the width of distribution of τ and is equal to $\ln(\tau_2/\tau_1)$. Variation of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij}

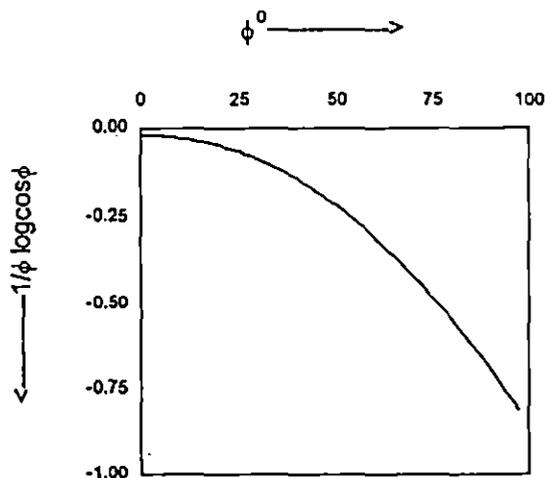


Fig. 7. Variation of $(1/\phi) \log(\cos \phi)$ against ϕ^0 .

χ_{oij} with w_j as seen in Figs. 5 and 6 are concave and convex in nature which are in accordance with Bergmann's eqs. (2) and (3) as observed elsewhere^{14,21}. The estimated c_2 is greater than c_1 for almost all the alcohols in Fröhlich's method, while the reverse is true for graphical technique. Formation of internal hydrogen bonding among -OH groups in polar alcohol molecules gives rise to inertia^{15,20} of the flexible part with respect to whole molecule which results in negative c_2 satisfying the condition $c_1 + c_2 \approx 1$ in graphical technique. For Fröhlich method $c_1 + c_2 > 1$, indicating the possibility of occurrence of more than two relaxation processes⁸ in them.

Dipole moments μ_1 and μ_2 estimated from dimensionless parameters b_1 and b_2 for measured τ_1 and τ_2 and linear coefficient β 's of $\chi'_{ij} - w_j$ curves of Fig. 3 are shown in the 5th and 5th columns of Table 1. Values of r 's and % of errors in terms of r 's gives reliable β to yield accurate μ_1 and μ_2 . Almost all the curves of Fig. 3 shows a tendency to become closer within the limit $0.00 \leq w_j \leq 0.05$ probably due to the same polarity of the molecules arising out of monomer and dimer formations^{13,15}.

The theoretical dipole moments μ_{theo} were, however, obtained from bond angles and bond moments of a number of dipolar groups like $H_3 \rightarrow C$, $C \rightarrow O$ and $O \leftarrow H$ of 1.23×10^{-30} , 3.33×10^{-30} and 1.30×10^{-30} Coulomb metre¹³ and are entered in 9th column of Table 1. The -OH group

in all the alcohols making an angle 105° with the C-C bond plays an important role to yield theoretical dipole moment μ_{theo} . In absence of reliable μ_j values Gopalakrishna's method were employed to get μ_j (reported data) to compare with μ_j 's estimated from the relation $\mu_1 = \mu_2 (c_1/c_2)^{1/2}$ assuming two relaxation processes are equally probable in them. But the agreement is poor probably due to the fact that sum of c_1 and c_2 as estimated from Fröhlich's method is not strictly equal to one. The close agreement between μ_1 from double relaxation method, μ_{theo} and reported μ 's establishes the basic soundness of the method¹⁹ for getting hf μ_j in addition to the fact that a part of the molecule is rotating¹⁵ under GHz electric field. Slight disagreement between μ_{theo} and μ_1 arises due to the formation of H bonds among the -OH groups in dipolar liquid molecules which results in solute-solute molecular association increasing thereby the value of μ_{theo} 's.

Conclusion :

The methodology so far developed in SI units with internationally accepted symbols of dielectric terminologies and parameters appears to be simple, straightforward and topical one to predict relaxation parameters as χ 's are directly linked with molecular orientational polarisation. The significant and interesting equations to evaluate relaxation parameters gives deep insight into the solute-solute and solute-solvent molecular interactions in a solution. The simple straight line eq. (6) provides one with microscopic and macroscopic relaxation times. Evaluation of τ_j from eq. (17) by ratio of slopes of individual variations of χ'_{ij} and χ''_{ij} against w_j in the limit $w_j = 0$ is a better representation of eq. (16) of Murthy *et al.* as it eliminates polar-polar interactions in a solution. The results obviously show that the former method in long straight chain hydrogen bonded associative alcohol molecules may be applicable to get the accurate τ 's of the molecules only due to orientational polarization. Validity of the method so far advanced to evaluate hf τ_j and μ_j is also supported by τ_j and μ_j values estimated from freshly calculated Gopalakrishna's method. The close agreement between measured τ_j and τ_{cs} confirms the non-rigid behaviour of the molecules which at once invites the applicability of Debye-Smyth model of dielectric relaxation in such alcohol molecules. Molecular association is however confirmed by conformational structure in which internal H bonding plays the prominent role. Graphical variation of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} with w_j as seen in Figs. 5 and 6 to estimate c_1 and c_2 are concave and convex in nature which are in accordance with Bergmann's equations. Reliable τ_1 and τ_2 obtained for alcohols at three electric

