

# DIELECTRIC RELAXATION PROCESS IN SOME PHENYL ACETONITRILES

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Dielectric relaxation studies on phenyl acetonitrile, *p*-chloro phenyl acetonitrile and *p*-nitro phenyl acetonitrile in dilute solution of benzene have been carried out in the temperature range, 288–320 K at 9.8 G. Hz frequency. The dielectric data obtained have been analysed by Gopala Krishna method to calculate  $\tau_{GK}$  and Higasi method to find the most probable relaxation time  $\tau_{OH}$  and distribution parameter ' $\alpha$ '. Having obtained the high value of distribution parameter the relaxation mechanism has further been resolved in terms of two independent Debye type relaxation times  $\tau_{(1)}$  and  $\tau_{(2)}$  using the method developed by Higasi, Koga and Nakamura. It appears that the molecules relax by molecular and intramolecular ( $-\text{CH}_2\text{CN}$ ) group rotation. For phenyl acetonitrile the resolved relaxation times are found to agree well with the existing literature data obtained by Cole-Cole analysis. The addition of -chloro and -nitro group at para position do not show any appreciable influence on the values of  $\tau_{(1)}$  which may will be associated with the intramolecular process.

## Introduction

Cyano compounds are known to possess interesting dielectric properties. On investigating the dielectric behaviour of some alkyl cyanides, RCN (where R =  $\text{CH}_3$ ,  $\text{CH}_3\text{CH}_2$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$ ) KRISHNAJI and MANSINGH [1] had found that the distribution parameter decreased with chain length and became zero for *n*-propyl and *n*-butyl cyanides in the temperature range 30–60°C. Dielectric measurements on phenyl cyanide by POLEY [2] yielded the distribution parameter  $\alpha=0$ , indicating the rigid nature of the molecule. The group moment of -CN group in aromatic compounds has been investigated as 3.9 D, while the group moment of acetonitrile  $-\text{CH}_2\text{CN}$  has been obtained [3] as 3.5 D indicating the influence of sandwiching  $\text{CH}_2$  group between carbon of aromatic ring and  $-\text{CN}$  group. In an attempt to investigate systematically the influence of sandwiching  $\text{CH}_2$  between carbon atom and  $-\text{CN}$  group on dielectric properties, FROST and SMYTH [4] studied phenyl acetonitrile and 1-naphthalene acetonitrile in the dilute solution of benzene in the temperature range 20–60°C. They found that phenyl acetonitrile relaxed by molecular and the intramolecular  $-\text{CH}_2\text{CN}$  group orientation and 1-naphthalene acetonitrile shows no evidence of group relaxation confirming the steric blocking of  $-\text{CH}_2\text{CN}$  group rotation. HASSAN *et al.* [5] on investigating the dielectric absorption of phenyl aceto-

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nitrile in pure liquid state noticed the occurrence of molecular and intramolecular-processes in the system.

An interesting part of the literature survey shows the absence of group rotation in phenyl acetonitrile in liquid as well as in dilute solution of benzene above 40 °C as investigated by HASSAN *et al.* [5] and FROST and SMYTH [4] respectively, using COLE-COLE [6] method. The unusual behaviour of phenyl acetonitrile made us interested in extending the work on cyanides by investigating the dielectric and thermodynamic behaviour of phenyl acetonitrile, *p*-chloro and *p*-nitro phenyl acetonitrile in dilute solution of benzene in the temperature range (288—320 K), this time, using single microwave frequency methods due to GOPALAKRISHNA [7] HIGASI [8] and HIGASI *et al.* [9]. Being a parent compound in the aromatic acetonitrile series, phenyl acetonitrile has been taken with a view to provide dielectric information about the compound using different methods of analyzing the permittivity data on one hand and to compare these results with those obtained by Cole-Cole's method on the other hand.

### Experimental

The dielectric constant  $\epsilon'$  and the dielectric loss  $\epsilon''$  of the solutes in the dilute solution of benzene have been measured on the x-band Microwave bench at 9.8 GHz, using the technique of ROBERTS and VON-HIPPLE [10] and later modified by DAKIN and WORKS [11]. The static dielectric constants  $\epsilon_0$  has been measured at 300 KHz by the dipolemeter based on the principle of heterodyne beat method. The refractive indices of the solutions have been measured by Abbe's refractrometer.  $\epsilon_\infty$  has been obtained by squaring the refractive indices ( $\epsilon_\infty = n^2$ ). The measurements of  $\epsilon'$  and  $\epsilon''$  are accurate up to  $\pm 2\%$  and  $\pm 5\%$  respectively.

The chemicals procured from Central Drug Research Institute, Lucknow, India, were of A. R. grade which were obtained from Aldrich Chemical Co. Inc, Milwaukee, Wis. The solvent benzene (A. R. grade) has been obtained from B. D. H., England. The benzene used has been distilled twice before use.

