

Chapter 7

**DIELECTRIC RELAXATION OF
PARA-POLAR LIQUIDS UNDER
HIGH FREQUENCY ELECTRIC FIELD**

DIELECTRIC RELAXATION OF PARA - POLAR LIQUIDS UNDER HIGH FREQUENCY ELECTRIC FIELD

1. INTRODUCTION

The dielectric relaxation phenomena of a polar liquid in nonpolar solvent have already gained much attention of a large number of workers¹⁻³. The process is thought to be a sensitive tool to investigate the molecular size, shape and structure of a polar liquid. The structural and associational aspects of the polar liquid can thus be inferred in terms of their measured relaxation time τ and hence dipole moment μ at different experimental temperatures in °C. The subsequent use of the temperature dependence of τ 's usually yields different thermodynamic energy parameters of a polar unit. The polar liquid having substituted polar groups in their para positions deserve a special property to be investigated. The μ 's of such para liquids are usually found to be zero⁴ due to symmetrical distribution of bond moments of the substituted polar groups in a plane. Sometimes they show resultant μ when the dipolar and free groups are out of plane with the parent ring.

Earlier investigations⁵ were made in substituted hydroxy and methoxy benzaldehydes in benzene to reveal that τ is generally governed by both molecular and intra-molecular rotations. However, no such study on the long chain substituted parabenzenaldehydes and phenones have been made so far. Dhar et al⁶ and Some vanshi et al⁷ have recently measured real ϵ'_{ij} and imaginary ϵ''_{ij} parts of complex dielectric constant ϵ_{ij}^* of p-hydroxypropiophenone, p-chloropropiophenone, p-acetamidobenzaldehyde, p-benzyloxybenzaldehyde in dioxane⁴ and p-anisidine, p-phenitidine, o-chloroparanitro aniline and p-bromonitro benzene in benzene respectively under 3 cm. wave length electric field at different experimental temperatures. The purpose of their study was only to observe the molecular and intra-molecular group rotations in the

molecules. Non spherical molecular liquids of such type also are known to be strongly non-Debye in their relaxation behaviour. we, therefore, concentrate our attention to these molecules⁶ to study dielectric relaxation phenomena by conductivity measurement technique⁸ based on the internationally accepted symbols of dielectric terminology and parameters. The phenones together with other di- or tri-substituted benzenes having rigid and free dipolar groups at their para positions are included in the present investigation to compare the dielectric relaxation properties with the benzaldehyde groups. Moreover, our aim is to observe how τ 's and μ 's vary with respect to sizes, shapes and structures of the molecules and to get an idea of molecular environment of such polar liquids too, in solvents. For most of the polar liquids the imaginary part σ''_{ij} varies linearly⁸ with the real part σ'_{ij} of hf complex conductivity σ_{ij}^* for different w_j 's of a solute. But in the present polar - nonpolar liquid mixtures the variation of σ''_{ij} with σ'_{ij} was not linear⁹ to yield τ_j . The ratio of the individual slopes of σ''_{ij} and σ'_{ij} against w_j 's curves at $w_j \rightarrow 0$, on the other hand, is used to get τ_j 's of these p - polar liquids in order to report them in Table 1.

The linear relationship of $\ln(\tau_j T)$ against $1/T$ as shown in Table 2, could, however, be used to obtain thermodynamic energy parameters like enthalpy of activation ΔH_τ , entropy of activation ΔS_τ and free energy of activation ΔF_τ of dielectric relaxation process of the rate theory of Eyring et al¹⁰. The enthalpy of activation ΔH_η due to viscous flow was, however, obtained from the slope γ of the linear relationship of $\ln(\tau_j T)$ against $\ln \eta$, where η is the coefficient of viscosity of the solvent to test the behaviour of solutes in solvents.

The values of ΔS_τ , ΔH_τ , and ΔF_τ of Table 2 give an insight into molecular dynamics of the systems. The estimated Debye factor $(\tau_j T/\eta)$ and Kalman factor $(\tau_j T/\eta^\gamma)$, in Table 2 signify the applicability of the required relaxation model for such p - liquids.

The dipole moments μ_j 's of all the liquids were finally worked out from the slopes β 's of hf conductivities σ_{ij} 's with w_j 's and dimensionless parameters

Table 1

The ratio of slopes of concentration variation of imaginary σ''_{ij} and real σ'_{ij} parts of high frequency complex conductivity σ^*_{ij} at $\omega_j \rightarrow 0$ estimated and reported τ_j in pico second, dimensionless parameter b [$= 1/(1 + \omega^2\tau_j^2)$], coefficients α, β, γ , of equation: $\sigma_{ij} = \alpha + \beta\omega_j + \gamma\omega_j^2$, estimated and reported dipole moment μ_j in Coulomb-metre at different experimental temperatures in $^{\circ}\text{C}$ and the theoretical dipole moment μ_{theo} in Coulomb-metre from bond angles and bond moments for different para compounds.^a