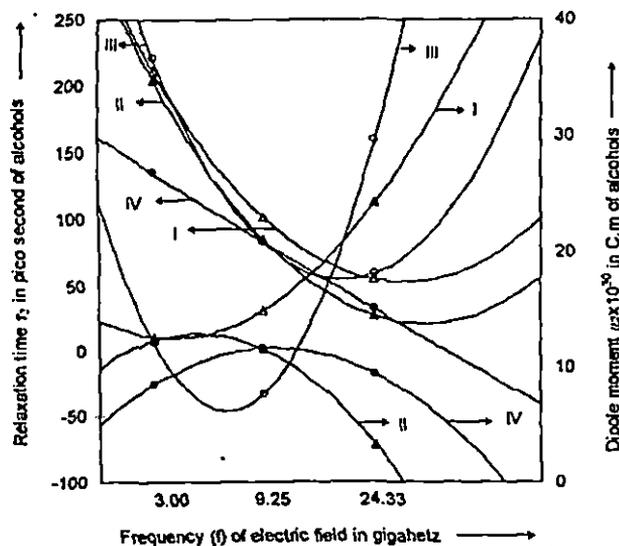


Fig. 8. Variation of relaxation time and dipole moment against frequency (f) of the applied electric field for some alcohols in *n*-heptane at 25 °C (I) 1-butanol (Δ), (II) 1-hexanol (\blacktriangle), (III) 1-heptanol (\circ), (IV) 1-decanol (\bullet).

field frequencies indicate the fact that double relaxation is a material property of the system. Although Figs. 1 to 6 appear to be crowdy, they provides a clear comparison between the results obtained for different systems. Some experimental points are found not to fall on the smooth curves of different figures probably due to various molecular associations between solute and solvent molecules which supports the physico-chemical behaviour of the systems. Concave and convex nature of curves of Fig. 8 shows that stability and instability of the alcohol molecules depends on frequency of the applied electric field ever shown. Thus the correlation between the conformational structures¹⁹ with the observed results enhances the scientific content to add a new horizon of understanding to the existing knowledge of dielectric relaxation phenomena in addition to physico-chemical properties of the polar liquid molecules.

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Structural aspects and physico-chemical properties of polysubstituted benzenes in benzene from relaxation phenomena

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Abstract : A brief report on the physico-chemical properties and structural aspects of some polysubstituted benzenes in benzene at different experimental temperatures under 10 GHz electric field is made to estimate relaxation times τ_j 's, dipole moments μ_j and thermodynamic energy parameters like enthalpy ΔH_τ , entropy ΔS_τ and free energy of activation ΔF_τ due to dielectric relaxation with formulations derived from orientational susceptibilities χ_{ij} 's, τ_j 's of the polar solutes obtained from the slope of the linear equation of χ''_{ij} and χ'_{ij} are, however, compared with those obtained from the ratio of the linear coefficients of individual variations of χ''_{ij} and χ'_{ij} with weight fractions w_j 's of the solute. τ_j 's from the later method are used to get thermodynamic energy parameters from the Eyring's rate process equation to shed more light on the physico-chemical properties of the polar liquid molecules concerned. The estimated μ_j 's in terms of linear coefficients β 's of χ'_{ij-w_j} equations and dimensionless parameters b 's involved with measured τ_j 's are finally compared with theoretical dipole moments μ_{theo} 's obtained from vector addition of available bond angles and bond moments of substituted polar groups. The estimated μ_{theo} gives valuable information regarding structures of the molecules. The slight disagreement between high frequency μ_j 's and μ_{theo} 's provides an interesting insight on the inductive, mesomeric and electromeric effects of the substituted polar groups attached to the parent molecules.

Keywords : Dipole moment, relaxation time, susceptibility.

Relaxation phenomena of polar liquid molecules in non-polar solvents under oscillating electric field in the GHz range at different experimental temperatures are of special importance as they are useful tools to investigate their physico-chemical properties as well as structural and associational aspects^{1,2}. The method is based on evaluation of relaxation time τ_j , dipole moment μ_j and thermodynamic energy parameters. There exists several methods^{3,4} to get τ_j 's and μ_j 's, but all these methods are not as simple as the present one in which a simultaneous determination of μ_j and τ_j is possible. Although several workers⁵⁻⁷ studied the relaxation mechanism of polar liquid molecules, but no such investigation on polysubstituted benzenes in terms of high frequency (hf) dielectric susceptibilities χ_{ij} 's has yet been made. The formulations derived so far may be used to study proteins, micelles, polymers and many other complex fluids⁸ including liquid crystals as well. Even binary mixtures of polar liquids can give rise to slow relaxation⁹. The formulations are concerned with the real χ'_{ij} ($= \epsilon'_{ij} - \epsilon_{\infty ij}$) and imaginary χ''_{ij} ($= \epsilon''_{ij}$) parts of hf complex dimensionless dielectric orientational susceptibility χ^*_{ij} .

