

DIPOLE RELAXATION AND SOLID ROTATOR PHASE INVESTIGATIONS IN SOME POLAR LIQUIDS IN DILUTE SOLUTION

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Dielectric relaxation time of the polar liquids viz. o-, m-, p-tolualdehyde and cuminaldehyde at 16, 25, 34 and 42 °C has been determined in dilute solution of benzene using recent Higasi, Koga and Nakamura method and discussed with reference to molecular structure. The relaxation time for each molecule has also been calculated with the equations proposed by DEBIE, WIRTZ et al., MURTY and SHIAMLAMBA et al. and compared with the corresponding experimental value. Dependence of the relaxation time over temperature has been utilized to study thermodynamics of dipole relaxation. It is found that molecules relax by molecular as well as intramolecular rotations and that the dipole relaxation is a cooperative process. A comparative study of the enthalpy of activation for dipole reorientation and for viscous flow has suggested that in all the molecules under investigation Solid rotator phase exists on solidification.

Introduction

Application of the dielectric properties of the materials for special purposes such as in energy source and pollution control [1] and fibre optics [2] have necessitated the exhaustive study of the dielectric behaviour of materials under a variety of physical conditions. Dielectric relaxation investigations are very helpful in studying the molecular structure and the molecular forces. Dependence of the dielectric relaxation time over the temperature is fundamental in determining the various thermodynamical parameters associated with dipole relaxation. Thermodynamics of dipole relaxation is used to study the disturbances in the local structure [3] of the medium. The knowledge of thermodynamics of dipole relaxation and viscous flow has been used to study the presence or absence of solid rotator phase in polar liquids.

The static dielectric constant (ϵ_0), dielectric constant (ϵ') and dielectric loss (ϵ'') and the refractive indices data have been analysed by a recent single microwave frequency method developed by HIGASI, KOGA and NAKAMURA [4]. The method consists in the evaluation of two relaxation times $\tau(1)$ and $\tau(2)$ defined by the equations

$$\tau(1) = \frac{a''}{\omega(a' - a_\infty)}, \quad (1)$$

$$\tau(2) = \frac{(a_0 - a')}{\omega a''}. \quad (2)$$

Where ω' is the angular frequency, a_0, a', a'' and a_∞ are defined by the following equations:

$$\epsilon_0 = \epsilon_{01} + a_0 w_2$$

$$\epsilon' = \epsilon'_1 + a' w_2$$

$$\epsilon'' = a'' w_2$$

$$\epsilon_\infty = \epsilon_{1\infty} + a_\infty w_2;$$

subscript 1 refers to pure solvent, 2 to the solute and the subscript ∞ refers to the value of relative permittivity at infinite frequency. w_2 is the weight fraction of the solute. The analysis reported in the paper [5] has shown that $\tau(1)$ is implicit function of τ_1, τ_2 and the relative contribution of τ_2 to the observed dielectric loss C_2 . It has been shown that in certain cases the molecular relaxation time $\tau(2)$ leads to τ_1 . It has been proved [6] that $\tau(1)$ is approximately equal to $\tau_{G.K}$ (*i. e.*, relaxation time by Gopala Krishna method). It follows therefore that $\tau_{G.K}$ depends on $\tau_1 \tau_2$ and C_2 . As a consequence the value of $\tau_{G.K}$ provides only an indication of the presence of intramolecular rotations in the molecule. The presence of these rotations is concluded only when $\tau(2)$ and $\tau_{G.K}$ differ significantly from each other.

MEHROTRA *et al.* [7] have investigated Anisaldehyde, Salisaldehyde and *O*-chlorobenzaldehyde for their dielectric behaviour by Gopala Krishna method [8]. DESHPANDE *et al.* [9] have also investigated dielectric behaviour of propionaldehyde and *p*-tolualdehyde at a single temperature and evaluated $\tau_{G.K}$. MOUNTAIN and WALKER [10] have investigated some *p*-halobenzaldehydes in dilute solution and analysed the results in terms of the molecular relaxation time τ_1 and intramolecular relaxation time τ_2 . SINGH and VIZ [11, 12] investigated some *p*-halobenzaldehydes and nitrobenzaldehydes and using the present method analysed the results in terms of two arbitrary relaxation times $\tau(2)$ which is molecular relaxation time and $\tau(1)$ which is an implicit function of $\tau_1 \tau_2$ and C_2 . They showed that their results and some of the inferences drawn agree with the results of MOUNTAIN and WALKER though they had studied the molecules at a single microwave frequency in the dispersion region. This provides a good test of the present method for analysing relative permittivity data.