System with SI. No. and Molecular weight M_j	Temp. in $^{\circ}\text{C}$	Ratio of slopes of σ''_{ij} & σ'_{ij} with ω_j ($d\sigma''_{ij}/d\omega_j$) $x/y = (d\sigma'_{ij}/d\omega_j)$	Estimated τ_j in p.sec	Reported τ_j in p.sec	Dimensionless parameter $b = 1/(1 + \omega^2\tau^2)$	Coefficients in the equation $\sigma_{ij} = \alpha + \beta\omega_j + \gamma\omega_j^2$			Estimated $\mu_j \times 10^{30}$ in Coulomb metre	Reported $\mu_j \times 10^{30}$ in Coulomb metre	Dipole moments $\mu_{\text{theo}} \times 10^{30}$ from bond angles and bond moments
						$\alpha \times 10^{-10}$	$\beta \times 10^{-11}$	$\gamma \times 10^{-12}$			
1. Para hydroxy-propiofenone $M_j = 0.150\text{kg}$	17	0.8287	19.86	-	0.4070	12.8647	-5.0205	42.5270	0.00		
	23	0.7451	22.08	25.40	0.3571	12.8887	0.0919	15.2643	2.36	10.20	8.27
	30	0.7028	23.41	24.20	0.3307	13.5236	-2.4503	-24.4312	0.00		
	37	1.1073	14.86	23.10	0.5508	12.9387	-19.8001	5.2591	15.03		
2. Para - chloropropiophenone $M_j = 0.1685\text{kg}$	19	0.7427	22.15	20.80	0.3556	12.7486	1.3145	6.8967	9.43		
	25	0.8261	19.92	19.70	0.4056	12.9382	-1.5409	16.8094	0.00	9.84	9.73
	31	0.7272	22.63	18.20	0.3458	12.8983	1.4290	0.2140	10.31		
	37	2.1799	7.55	17.10	0.8261	12.5003	13.8819	-64.5742	21.14		
3. Para acetamido-benzaldehyde $M_j = 0.163\text{kg}$	17	0.5756	28.58	21.80	0.2490	13.0577	0.7906	6.5180	8.55		
	23	0.7736	21.27	20.80	0.3744	13.0602	2.5550	-7.2309	12.75	10.37	13.12
	30	0.7260	22.66	19.00	0.3453	12.9053	5.8673	17.9855	20.51		
	37	1.0111	16.27	18.60	0.5056	12.6908	13.9352	-50.5510	26.62		
4. Para benzoyloxy benzaldehyde $M_j = 0.212\text{kg}$	20	0.5865	28.06	20.00	0.2259	12.9919	1.3256	-3.8704	12.56		
	25	0.6247	26.34	19.40	0.2807	13.1236	1.0601	-	10.87	10.63	6.23
	30	0.8358	19.69	18.00	0.4112	13.2032	1.3264	-	10.19		
	35	1.2238	13.44	16.90	0.5998	13.3518	0.8984	-	7.04		
5. Paraanisidine $M_j = 0.123\text{kg}$	20	2.2120	7.43	3.89	0.8306	12.8499	6.1740	-16.7410	12.23	5.20	
	30	2.4152	6.81	3.67	0.8537	13.1252	1.8955	-	6.87	10.33	6.28
	40	3.4952	4.71	3.17	0.9243	13.1862	1.9022	-	6.79	8.87	
6. Parapentidine $M_j = 0.137\text{kg}$	20	1.5288	10.76	11.08	0.7005	13.3177	5.4487	-	13.21	7.47	15.04
	30	1.9049	8.64	10.63	0.7839	12.7717	14.0691	-24.4860	20.61	9.27	
	40	2.1036	7.82	9.95	0.8158	13.6273	3.9487	-2.2744	10.98	10.47	
7. Ortho-chloro- paranitroaniline $M_j = 0.1725\text{kg}$	20	1.5124	10.88	10.57	0.6958	12.3443	1.2822	-0.9397	7.21	8.13	15.93
	30	1.9522	8.43	9.89	0.7921	12.7291	0.1756	-	2.57	10.93	
	40	2.2126	7.44	9.18	0.8302	12.8787	0.0908	-	1.85	13.10	
8. Para-bromo- nitrobenzene $M_j = 0.202\text{kg}$	20	1.6446	10.01	-	0.7299	13.3533	0.6908	0.2145	5.59	-	
	30	1.7818	9.24	-	0.7603	13.7402	-0.6908	2.5184	0.00	-	8.40
	40	1.9503	8.44	-0.7917	13.8959	-0.5847	2.5301	0.00	-	-	