The real ϵ'_{ij} and imaginary ϵ''_{ij} parts of high frequency permittivity ϵ^*_{ij} of polysubstituted benzenes like 1,3-diisopropyl benzene, *p*-methyl benzoyl chloride and *o*-chloroacetophenone in benzene at different weight fractions w_j 's of solutes in the temperature range of 30 to 45 °C under 10 GHz electric field were measured by Paul *et al.*¹⁰. The useful optical relative permittivities $\epsilon_{\infty ij}$'s to get concentration variation of χ'_{ij} were generated from Debye-Pallet's equations¹¹.

$$\epsilon'_{ij} = \epsilon_{\infty ij} + \frac{\epsilon_{0ij} - \epsilon_{\infty ij}}{1 + \omega^2 \tau_j^2} \quad (1)$$

and

$$\epsilon''_{ij} = \frac{\epsilon_{0ij} - \epsilon_{\infty ij}}{1 + \omega^2 \tau_j^2} \omega \tau_j \quad (2)$$

with the available τ_j 's previously determined by conductivity measurements¹². Paul *et al.*¹⁰ used the Gopalakrishna's method¹³ to measure τ_j 's from ϵ_{ij} 's in which all the polarisations including the fast polarisation

exist. If 1 is subtracted from low frequency ϵ_{0ij} and real ϵ'_{ij} , the corresponding static susceptibilities χ_{0ij} and real χ'_{ij} contain all the polarizations. When hf $\epsilon_{\infty ij}$ is subtracted from ϵ'_{ij} or static ϵ_{0ij} one obtains susceptibilities χ'_{ij} or χ_{0ij} respectively, involved with the orientational polarization alone to get accurate τ_j 's and μ_j 's.

Both the real ϵ'_{ij} and imaginary ϵ''_{ij} parts of ϵ^*_{ij} are related by¹⁴

$$\epsilon'_{ij} = \epsilon'_{\infty ij} + (1/\omega\tau_j) \epsilon''_{ij} \quad (3)$$

which in terms of established symbols of χ'_{ij} and χ''_{ij} becomes

$$\chi''_{ij} = \omega\tau_j \chi'_{ij} \quad (4)$$

Eq. (4) exhibit linear relationship between χ''_{ij} and χ'_{ij} as seen in Fig. 1. The slope $\omega\tau_j$ is used to get τ_j of a polar solute¹⁵. For most of the associative liquids studied elsewhere¹⁶, however, the variation of χ''_{ij} against χ'_{ij} is not strictly linear as seen in Figs. 2 and 3. Hence the slope of eq. (4) can be written as :

$$\frac{(d\chi''_{ij} / d\omega_j)_{\omega_j \rightarrow 0}}{(d\chi'_{ij} / d\omega_j)_{\omega_j \rightarrow 0}} = \omega\tau_j \quad (5)$$

containing τ_j 's of the present polar solutes. The τ_j 's estimated using eqs. (5) and (4) from both the methods are presented in Table 1. The excellent agreement between

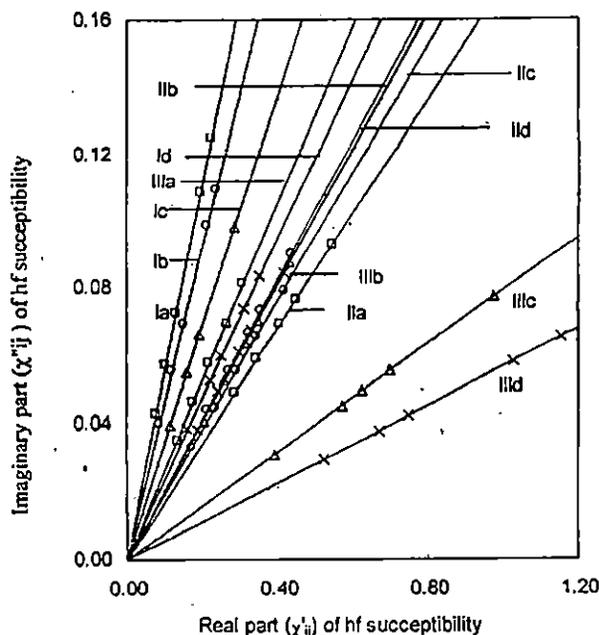


Fig. 1. Variation of imaginary part χ''_{ij} against real part χ'_{ij} of the complex hf dielectric orientational susceptibility χ^*_{ij} of some polysubstituted benzenes in C_6H_6 under 10 GHz electric field at various experimental temperatures. *m*-Di-isopropylbenzene : Ia (\square) at 30°, Ib (O) at 35°, Ic (Δ) at 40°, Id (\times) at 45°; *p*-methylbenzylchloride : IIa (\square) at 30°, IIb (O) at 35°, IIc (Δ) at 40°, IIId (\times) at 45°; *o*-chloroacetophenone : IIIa (\square) at 30°, IIIb (O) at 35°, IIIc (Δ) at 40°, IIIId (\times) at 45°C.