Many polar liquids have not been investigated for their rotational behaviour on solidification. Therefore in the present study a series of substituted benzaldehydes namely *o*-, *m*-, and *p*-tolualdehyde and cuminaldehyde in benzene solution at different temperatures has been investigated for their rotational behaviour on solidification, dielectric and thermodynamic behaviour.

Experimental

The dielectric constant (ϵ') and the dielectric loss (ϵ'') have been measured at *X*-band by a technique due to ROBBERT and VON HIPPLE [13] and later modified by DAKIN and WORKS [14]. The static dielectric constant (ϵ_0) at 300 kHz has been measured by a dipolemeter based on the principle of heterodyne beat method. The refractive indices of all the solutions have been measured by Abbe's refractometer. The viscosity and density measurements have been carried out by Ostwald viscometer and pykno-

meter respectively. The relaxation times have been calculated using Higasi, Koga and Nakamura method. Thermodynamical energy parameters have been calculated using EYRING's theory [15] of rate process for the molecular relaxation time $\tau(2)$. The measurements for ϵ' and ϵ'' are accurate upto $\pm 1\%$ and $\pm 5\%$ respectively.

The chemicals were obtained from Aldrich Chemicals Co. The physical cal properties of the chemicals were checked against the literature values. The solvent obtained from B. D. H. England was distilled twice before use.

Results and Discussions

The values of $a_0, a' a'', a_\infty, \tau(1)$ and $\tau(2)$ for each molecule at different temperatures have been reported in Table I. Literature values of $\tau_{G,K}$ where available for the molecules under investigation have also been included in Table I. Table II gives various thermodynamical parameters associated with dipole reorientation and viscous flow. Relaxation times calculated theoretically from various equations together with the experimental values of relaxation times have been presented in Table III. Expected rotational behaviour on solidification of various molecules under investigation has been reported in Table IV.

Dipole relaxation: A perusal of table 1 shows that at a particular temperature for each molecule $\tau(1)$ and $\tau(2)$ are distinct from each other beyond experimental errors. This suggests that dielectric absorption by molecules under investigation is not solely contributed by the rotation of molecule as a single unit but also by intramolecular rotation of $-\text{CHO}$ group about the $\text{C}_{\text{aro}}-\text{C}_{\text{ali}}$ bond. Therefore it is concluded that molecules relax by both molecular and intramolecular relaxation processes. Similar results have been observed by HIGASI *et al.* [16] on a number of aromatic polar molecules. At the same time it is quite interesting to note that the literature value of $\tau_{G,K}$ for p-tolualdehyde is approximately equal to $\tau(1)$ and significantly differs from $\tau(2)$. This further supports that p-tolualdehyde relax by more than one relaxation mechanism.

An examination of the same table reveals that for each molecule the relaxation time for overall rotation $\tau(2)$ decreases with increasing temperature. This is due to decrease in viscosity of the solvent as temperature increases. It is worthwhile to mention here that for each molecule the rate of variation of $\tau(2)$ with temperature is more marked than the rate of variation of $\tau(1)$ with temperature. This suggests that probably among the investigated molecules temperature variation markedly influences overall rotation of the molecule as compared to the internal group rotation. SINGH and VIZ [11] have also reported similar results on substituted benzaldehydes.

On comparing the relaxation time of the investigated molecules it is found that the relaxation time of the cuminaldehyde is the highest. This is as expected because cuminaldehyde has the largest size amongst the molecules under investigation. Also amongst the isomers of tolualdehyde the relaxation time is found to be the highest for o-tolualdehyde and decreases as the substituent $-\text{CH}_3$ group moves from o- to m- and from m-, to p-position respectively. Presumably this is due to the greater steric hinderance of $-\text{CH}_3$ group at ortho position as compared to meta and para position respectively. Similar results have been obtained by others on a number of organic compounds [17, 18].

Theoretical and Experimental relaxation time

DEBYE [19] has given a relation for calculating relaxation time (τ) of a molecule of radius 'a' as

$$\tau = \frac{4\bar{\Lambda}a\eta}{kT} \quad (3)$$

WIRTZ and his coworkers [20] elaborating PERIN's idea [21] modified the Debye equation to denote relaxation time as

$$\tau = \frac{4\bar{\Lambda}\eta a_2^3}{kT} \left[\frac{6a_1}{a_2} + \left(1 + \frac{a_1}{a_2}\right)^{-3} \right]^{-1} \quad (4)$$

Here a_1 and a_2 are the radii of the rotating unit of the solvent and solute respectively and are given as

$$a_i = \left[\frac{5.56 M_i}{6.06 d_i} \right]^{1/3} \times 10^{-8} \text{ cm} \quad i = 1 \text{ or } 2$$

SHYAMLAMBA and PREMSWAROOP [22] using interfield correction term to Debye equation obtained for relaxation time τ

$$\tau = \frac{3M\eta}{RTd} \frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon^2} \quad (5)$$