Table 2

The intercepts and slopes of $\ln \tau_j T$ against $1/T$ curves, energy parameters like enthalpy of activation ΔH_{τ} in Kilo Joule mole⁻¹, the entropy of activation ΔS_{τ} in Joule mole⁻¹ K⁻¹, free energy of activation ΔF_{τ} in Kilo-Joule-mole⁻¹ for dielectric relaxation process, enthalpy of activation ΔH_{η} in Kilo Joule mole⁻¹ due to viscous flow, γ as the ratio of ΔH_{τ} and ΔH_{η} , Kalman factor ($\tau_j T/\eta^2$), Debye factor ($\tau_j T/\eta$) at different experimental temperatures in $^{\circ}\text{C}$ and the coefficients of μ_j -t equations $\mu_j = a + bt + ct^2$ of different para compounds

System with SI. No.	Temp. in $^{\circ}\text{C}$	Intercept & slope of $\ln \tau_j T$ Vs $1/T$ Curve		ΔH_{τ} in KJ mole ⁻¹	ΔS_{τ} in J mole ⁻¹ K ⁻¹	ΔF_{τ} in KJ mole ⁻¹	$\gamma = (\Delta H_{\tau}/\Delta H_{\eta})$	ΔH_{η} in KJ mole ⁻¹	Kalman Factor $\tau_j T/\eta^2$	Debye Factor $(\tau_j T/\eta) \times 10^6$	Coefficients in the equation $\mu_j \times 10^{30} = a + bt + ct^2$		
		Intercept	Slope								a	b	c
1. Para hydroxy propiofenone	17			-19.02	11.53			11.15	19.75×10^{-8}	4.0135	35.4250	-3.2286	0.0716
	23	-21.36	-724.41	6.02	-20.49	12.08	0.54		23.64×10^{-8}	5.0274			
	30				-21.64	12.58			27.55×10^{-8}	6.2221			
	37				-18.51	11.76			19.36×10^{-8}	4.6767			
2. Para chloro-propiofenone	19			79.57	11.90			13.36	0.2112	4.6531	92.9880	-7.1216	0.1407
	25	-33.17	4227.52	35.13	77.86	11.93	2.63		0.2535	4.7300			
	31				74.30	12.54			0.2938	6.1424			
	37				81.03	10.01			0.1890	2.3761			
3. Para acetamido benzaldehyde	17			7.92				13.37	11.12×10^{-6}	5.7757			
	23	-24.76	1770.09	14.71	9.17	12.41	1.10		9.41×10^{-6}	4.8430	-4.2996	0.6554	0.0050
	30				7.31	11.99			11.86×10^{-6}	6.0228			
	37				8.77	12.49			10.23×10^{-6}	5.1205			
4. Para benzoyloxy benzaldehyde	20			71.34	12.52			17.68	19.57×10^{-4}	5.7293	9.0620	0.4582	0.0146
	25	-32.27	4022.34	33.43	69.81	12.62	1.89		22.42×10^{-4}	6.0379			
	30				70.24	12.14			22.09×10^{-4}	5.2333			
	35				71.49	11.41			20.70×10^{-4}	4.2025			
5. Paraanisidine	20			18.54	9.29			9.08	3.20×10^{-4}	3.3647	38.7900	-1.8560	0.0264
	30	-25.94	1771.20	14.71	17.33	9.47	1.62		3.82×10^{-4}	3.6781			
	40				18.57	8.91			3.07×10^{-4}	2.8188			
6. Parapentidine	20	-23.58	1167.25	9.70	-1.67	10.19	1.21	8.02	22.87×10^{-6}	4.8728	-52.6800	4.9975	-0.0851
	30				-1.22	10.07			22.49×10^{-6}	4.6665			
	40				-1.68	10.22			22.87×10^{-6}	4.6800			
7. Ortho chloro-para nitroaniline	20			6.19	10.22			8.07	17.99×10^{-5}	4.9271	28.2500	-1.4440	0.0196
	30	-24.52	1447.51	12.03	6.88	10.00	1.49		17.86×10^{-5}	4.5531			
	40				6.18	10.09			18.05×10^{-5}	4.4526			
8. Para bromo-nitrobenzene	20			-20.58	10.01			8.47	9.25×10^{-8}	4.5331	33.5400	-1.9865	0.0280
	30	-21.28	479.23	3.98	-20.64	10.24	0.47		9.44×10^{-8}	4.9906			
	40				-20.58	10.42			9.21×10^{-8}	5.0511			

b's with the estimated τ_j at all the temperatures. All the μ_j 's as placed in Table 1, are found, to be temperature dependent quantities. The coefficients a, b and c of $\mu_j - t$ curves of Fig. 2, are, however, placed in Table 2, in order to compare with the reported μ_j 's as well as theoretical μ_{theo} 's, obtained from bond angles and bond moments of substituent polar groups attached with the parent ones of Fig. 3. The disagreement of the measured μ_j 's with μ_{theo} 's as obtained from Fig. 3, for these compounds establishes the fact that the inductive moments combined with the mesomeric moments of the substituent polar groups with the parent molecules is a function of temperature.