Table 1. Estimated relaxation times τ_j 's, enthalpy ΔH_τ , entropy ΔS_τ and free energy ΔF_τ of activation due to dielectric relaxation, dimensionless parameter $\gamma (= \Delta H_\tau / \Delta H_{\eta_i})$ from slope of $\ln \tau_j T$ vs $\ln \eta_i$ equation, enthalpy of activation ΔH_{η_i} due to viscous flow of the solvent, estimated hf dipole moment μ_j and theoretical dipole moment μ_{theo} in coulomb metre (c.m.) of some polysubstituted benzenes in solvent C_6H_6 at different experimental temperatures in °C under 10 GHz electric field frequency

System with sl. no. and mol. wt. (kg)	Temp. (°C)	τ_j in psec (eq. 4)	τ_j in psec from eq. (5)	ΔH_τ (kJ mol ⁻¹)	ΔS_τ (J mol ⁻¹ K ⁻¹)	ΔF_τ (kJ mol ⁻¹)	Value of δ	$\Delta H_{\eta_i} = (\Delta H_{\tau_j})$ (kJ mol ⁻¹)	Estimated dipole moment $\mu \times 10^{30}$ c.m. with τ_j from eq. (5)	$\mu_{theo} \times 10^{30}$ c.m. from bond angles and reduced bond moments
(I) <i>m</i> -Di-isopropyl-benzene ($M_j = 0.162$)	30	8.80	8.80		109.01	10.12			12.70	
	35	7.33	7.33		108.09	9.86			13.87	
	40	5.46	5.46	43.15	108.16	9.30	6.96	6.20	13.99	3.77
	45	3.74	3.76		109.01	8.49			14.76	
(II) <i>p</i> -Methylbenzoyl chloride ($M_j = 0.156$)	30	2.72	2.72		-59.09	7.16			9.63	
	35	3.30	3.30		-60.26	7.82			9.82	
	40	3.23	3.23	-10.74	-59.66	7.93	-1.61	6.67	9.95	8.80
	45	3.24	3.24		-59.28	8.11			10.10	
(III) <i>o</i> -Chloroacetophenone ($M_j = 0.156$)	30	4.20	4.20		255.12	8.26			6.83	
	35	3.04	3.04		253.09	7.61			7.72	
	40	1.26	1.26	85.56	255.84	5.48	13.56	6.31	7.05	7.40
	45	0.90	0.90		254.21	4.72			6.48	

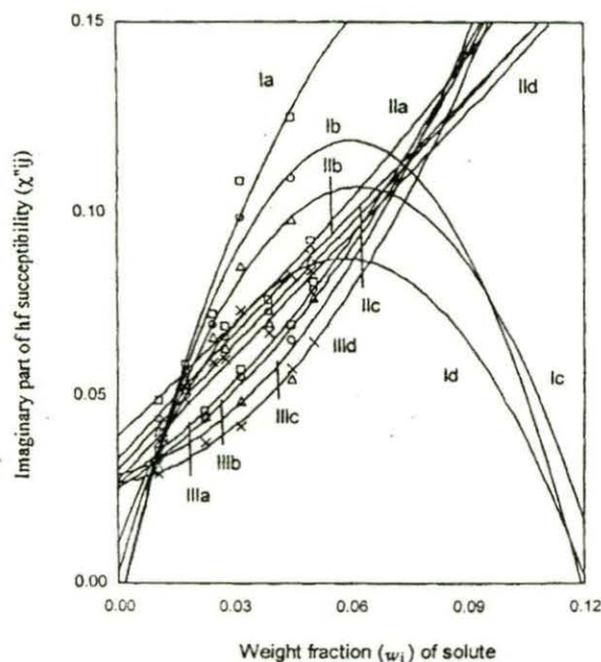


Fig. 2. Variation of imaginary part χ''_{ij} of hf susceptibility with weight fraction w_j 's of some polysubstituted benzenes in C_6H_6 under 10 GHz electric field at various experimental temperatures. *m*-Di-isopropylbenzene : Ia (\square) at 30°, Ib (O) at 35°, Ic (Δ) at 40°, Id (\times) at 45°; *p*-methylbenzylchloride : IIa (\square) at 30°, IIb (O) at 35°, IIc (Δ) at 40°, IID (\times) at 45°; *o*-chloroacetophenone : IIIa (\square) at 30°, IIIb (O) at 35°, IIIc (Δ) at 40°, IIId (\times) at 45°C.