Table I

Values of a_0 , a' , a'' , a_∞ , $\tau(1)$ and $\tau(2)$, $\tau_{G.K.}^{Lit.}$ for the materials in benzene solution at different temperatures

T(K)	a_0	a'	a''	a_∞	$\tau(1)$ ps	$\tau(2)$ ps	$\tau_{G.K.}^{Lit. [10]}$
o-tolualdehyde							
289	5.90	2.87	2.12	0.188	13.0	23.0	
398	5.46	2.75	1.96	0.178	12.5	22.7	
307	5.39	2.77	1.96	0.190	12.5	22.0	
315	5.23	2.81	1.89	0.180	11.8	21.1	
m-tolualdehyde							
289	8.62	4.12	3.22	0.198	13.5	23.0	
298	8.21	4.02	3.12	0.188	13.4	22.1	
307	8.10	4.18	3.08	0.190	12.7	20.9	
p-tolualdehyde							
289	13.53	6.32	5.20	0.212	14.0	22.8	
298	13.09	6.37	5.05	0.212	13.5	21.9	
307	12.20	6.29	4.69	0.216	12.7	20.7	12.0
315	12.18	6.35	4.77	0.221	12.8	20.1	
Cummaldehyde							
289	8.58	3.53	3.05	0.187	15.0	27.2	
298	8.05	3.45	2.89	0.212	14.7	26.2	
307	7.95	3.56	2.92	0.200	14.3	24.7	
315	7.38	3.60	2.69	0.195	13.0	23.1	

Table II
Values of $\tau(2)$ and Thermodynamical Energy parameters

T(K)	$\tau(2)$ ps	ΔF_e Kcal/mol	ΔH_e Kcal/mol	ΔS_e cal/mol	ΔF_η Kcal/mol	ΔH_η Kcal/mol	ΔS_η cal/mol
o-tolualdehyde							
289	23.5	2.85	0.18	-9.25	2.93	2.52	-1.42
298	22.7	2.93	0.18	-9.22	2.95	2.52	-1.44
307	22.0	3.02	0.18	-9.18	2.96	2.52	-1.43
315	21.1	3.09	0.18	-9.24	2.98	2.52	-1.46
m-tolualdehyde							
289	23.0	2.84	0.33	-8.68	2.93	2.52	-1.42
298	22.1	2.92	0.33	-8.69	2.95	2.52	-1.44
307	20.9	2.99	0.33	-8.66	2.96	2.52	-1.43
p-tolualdehyde							
289	22.8	2.83	0.29	-8.79	2.93	2.52	-1.42
298	21.9	2.90	0.29	-8.75	2.95	2.52	-1.44
307	20.7	2.98	0.29	-8.77	2.96	2.52	-1.43
315	20.1	3.05	0.29	-8.77	2.98	2.52	-1.46
Cummaldehyde							
289	27.2	2.93	0.63	-7.94	2.93	2.52	-1.42
298	26.2	3.02	0.63	-8.02	2.95	2.52	-1.44
307	24.7	3.09	0.63	-8.01	2.96	2.52	-1.43
315	23.1	3.15	0.63	-7.99	2.98	2.52	-1.46

Table III
Comparison of experimental and theoretical relaxation times

Compound	$\tau^*(1)$ (ps)	$\tau^*(1)$ (ps)	$\tau_{G,K}^{Lit}$ (ps)	τ_{theo}^{**} (ps)				
				Debye Eqn. using η	0.86 η	Wirtz <i>et al.</i>	Murty <i>et al.</i>	Shyam- lamba
o-tolualdehyde	13.0	23.5	—	92.1	33.1	17.6	13.6	13.7
m-tolualdehyde	13.5	23.0	—	93.6	33.7	19.9	13.5	13.9
p-tolualdehyde	14.0	22.8	12.0	94.1	33.9	20.0	13.5	14.0
Cummaldehyde	15.0	27.2	—	117.6	42.3	31.9	13.7	17.5

* — values of experimental relaxation at 16 °C

** — Values of relaxation time at 20 °C

Table IV
Expected rotational behaviour of the molecules

compound	ΔH_e	ΔH_η	x	class of liquid	rotational behaviour
	Kcal/mol				
o-tolualdehyde	0.18	2.52	0.07	Class II	Solid rotator phase
m-tolualdehyde	0.33	2.52	0.13	Class II	Solid rotator phase
p-tolualdehyde	0.29	2.52	0.11	Class II	Solid rotator phase
Cummaldehyde	0.63	2.52	0.25	Class II	Solid rotator phase

Here M and d are the molecular weight and density of the solute respectively. ϵ is the static dielectric constant of the solvent.