2. THEORETICAL FORMULATIONS

Under the hf electric field the dimensionless complex dielectric constant k_{ij}^* is :

$$k_{ij}^* = k_{ij}' - jk_{ij}'' \quad \dots\dots\dots (1)$$

where $k_{ij}' = \frac{\epsilon_{ij}'}{\epsilon_0}$ = real part of dielectric constant and $k_{ij}'' = \frac{\epsilon_{ij}''}{\epsilon_0}$ = dielectric

loss factor, respectively, ϵ_{ij}' and ϵ_{ij}'' are real and imaginary parts of complex permittivity ϵ_{ij}^* having dimension of Farad meter⁻¹ (F.m.⁻¹) and ϵ_0 = permittivity of free space = 8.854×10^{-12} Fm⁻¹. Hence Murphy-Morgan relation for the complex hf conductivity σ_{ij}^* of a solution of a polar - nonpolar liquid mixture of weight fraction w_j 's is :

$$\sigma_{ij}^* = \omega \epsilon_0 k_{ij}'' + j\omega \epsilon_0 k_{ij}' \quad \dots\dots\dots (2)$$

where $\sigma_{ij}' (= \omega \epsilon_0 k_{ij}'')$ and $\sigma_{ij}'' (= \omega \epsilon_0 k_{ij}')$ are the real and imaginary parts of complex conductivity and j is a complex number = $\sqrt{-1}$.

The hf conductivity σ_{ij} is however obtained from :

$$\sigma_{ij} = \omega \epsilon_0 \sqrt{k_{ij}''^2 + k_{ij}'^2} \quad \dots\dots\dots (3)$$

The imaginary part of hf conductivity σ_{ij}'' is related to the real part of hf conductivity σ_{ij}' by

$$\sigma_{ij}'' = \sigma_{\infty ij} + \left(-\frac{1}{\omega\tau} \right) \sigma_{ij}' \quad \dots\dots\dots (4)$$

where $\sigma_{\infty ij}$ is the constant conductivity at $w_j = 0$ and τ is the relaxation of a polar unit $= \tau_j$.

Equation (4) on differentiation with respect to σ_{ij}' becomes.

$$\frac{d\sigma_{ij}''}{d\sigma_{ij}'} = \frac{1}{\omega\tau_j} \quad \dots\dots\dots(5)$$

to yield τ_j of a polar solute. It is often better to use the ratio of the individual slopes of variations of σ_{ij}'' and σ_{ij}' with w_j at $w_j \rightarrow 0$ to avoid the effect of polar-polar interactions in a liquid mixture to get τ_j from :

$$\begin{aligned} & \left(\frac{d\sigma_{ij}''}{dw_j} \right)_{w_j \rightarrow 0} / \left(\frac{d\sigma_{ij}'}{dw_j} \right)_{w_j \rightarrow 0} = \frac{1}{\omega\tau_j} \\ \text{or, } x/y &= \frac{1}{\omega\tau_j} \quad \dots\dots\dots(6) \end{aligned}$$

Again, it is observed experimentally that σ_{ij}'' is nearly equal to σ_{ij}' of Eq (3) under hf alternating electric field. Hence Eq (4) becomes :

$$\begin{aligned} \sigma_{ij} &= \sigma_{\infty ij} + \left(-\frac{1}{\omega\tau_j} \right) \sigma_{ij}' \\ \text{or } \left(\frac{d\sigma_{ij}}{dw_j} \right)_{w_j \rightarrow 0} &= \omega\tau_j \beta \quad \dots\dots\dots (7) \end{aligned}$$

where $\beta = (d\sigma_{ij}/dw_j)$ the slope of $\sigma_{ij} - w_j$ curve at $w_j \rightarrow 0$.

All the β 's are however, presented in Table 2 for all the liquids. The real part of hf conductivity ^{9,12}, σ_{ij}' at T K of a given solution of w_j is :

$$\sigma_{ij}' = \left(\frac{N\rho_{ij} \mu_j^2}{27 \epsilon_0 k_B M_j T} \right) \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) (\epsilon_0 k_{oij} + 2) (\epsilon_0 k_{\infty ij} + 2) w_j \quad \dots\dots (8)$$

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

$$(d\sigma_{ij}'/d\omega_j)_{w_j \rightarrow 0} = \frac{N\rho_i \mu_j^2}{3\epsilon_0 k_B T M_j} \left(\frac{\epsilon_i + 2}{3} \right)^2 \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) \dots\dots (9)$$

where

N = Avogadro's Number

ρ_i = density of solvent

ϵ_i = dielectric permittivity of the solvent

M_j = molecular weight of solute and

k_B = Boltzmann Constant.

All the symbols stated above are expressed in S.I. unit. From Eqs (7) and (9) one gets μ_j in coulomb meter under hf electric field as :

$$\mu_j = \left(\frac{27 \epsilon_0 k_B T M_j \beta}{N \rho_i (\epsilon_i + 2)^2 \omega b} \right)^{\frac{1}{2}} \dots\dots\dots (10)$$

in terms of a dimensionless parameter 'b'

$$b = \frac{1}{1 + \omega^2 \tau^2} \dots\dots\dots (11)$$

involved with the measured τ of the liquid.