τ_j 's indicates that the polar-polar interactions are almost eliminated in the limit of $w_j = 0$ to give reliable τ_j by the latter method¹⁷. The correlation coefficients r 's and relative errors of both the plots in Figs. 2 and 3 were obtained by regression analysis. They are within the range of 0.93 to 0.99 and 0.0008 to 0.0001 respectively, hereby indicating how far both χ''_{ij} 's and χ'_{ij} 's are correlated with w_j 's. It is evident from Table 1 that τ_j 's decrease with temperature. At constant temperature τ_j depends on the energy difference between the activated and normal states. At higher temperatures thermal agitation causes an increase in energy loss due to larger number of collisions and thereby decreases the values of τ_j 's. For *m*-diisopropyl benzenes the τ_j 's are greater in comparison to *p*-methyl benzoyl chloride and *o*-chloro acetophenone probably due to bigger size of the molecules containing higher number of carbon atoms. For systems II and III τ_j 's do not vary much with temperature because of the presence of the same number of C-atoms in both the molecules. *p*-Methyl benzoyl chloride shows reverse variation of τ_j with temperature. Inductive effect of CH_3 group put the $C=O$ group of $COCl$ to exist as dipolar structure

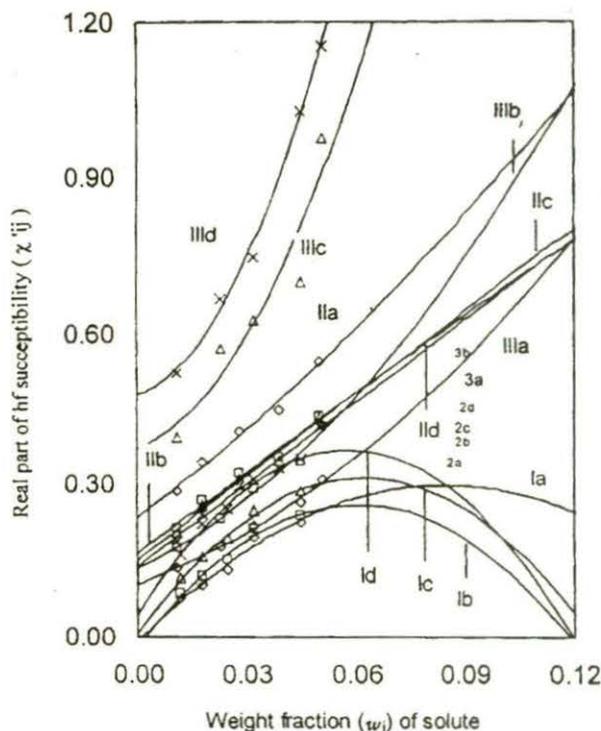


Fig. 3. Variation of imaginary part χ'_{ij} of hf susceptibility with weight fraction w_j 's of some polysubstituted benzenes in C_6H_6 under 10 GHz electric field at various experimental temperatures. *m*-Di-isopropylbenzene : Ia (\diamond) at 30°, Ib (\square) at 35°, Ic (Δ) at 40°, Id (\times) at 45°; *p*-methylbenzylchloride : IIa (\diamond) at 30°, IIb (\square) at 35°, IIc (Δ) at 40°, IID (\times) at 45°; *o*-chloroacetophenone : IIIa (\diamond) at 30°, IIIb (\square) at 35°, IIIc (Δ) at 40°, IIId (\times) at 45°C.

($>C^+-O^-$), therefore increase in temperature has no significant effect on τ_j of this system.

Dielectric relaxation is a process of rotation of polar molecule under hf electric field and it requires an activation energy ΔF_τ to overcome the potential energy barrier between two equilibrium positions. ΔF_τ is related to estimated τ_j by¹⁹

$$\tau_j = (A/T) e^{\Delta F_\tau/RT} \quad (6)$$

$$\text{where } \Delta F_\tau = \Delta H_\tau - T\Delta S_\tau \quad (7)$$

From eqs. (6) and (7) it follows that

$$\ln \tau_j T = \ln A' + (\Delta H_\tau/R) 1/T \quad (8)$$

$$\text{where } A' = Ae^{-\Delta S_\tau/R}$$

Eq. (8) is a straight line when $\ln(\tau_j T)$ is plotted against $1/T$ as seen in Fig. 4, the slope and intercept are used to get enthalpy of activation ΔH_τ , entropy of activation ΔS_τ and free energy of activation ΔF_τ due to dielectric relaxation as presented in Table 1. The enthalpy of activation ΔH_τ