MURTY [23] also modified the Debye equation to give relaxation time of the molecule as

$$\tau = \frac{6\bar{A}\eta\alpha}{kT(\epsilon+2)} \quad (6)$$

Where α is the polarizibility of the solute molecule and is obtained from molar refraction and ϵ is the dielectric constant of the solvent.

The relaxation times of the molecules under investigations have been calculated using the Eqs. (3), (4), (5) and (6) and tabulated in Table III. A perusal of Table III suggests that for each molecule the experimental value of molecular relaxation time $\tau(2)$ is found to be much smaller as compared to the theoretical value obtained by Debye equation. AHMAD *et al.* [24] using Debye equation obtained relaxation time to be 3 to 4 times their values for experimental values. However the difference in the experimental value of relaxation time $\tau(2)$ and the relaxation time obtained using Debye equation is reduced if η is replaced by 0.36η as suggested by FISCHER [25]. The values of τ calculated using WIRTZ *et al.*, MURTY and SHYAMLAMBA *et al.* give smaller values of τ as compared to the experimental molecular relaxation time $\tau(2)$. However, it is interesting to note that the relaxation time obtained by WIRTZ *et al.*, Murty and Shyاملamba equations is close to the experimental values of $\tau(1)$ which has been found to agree with the relaxation time obtained by Gopalakrishna method.

The discrepancies between the experimental values and those calculated by different equations may be due to (i) the internal rotation in the molecule concerned and (ii) the use of macroscopic viscosity of the medium in place of unknown inner friction coefficient for dipolar rotation which are not taken into account in these equations.

Thermodynamics of dipole relaxation

An examination of Table II shows that the free energy of activation for dipole relaxation and viscous flow processes increases as temperature increases. This has been observed for most of the substances examined by MISRA *et al.* [26]. This is because as temperature increases thermal agitation increases and molecules require more energy to come to the activated state. From the same table it is clear that the free energy of activation for dipole orientation (ΔF_p) is the highest for cuminaldehyde. This may be attributed to the size of the cuminaldehyde which is the largest amongst the molecules under investigation. Similar results have been reported by SHUKLA *et al.* [27]. It is found from the same table that the enthalpies of activation (ΔH_e) are less than the corresponding free energy of activation ΔF_e which implies that a large number of molecules in groups surrounding one, which rotates, are involved in the process of dipole orientation. It is possible that the rotation of a dipolar molecule requires some rearrangement of other molecules before the rotation can take place. The arrangement of the molecules in the activated state is described by their entropy values. For the molecules under investigation entropy values have been found to be negative. BRANIN and SMYTH [28] explained the negative entropy due to the existence of cooperative orientation of the molecules resulting from steric forces.

Solid Rotator Phase

It is interesting to note from Table IV that for all the molecules under investigation the value of x which is the ratio of enthalpy of activation for dipole orientation and enthalpy of activation for viscous flow is found to be less than 0.45. Other workers [29, 30] have classified polar liquids into two groups. The liquids for which x lies between 0.5 & 1.0 belong to class I liquids. In these liquids it is expected that dipole freezing may occur immediately after solidification resulting in the sudden drop in the value of static dielectric constant. The liquids for which x lies between 0.0 and 0.45 belong to class II liquids. These liquids are expected to have solid rotator phase and for these liquids dipole rotation is possible even at freezing point. It is therefore suggested that solid rotator phase may exist in all the polar molecules under investigation.

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**ИССЛЕДОВАНИЕ ДИПОЛЬНОЙ РЕЛАКСАЦИИ И ХРУПКОЙ ВРАЩАТЕЛЬНОЙ
ФАЗЫ В РАЗБАВЛЕННЫХ РАСТВОРАХ НЕКОТОРЫХ ПОЛЯРНЫХ
ЖИДКОСТЕЙ**

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Определено время диэлектрической релаксации полярных жидкостей в том числе *o*-, *m*-, *p*-толуальдегидов и куминальдегида при температурах 16, 25, 34 и 42 °С в разбавленных растворах бензола с помощью нового метода Хигаши, Кога и Накамура и обсуждается на основании строения молекул. Релаксационное время каждой молекулы было рассчитано способом Дзэбая, Виртца, Марти и Шиахламбе и др. и сравнивалось с результатами эксперимента. Зависимость релаксационного времени при высоких температурах была использована для определения термодинамики дипольной релаксации. Найдено, что релаксация молекул происходит как на молекулярных, так и на внутримолекулярных вращениях и дипольная релаксация поэтому является кооперативным явлением. Сравнительное изучение энтальпии активации дипольной ре-ориентации и вязкого течения показывает, что во всех исследованных молекулах хрупкая вращательная фаза присутствует при затвердевании.