The dielectric data has been analysed for the Debye relaxation time  $\tau_{GK}$  by the GOPALAKRISHNA method [7] which consist of evaluation of  $X$  and  $Y$  given by

$$X = P + \frac{Y}{\omega\tau_{GK}} \quad (1)$$

where

$$X = \frac{\epsilon'^2 + \epsilon''^2 + \epsilon' - 2}{(\epsilon' + 2)^2 + \epsilon''^2} \quad ($$

$$Y = \frac{3\epsilon''}{(\epsilon' + 2)^2 + \epsilon''^2} \quad ($$

$$P = \frac{(\epsilon_\infty - 1)}{(\epsilon_\infty + 1)} \quad ($$

$P$  is assumed to be constant for dilute solutions. The slope  $\frac{dY}{dX}$  of equation (1) gives the relaxation time,

$$\tau_{GK} = \frac{\lambda}{2\pi C} \frac{dy}{dx} \quad (3)$$

where  $\omega = \frac{2\pi C}{\lambda}$ ,  $\lambda$  being the free space wavelength.

The most probable relaxation time  $\tau_{OH}$  and the distribution parameter ' $\alpha$ ' have also been estimated by HIGASI method [8] using the equations

$$\tau_{OH} = \frac{1}{\omega} \left[ \frac{A^2 + B^2}{C^2} \right]^{1/2(1-\alpha)} \quad (4)$$

$$1 - \alpha = \frac{2}{\pi} \tan^{-1}(A/B)$$

where

$$\begin{aligned} A &= a''(a_0 - a_\infty) \\ B &= (a' - a_\infty)(a_0 - a') - a''^2 \\ C &= (a' - a_\infty)^2 + a''^2 \end{aligned} \quad (5)$$

where  $a'$ ,  $a''$ ,  $a_0$  and  $a_\infty$  are determined by the set of equations given by

$$\begin{aligned} \epsilon' &= \epsilon'_1 + a'w_2 \\ \epsilon'' &= a''w_2 \\ \epsilon_0 &= \epsilon_{10} + a_0w_2 \\ \epsilon_\infty &= \epsilon_{1\infty} + a_\infty w_2 \end{aligned} \quad (6)$$

where the subscript 1 refers to pure solvent and  $w_2$  the concentration of solute.

The dielectric absorptions have been further resolved by HIGASI, KOGA and NAKAMURA method [9], in terms of two independent Debye type relaxation time  $\tau_{(2)}$  and  $\tau_{(1)}$ .  $\tau_{(1)}$  and  $\tau_{(2)}$  have been estimated by using the following equations:

$$\tau_{(1)} = \frac{a''}{\omega(a' - a_\infty)} \quad (7)$$

$$\tau_{(2)} = \frac{1}{\omega} \frac{(a_0 - a')}{a''} \quad (8)$$

where  $a_0$ ,  $a'$ ,  $a''$  and  $a_\infty$  have their usual meanings.

Eyring's rate equations [12] have been utilized in evaluating the energy parameters associated with the dipole relaxation and viscous flow processes. The enthalpy of activation corresponding to the relaxation time  $\tau_{GK}$ ,  $\tau_{(1)}$ ,  $\tau_{(2)}$ ,  $\tau_{(0)} = [\sqrt{\tau_{(1)} \cdot \tau_{(2)}}]$  and  $\tau_{OH}$  have been determined respectively from the slopes of the plots of  $\log[\tau_{GK} T]$ ,  $\log[\tau_{(1)} T]$ ,  $\log[\tau_{(2)} T]$ ,  $\log[\tau_{(0)} T]$  and  $\log[\tau_{OH} T]$  versus  $\frac{1}{T}$  and enthalpy for viscous flow has been evaluated from the slope of  $\log \eta$  versus  $\frac{1}{T}$ .

### Results and Discussions

Table I reports the slopes  $a_0$ ,  $a'$ ,  $a''$  and  $a_\infty$  of the solutes in benzene at different temperatures. In Table II the relaxation time  $\tau_{OH}$ ,  $\tau_{(1)}$ ,  $\tau_{(2)}$ ,  $\tau_{(0)}$  and  $\tau_{GK}$  have been reported. Enthalpy of activation corresponding to the different processes associated with the molecules have been reported in Table III. The free energies, enthalpies and entropies corresponding to the various relaxation processes and also for the viscous flow process have been reported and compared in Table IV.