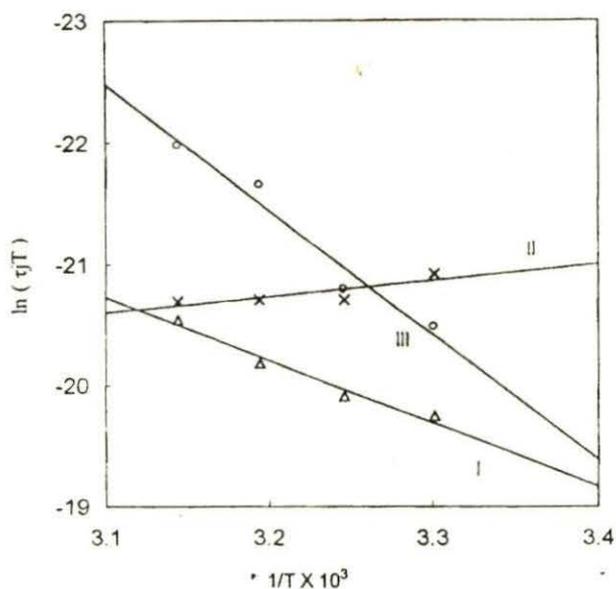


Fig. 4. The linear plot of $\ln(\tau_j T)$ against $1/T$ of some polysubstituted benzenes in C_6H_6 under 10 GHz electric field. (I) *m*-Diisopropylbenzene (Δ) using τ_j of eq. (2), (II) *p*-methylbenzylchloride (\times) using τ_j of eq. (2), (III) *o*-chloroacetophenone (O) using τ_j of eq. (2).

due to viscous flow of the solvent is ascertained from the slope $\delta (= \Delta H_\tau / \Delta H_{\eta_i})$ of the linear equation of $\ln \tau_j T$ against $\ln \eta_i$, where η_i is the coefficient of viscosity of the solvent used.

It is evident from Table 1 and Fig. 4 that for system II the linear eq. (8) has negative slope to give negative ΔH_τ because for that system τ_j 's increases with temperature. The systems I and III shows positive ΔS_τ 's which suggest that the configuration involved in dipolar rotation has an activated state which is less ordered than the normal state²⁰. Unlike *p*-methyl benzoyl chloride both systems I and III show $\delta > 0.50$ (as seen in Table 1) indicating solvent environment around solute molecules to behave as solid phase rotators^{18,20}. ΔH_{η_i} in Table 1 involved with translational and rotational motions of the molecule is of lower value than those of ΔH_τ 's in which only the rotational motion occurs. The Debye factors $\tau_j T / \eta_i$ unlike Kalman factors $\tau_j T / \eta_i^\gamma$ at all temperatures are of constant orders for each system. This at once reflects the validity of Debye model¹⁸ of dielectric relaxation for such compounds in benzenes under 10 GHz electric field.

Theoretical formulations :

In order to obtain hf dipole moment μ_j , the Debye-Smyth's relation^{21,22} in terms of hf χ_{ij} 's is used

$$\chi''_{ij} = \frac{N\rho_{ij}\mu_j^2}{27\epsilon_0 M_j k_B T} \left(\frac{\omega\tau_j}{1 + \omega^2\tau_j^2} \right) (\epsilon_{ij} + 2)^2 w_j \quad (9)$$

where M_j = molecular weight of the solute in kg.

ϵ_{ij} = relative permittivity of solution (ij)

ρ_{ij} = density of solution (ij)

k_B = Boltzmann constant

Eq. (9) on differentiation with respect to w_j and at $w_j \rightarrow 0$

$$\left(\frac{d\chi''_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_i\mu_j^2}{27\epsilon_0 M_j k_B T} \left(\frac{\omega\tau_j}{1 + \omega^2\tau_j^2} \right) (\epsilon_j + 2)^2 \quad (10)$$

in the limit $w_j = 0$, because $\rho_{ij} \rightarrow \rho_i$, $\epsilon_{ij} \rightarrow \epsilon_i$ are the density, relative permittivity of solvent benzene. From eqs. (5) and (10) one obtains

$$\mu_j = \left[\frac{27\epsilon_0 M_j k_B T \beta}{N\rho_i (\epsilon_i + 2)^2 b} \right]^{1/2} \quad (11)$$

where $b = 1/(1 + \omega^2\tau_j^2)$ is a dimensionless parameter associated with estimated τ_j of eq. (5), β is the linear coefficient of $\chi'_{ij} - w_j$ curves of Fig. 3.

Experimental

The microwave radiations of frequency 10 GHz, generated by a Gunn oscillator fed by 10 volt dc power supply were passed through the isolator, tuner, frequency meter, attenuator and a slotted line fitted with a probe connected with a crystal detector and a VSWR meter. The other end of the slotted line was connected to a 6.4 cm long silvered waveguide cell which was connected to a thermostat by a 90° bend to carry out the experimental values of ϵ'_{ij} and ϵ''_{ij} at different temperatures¹⁰.