All the measured μ_j 's in terms of β 's and b's of Eqs (10) and (11) are, however, placed in table 2 and compared with the reported μ 's and μ_{theo} 's the latter ones are obtained from bond angles and bond moments of the substituted groups of the molecules as shown in Fig. 3.

3. RESULTS AND DISCUSSIONS

The relaxation time τ_j 's of the para polar liquids as reported in Table 1 and 2 in dioxane and benzene respectively were estimated from the ratio of the individual slopes of both the imaginary σ_{ij}'' and real σ_{ij}' parts of high frequency conductivity

σ_{ij}^* with weight fraction w_j of polar solutes at different experimental temperatures in $^{\circ}\text{C}$ under 3 cm. wave length electric field. τ_j 's of these liquids could not be obtained directly from the slope of Eq (5) of σ_{ij}'' with σ_{ij}' because of the non linear character⁸. Thus the individual slopes of $\sigma_{ij}'' - w_j$ and $\sigma_{ij}' - w_j$ curves at $w_j \rightarrow 0$ were used to get τ 's of these para polar liquids from Eq (6) in order to minimize the effects of dipole - dipole interactions, macroscopic viscosity, internal field etc.

The estimated slopes of σ_{ij}'' and σ_{ij}' curves with w_j 's together with estimated and reported τ_j 's are placed in the 3rd, 4th and 5th columns of Table 1. The τ_j 's thus obtained agree well with the reported τ 's where such are available^{6,7} based on Gopalakrishna's method¹³. As observed in Table 1, the τ 's of molecules having phenone and benzaldehyde groups are higher in comparison to other di- and tri - substituted para polar molecules. This is probably due to larger sizes of rotating units. It is also interesting to note that variation of τ of such molecules as presented in Table 1 are irregular in disagreement with the Debye model of relaxation as observed elsewhere⁴. This may be explained by the fact that stretching of bond angles and bond moments of polar groups with temperature and the distribution of bond moments around the parent molecules to yield either symmetric or asymmetric shape of the molecules. The rest of the molecules show the lower values of τ decreasing with increase of temperature in agreement of the Debye relaxation in spite of the fact that they are nonspherical.

The process of rotation of the rotating dipoles requires an activation energy sufficient to overcome the energy barrier between two equilibrium positions, one can write according to Eyring et al¹⁰ with the known τ_j by :

$$\tau_j = \frac{A}{T} e^{\Delta F_r / RT} \quad (\because \Delta F_r = \Delta H_r - T \Delta S_r)$$

$$\text{or, } \ln(\tau_j T) = \ln(Ae^{-\Delta S_r/R}) + \frac{\Delta H_r}{RT}$$

$$= \ln A' + \frac{\Delta H_{\tau}}{R} \frac{1}{T} \dots\dots\dots (12)$$

Equation (12) is a straight line of $\ln(\tau_j T)$ against $1/T$ having intercept and slope to measure the thermodynamic energy parameters like enthalpy of activation (ΔH_{τ}), entropy of activation (ΔS_{τ}) and free energy of activation (ΔF_{τ}) of dielectric relaxation process of the molecules. The intercepts and slopes of the least square fitted $\ln(\tau_j T)$ against $1/T$ curves as illustrated graphically in fig 1, were accurately obtained and placed in the 3rd and 4th columns of Table 2. The variation of $\ln \tau_j T$ against $1/T$ are linear for almost all the liquids with the available experimental data. The enthalpy of activation ΔH_{η} due to viscous flow of the solvent was, however, estimated from the slope of the linear equation of $\ln(\tau_j T)$ against $\ln \eta$ at different experimental temperatures. As evident from Table 2, the values of $\gamma (= \Delta H_{\tau} / \Delta H_{\eta}) > 0.50$ for all the liquids except para bromonitrobenzene exhibit the solvent environment around the solute molecules which behave as solid phase rotators. The low value of γ , on the other hand, for p-bromonitrobenzene may indicate the weak molecular interaction of such dipole with benzene. The values of ΔS_{τ} 's for the system like p-hydroxypropiophenone, p-phenitidine and p-bromonitrobenzene are negative. This is due to the fact that activated states are more ordered than the normal states unlike other molecules. The high values of ΔH_{τ} of p-chloropropiophenone and p-benzyloxybenzaldehyde indicate the activated states are not stable probably due to internal resistance suffered by larger dipole rotations. The rest of the molecules possesses ΔH_{τ} of nearly the same magnitude. The ΔF_{τ} 's between the activated and unactivated states of all the systems are, however, the same as the activation is accomplished by rupture of bonds of dipolar groups in the same degree of freedom^{6,7}. Unlike Kalman factor $(\tau_j T / \eta^{\gamma})$ at different temperatures, Debye factor $(\tau_j T / \eta)$ are almost constant signifying the applicability of Debye model of relaxation behaviour for such para liquids¹⁴. The μ_j 's (Eq 10) of all the p-liquids were obtained from slopes β 's of $\sigma_{ij} - w_j$ curves and dimensionless parameters b's of Eq (11) involved with measured τ_j 's (Eq. 6). The slopes and intercepts of σ_{ij} against w_j as presented in Table 1 were obtained by careful regression technique and are found to be almost constant ($\sim 10^{-12} \Omega^{-1} \text{m}^{-1}$) at all the experimental temperatures

under 3 cm. wave length electric field perhaps for their same polarity. Thus σ_{ij}' , σ_{ij}'' and σ_{ij} could not be shown graphically. Para-hydroxypropiophenone (curve 1) and p-acetamidobenzaldehyde (curve III) showed the monotonic increase of μ_j with temperature (Fig 2) for their increasing molecular asymmetry at higher temperatures. The $(\mu_j - t)$ curves of p-benzyloxybenzaldehyde (curve IV) and p-phenitidine (curve VI) are convex in nature¹⁵ showing zero values at lower and higher temperatures unlike the other four assuming minimum values at different temperatures as seen in fig. 2. The above nature of $(\mu_j - t)$ curves are explained by the rupture of solute-solvent (monomer) and solute-solute (dimer) association due to stretching of bond angles and bond moments of substituted polar groups at different temperatures.

The theoretical dipole moments μ_{theo} 's of all the p - liquids were also calculated from the vector addition of the available bond moments 4.67, 10.33, 4.40, 4.40, 1.00, 8.00, 5.63, 1.50, 14.10 and 5.70 multiples of 10^{-30} coulomb metre (C.m.) for C \rightarrow OH, C \rightarrow CHO, C \rightarrow OCH₃ and C \rightarrow NH₂ bonds making angles 62°, 55°, 57°, and 142° and 0° for the rest C \rightarrow H, C \rightarrow O, C \rightarrow Cl, C \rightarrow N, C \rightarrow NO₂ and C \rightarrow Br bonds respectively with C atom of the parent molecules which are assumed to be planar structures, as shown in Fig 3, The μ_{theo} 's thus obtained are finally placed in the 12th column of Table 1. The slight disagreement between measured μ_j 's and μ_{theo} 's reveals the presence of inductive and mesomeric moments of the substituent polar groups due to their aromaticity. In p-acetamido-benzyldehyde, p-phenitidine, orthochloro para nitro aniline and p-bromonitrobenzene, the μ_{theo} 's are larger while for others μ_{theo} 's are smaller than the measured values. This fact at once predicts that the substituent polar groups in former molecules push the electrons towards the electro negative atoms and there by inductive effect is less than in latter systems where they pull the electrons. The electromeric effect is also prominent in the system containing C \rightarrow O groups.

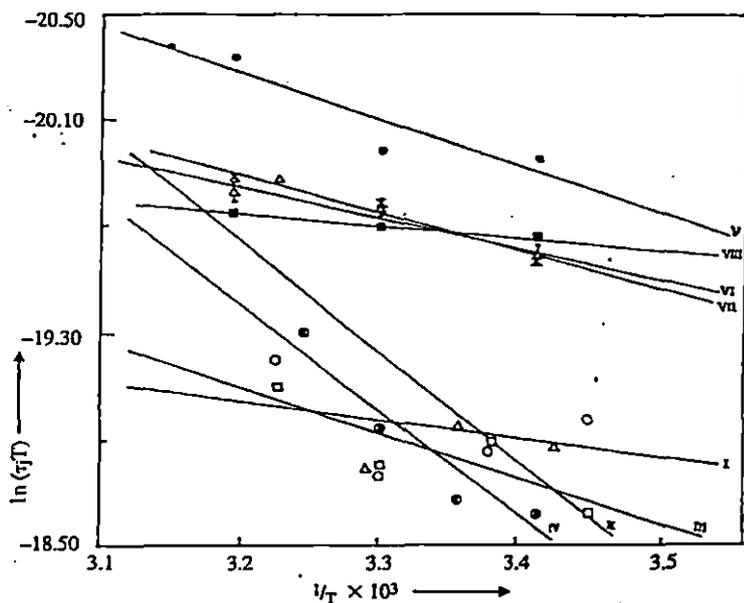


Figure 1. Straight line plots of $\ln(\tau T)$ against $1/T$. (I) parahydroxypropiophenone ($-\circ-$), (II) parachloropropiophenone ($-\triangle-$), (III) paraacetamidobenzaldehyde ($-\square-$), (IV) parabenzoyloxybenzaldehyde ($-\odot-$), (V) paraanisidine ($-\bullet-$) (VI) paraphenitidine ($-\triangle-$), (VII) orthochloroparanitroaniline ($-\times-$) and (VIII) parabromonitrobenzene ($-\blacksquare-$)