The viscosity η_i and density ρ_i of benzene at various experimental temperatures were measured using an Ubbelohde viscometer and a pycnometer respectively. The analytical grade polysubstituted benzenes like 1,3-diisopropyl benzene, *p*-methyl benzoyl chloride and *o*-chloroacetophenone as well as the solvent benzene were supplied by Central Drug Research Institute, Lucknow. They were further purified by repeated fractional distillations and the physical constants like density, viscosity and relative permittivity ϵ_i of solvent C_6H_6 were checked in agreement with the literature values¹⁰. The polar liquids were kept over molecular sieve of mesh 4 Å for 48

h with occasional shaking. They were then distilled through a long vertical fractionating column and the middle fractions were used for the present study. Benzene (B.D.H., Analar) was purified by refluxing over sodium metal for 6 h and then distilled through a long vertical fractionating column. The middle fraction of the solvent was used to make solutions of different w_j 's of the respective solutes at different experimental temperatures²⁶.

Results and discussion

The μ_j 's thus measured at all temperatures are entered in Table 1. Almost all the $\chi'_{ij}-w_j$ curves have a tendency to come closer within the range $0.00 < w_j < 0.03$ probably due to almost same polarity of the molecules²² arising out of solute-solvent or solute-solute molecular association which may be supposed to be physico-chemical properties¹⁴ of the systems. This can be inferred from the nonlinear variation of μ_j-t curves of Fig. 5. Unlike the system I and II, *o*-chloroacetophenone (system III) shows minimum μ_j 's at lower and higher temperatures. In the vicinity of $-\text{COCH}_3$ and Cl, the electronic factor may operate between the carbonyl oxygen and Cl atom at *ortho* position may be the reason for its anomalous behaviour towards μ_j value as seen in Fig. 6. The minimum μ_j 's indicate the attainment of slight symmetry in the molecules at those temperatures¹⁸. The monotonic increase of μ_j with temperature for *p*-methyl benzoyl chloride oc-

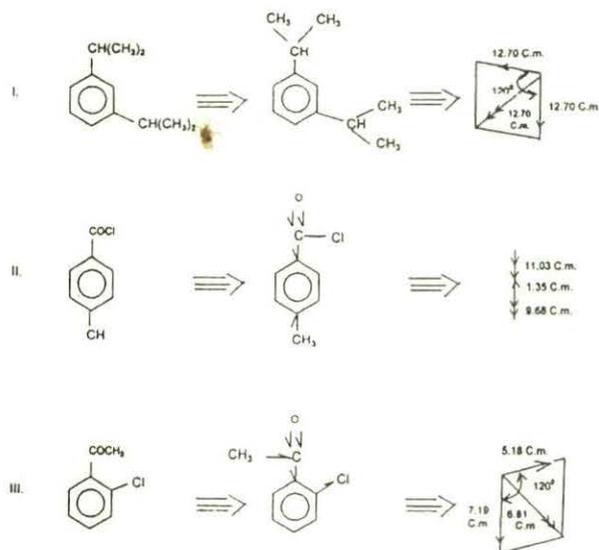


Fig. 6. Conformational structures of different polysubstituted benzenes with dipole moment $\mu_{\text{theo}} \times 10^{30}$ in Coulomb metre (c.m.). (I) *m*-Di-isopropylbenzene, (II) *p*-methylbenzoylchloride, (III) *o*-chloroacetophenone.

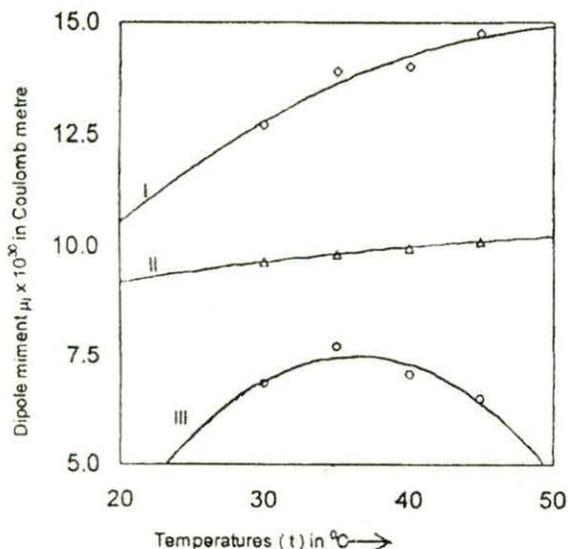


Fig. 5. Plot of measured dipole moment μ_j in Coulomb metre [using τ_j by our method i.e. eq. (5)] with temperatures t in $^{\circ}\text{C}$ of some polysubstituted benzenes in C_6H_6 under 10 GHz electric field. (I) *m*-Di-isopropylbenzene (\square) using τ_j of eq. (2), (II) *p*-methylbenzoylchloride (Δ) using τ_j of eq. (2), (III) *o*-chloroacetophenone (O) using τ_j of eq. (2).

curs for its increasing molecular asymmetry at higher temperatures. The above nature of μ_j-t curves arises due to alignment of different types of bondings among the solute and solvent molecules which are either formed or broken to some extent^{23,24}. Thus the measured μ_j 's reflects the stability or instability of the molecules. This is confirmed by different thermodynamic energy parameters in order to make a strong comment on their physico-chemical properties.