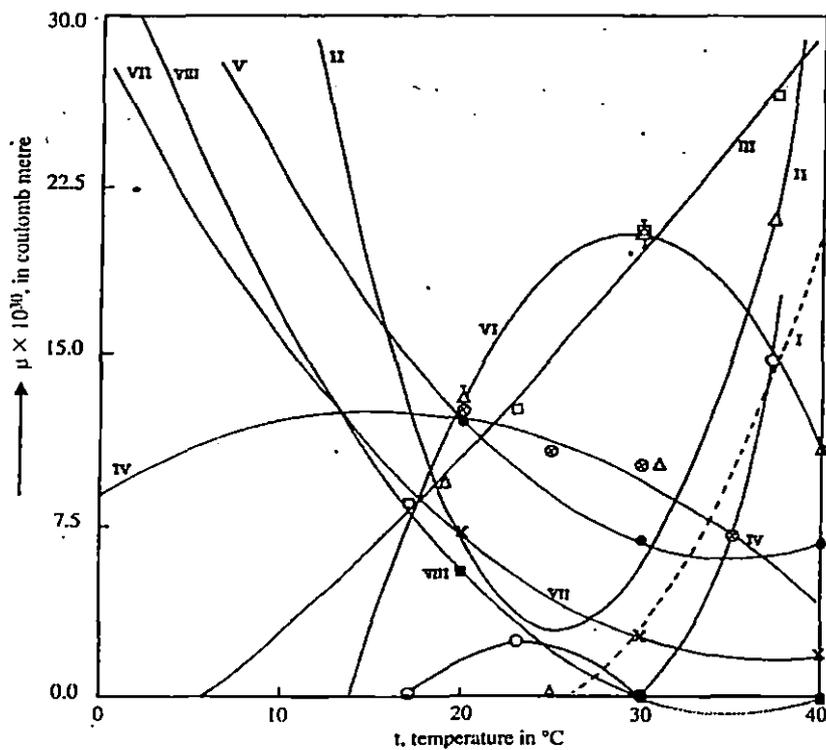


Figure 2. Variation of dipole moments $\mu, \times 10^{30}$ in Coulomb metre against t in $^{\circ}\text{C}$. (I) parahydroxypropiophenone ($-\circ-$), (II) parachloropropiophenone ($-\triangle-$), (III) paraaceta-midobenzaldehyde ($-\square-$), (IV) parabenzoyloxybenzaldehyde ($-\odot-$), (V) paraanisidine ($-\bullet-$), (VI) paraphenitidine ($-\triangle-$), (VII) orthochloroparanitroaniline ($-\times-$) and (VIII) parabromonitrobenzene ($-\blacksquare-$).

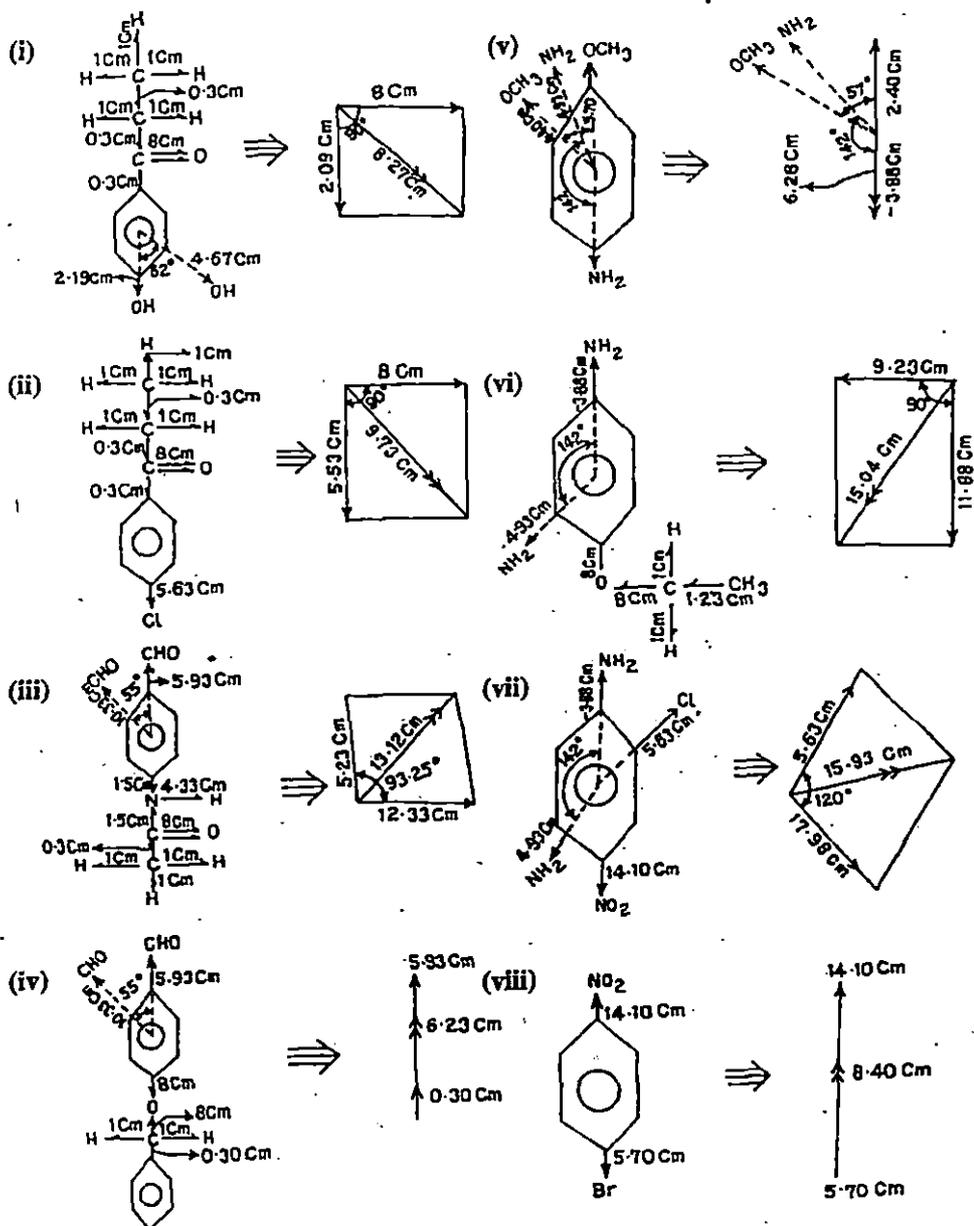


Figure 3. Conformational structures from available bond moments and bond angles of para compounds : (i) para-hydroxypropiofenone (ii) para-chloropropiofenone (iii) para-acetamidobenzaldehyde (iv) para-benzyl-oxybenzaldehyde (v) para-anisidine (vi) para-phenitidine (vii) ortho-chloroparanitroaniline and (viii) para-bromonitrobenzene.

4. CONCLUSION

A very convenient method to evaluate τ_j 's from the ratio of the individual slopes of $\sigma_{ij}'' - w_j$ and $\sigma_{ij}' - w_j$ curves at $w_j \rightarrow 0$ and the corresponding μ_j 's in SI unit of several chain like para liquids at different experimental temperatures is suggested in order to avoid polar - polar interactions. The slopes of $\sigma_{ij}'' - \sigma_{ij}'$ curves are very often not linear in almost all liquids and hence could not be used to obtain τ_j 's. Both τ_j 's and hence μ_j 's within the accuracy of 10% and 5% are now reliable. Para - hydroxypropiophenon and p - chloropropiophenone show zero values of μ at certain temperatures owing to their symmetry gained at that temperatures. The variation of μ with temperature in $^{\circ}\text{C}$ is not a new concept, but for p-liquids, the convex, concave or gradual increase occur probably due to association or dissociation of solute - solute and solute - solvent molecular associations and stretching of bond moments of the substituent polar groups at different temperatures. Different thermodynamic energy parameters, could therefore, be estimated from the stand point of Eyring's rate theory¹⁵⁻¹⁶, to infer molecular dynamics of the nonspherical liquids, μ_{theo} 's of the molecules could, however, be found out from the available bond angles and bond moments of the substituent polar groups attached to the parent molecules. They are usually found to differ from the measured μ_j 's indicating the existence of mesomeric and inductive effects in polar liquids due to their aromaticity.

REFERENCES

1. Kastha G S, Dutta J, Bhattacharyya J and Roy S B 1965 Ind J Phys **43**, 14.
2. Acharyya C R, Chatterjee A K, Sanyal P K and Acharyya S 1986 Ind J. Pure & Appl Phys, **24** 234.
3. Saha U & Acharyya S. 1993 Ind. J. Pure & Appl Phys **31** 181.
4. Acharyya S. Chatterjee A K, Acharyya P and Saha I. L (1982) Ind J Phys. **56** B 291.
5. Shukla J P, Ahmad S I, Shukla D D & Saxena M C, 1968 J. Phys. Chem **72**, 1013.

6. Dhar R L, Mathur A, Shukla J P and Saxena M C 1973 Ind J. Pure & Appl Phys. **11**, 568.
7. Some vanshi S K S, Misra S B I & Mehrotra N K (1978) Ind J Pure & Appl Phys **16** 57.
8. Murthy M B R, Patil R L and Desh Pande D K, (1989) Indian J. Phys. **63** B, 491.
9. Basak R C, Karmakar A, Sit S K and Acharyya S (1999) Ind J Pure & Appl Phys. **37** 224.
10. Eyring H, Glasstone S and Laidler - (1941) The theory of rate process (Mc Graw Hill N Y)
11. Murphy F J and Morgan S O, Bull Syst Tech J **18** (1939) 502.
12. Smyth C P, Dielectric behaviour and structure (Mc Graw Hill New York) 1955.
13. Gopala Krishna K. V Trans Faraday Soc. **53** (1957) 767
14. Dutta K, Sit S. K. and Acharyya S, Ind. J. Pure & Appl Phys. Communicated
15. Eyring H : J. Chem Phys. **4** (1936) 283
16. Kauzmann W : Rev. mod. Phys. **14** (1942) 12.