Theoretical dipole moment's μ_{theo} 's, as seen in Fig. 6. are, however, considered by vector addition of bond moments of substituted polar groups of molecules from the available infrared spectroscopic data of bond moments assuming the molecules to be planar ones. They are placed in Table 1 to compare them with the measured hf μ_j 's. The molecules under study have polar groups and there is large probability of intramolecular group rotations and, therefore, these molecules may not be represented by simple Debye type dielectric dispersions. On the otherhand, Higasi's equation⁷ for single frequency in dilute solutions or Higasi's frequency variation method could, however, be used to evaluate those group rotations for such molecules. But the molecules are very simple and the purpose of the paper is to see the applicability of Debye type dispersions in them in evaluating τ_j and μ_j which are claimed to be accurate with 10% and 5% respectively. The molecules of polysubstituted benzenes

referred to tables and figures are planar and have the property of cyclic delocalization of π electrons on each C-atom. The solvent benzene is a cyclic and planar compound with three double bonds and six p -electrons on six carbon atoms of the benzene ring. Hence π - π interaction or resonance effect combined with an inductive effect commonly known as mesomeric effect in excited state called the electromeric effect is expected to play the prominent role in μ_j 's. The slight disagreement between hf μ_j 's and μ_{theo} 's of Fig. 6 is explained on the basis of the fact that the flexible polar groups of the molecules are greatly influenced by hf electric field to yield the inductive, mesomeric and electromeric effects in them to give higher μ_j values, especially for *m*-diisopropyl benzene. All these effects, are, however, incorporated in their structures by multiplying the bond moments by a factor μ_j/μ_{theo} to make μ_{theo} 's closer to μ_j 's as sketched in Fig. 6. The electromeric effect caused by $>C=O$ in the 2nd and 3rd molecules may be the reason to make μ_j 's more closer to μ_{theo} 's²⁵.

Conclusion :

The theoretical formulations in terms of internationally accepted and established symbols of established dielectric terminologies and parameters in SI units are more topical, significant and simpler one to have deep insight into the physico-chemical, structural and associational aspects of polysubstituted benzenes in C_6H_6 at different temperatures under 10 GHz electric field. The conformational structures so far sketched in Fig. 6 are also significant because they enhance the scientific content of the existing knowledge of dielectric relaxation processes. The curves satisfied by experimental points in all the figures reflect the validity of the theoretical formulations based on Debye model to estimate several physical parameters such as τ_j 's, μ_j 's and ΔH_τ , ΔF_τ , ΔS_τ etc. which are more of archival values to study the temperature variation of physico-chemical properties of dipolar molecules. The uncertainty in the evaluated τ_j and μ_j values are of 10% and 5% errors which are claimed to be accurate.

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The Structural Aspects and Physico Chemical Properties of Binary Polar Liquids in Nonpolar Solvent under a Gigahertz Electric Field

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The mixtures of two polar liquids N,N-dimethyl formamide DMF(j) and N,N-dimethyl sulphoxide DMSO(k) in a nonpolar solvent benzene C_6H_6 (i) are studied in terms of the ternary(ijk) high frequency (hf) orientational susceptibilities χ_{ijk} 's at different experimental temperatures in $^{\circ}C$ to arrive at the structural and associational aspects of those polar liquids. The estimation of binary relaxation time τ_{jk} and dipole moment μ_{jk} and several thermodynamic energy parameters like the enthalpy of activation $(\Delta H\tau)_{jk}$, the entropy of activation $(\Delta S\tau)_{jk}$, the free energy of activation $(\Delta F\tau)_{jk}$ of the binary solutes are, however, obtained in order to reach the conclusion. The dimensionless parameter $\delta = (\Delta H\tau)_{jk} / \Delta H\eta_i$ estimated from the slope of the linear equation of $\ln\tau_{jk}T$ against $\ln\eta_i$ where η_i is the coefficient of viscosity of the solvent used, provides one with the information of the solute-solute and solute-solvent molecular associations among the molecules concerned. Almost constant values of Debye factor $\tau_{jk}T / \eta_i$ unlike Kalman factors $\tau_{jk}T / \eta_i^{\delta}$ indicate the Debye relaxation mechanism obeyed by the solutions of binary associated molecules in C_6H_6 . The measured hf binary dipole moment μ_{jk} in terms of estimated binary relaxation time τ_{jk} are compared with the theoretical dipole moments μ_{theo} 's obtained from the bond moments of the substituent polar groups attached to the parent molecules only to support their conformations of associations. The disagreement between μ_{jk} 's and μ_{theo} 's indicates the inductive, mesomeric and electromeric effects of the substituent polar groups in addition to their H-bonding in a gigahertz electric field.

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