Table I

The slopes  $a_0$ ,  $a'$ ,  $a''$  and  $a_\infty$  for the compounds in the dilute solution of benzene

	Temp. K	$a_0$	$a'$	$a''$	$a_\infty$
(A) Phenyl acetonitrile	296	19.50	10.80	6.00	1.60
	304	18.20	10.50	5.80	1.25
	312	15.80	9.50	5.30	1.00
	320	12.70	8.00	4.40	0.77
(B) <i>p</i> -chloro phenyl acetonitrile	296	18.20	9.30	5.30	0.67
	304	16.10	8.50	4.80	0.52
	312	13.70	7.70	4.00	0.38
	320	12.70	7.30	3.85	0.28
(C) <i>p</i> -Nitro phenyl acetonitrile	288	22.80	11.10	5.71	0.058
	296	17.40	8.60	4.50	0.096
	304	14.80	7.90	3.75	0.16
	312	12.50	7.00	3.03	0.21

Table II

Relaxation times  $\tau_{OH}$ ,  $\tau_{(1)}$ ,  $\tau_{(2)}$ ,  $\tau_{(0)}$ ,  $\tau_{GK}$  and distribution parameters using Higasi, Higasi, Koga and Nakamura method and Gopalakrishna method

Compound	Temperature K	$\alpha$	$\tau_{OH}$ ps.	$\tau_{(1)}$ ps.	$\tau_{(2)}$ ps.	$\tau_{(0)}$ ps.	$\tau_{GK}$ ps.
(A) Phenyl acetonitrile	296	0.23	15.5	10.8	23.2	15.8	23.7
	304	0.19	13.9	10.4	22.0	15.1	22.1
	312	0.19	13.0	10.3	19.7	14.2	19.5
	320	0.18	11.8	10.1	17.7	13.4	18.4
(B) <i>p</i> -chloro phenyl acetonitrile	296	0.31	17.1	10.2	28.8	17.1	8.3
	304	0.30	15.8	9.9	26.3	16.1	7.7
	312	0.31	15.1	9.1	24.9	15.1	6.9
	320	0.29	12.8	9.1	23.3	14.6	6.1
(C) <i>p</i> -nitro phenyl acetonitrile	288	0.41	18.5	8.9	35.3	17.7	27.5
	296	0.39	17.2	8.8	32.7	17.0	23.5
	304	0.40	14.9	8.2	31.0	16.0	21.6
	312	0.37	12.8	7.4	27.9	14.9	19.2

Table III

Enthalpies of activation for  $\tau_{(1)}$ ,  $\tau_{(2)}$ ,  $\tau_{(0)}$ ,  $\tau_{OH}$ ,  $\tau_{GK}$  and viscous flow

	$\Delta H\tau_{(1)}$ kJ mol <sup>-1</sup>	$\Delta H\tau_{(2)}$ kJ mol <sup>-1</sup>	$\Delta H\tau_{(0)}$ kJ mol <sup>-1</sup>	$\Delta H\tau_{OH}$ kJ mol <sup>-1</sup>	$\Delta H\tau_{GK}$ kJ mol <sup>-1</sup>	$\Delta H\eta$ kJ mol <sup>-1</sup>
(A) Phenyl acetonitrile	—	5.3	3.2	5.8	7.4	10.6
(B) <i>p</i> -chloro phenyl acetonitrile	1.6	5.3	4.6	7.6	7.6	10.6
(C) <i>p</i> -nitro phenyl acetonitriles	—	6.0	5.0	9.3	8.7	10.6

## (A) Phenyl acetonitrile

The most probable relaxation time  $\tau_{OH}$  for this molecule in the solution of benzene, using Higasi method has been found to be 15.5 ps. at 296 K. Having obtained high value of the distribution parameter ' $\alpha$ ' ranging from (0.23—0.18), the dielectric absorptions were further resolved in terms of two independent Debye type relaxation times using the HIGASI, KOGA and NAKAMURA method. The molecular relaxation time  $\tau_{(2)}$  and the other relaxation time  $\tau_{(1)}$  presumably associated with the rotation of  $-\text{CH}_2\text{CN}$  group around C—C bond have been found to be 23.2 ps. and 10.8 ps. respectively at 296 K. The average relaxation time  $\tau_{(0)} = \sqrt{\tau_{(1)} \cdot \tau_{(2)}}$  for the molecule has been evaluated as 15.8 ps. which agrees well with  $\tau_{OH} = 15.5$  ps.

Since the two values of the relaxation times,  $\tau_{(2)} (= 23.2$  ps.) and  $\tau_{(1)} (= 10.8$  ps.) are appreciably different, the absorption appears to have been caused by both the molecular and the group rotations in the system, in which  $\tau_{(1)}$  and  $\tau_{(2)}$  may be assigned to the group and molecular process respectively. These results are consistent with the earlier studies by HIGASI *et al.* [13] on alkyl acetates and MISRA *et al.* [14] on substituted amides. The relaxation time  $\tau_{GK}$  of the molecule as evaluated by using Gopalakrishna method has been found to be 23.7 ps. at 296 K which is in close agreement with the molecular relaxation time  $\tau_{(2)} (= 23.2$  ps.) at the same temperature. It has also been observed that  $\tau_{(2)}$  is about two times longer than  $\tau_{(1)}$  for the molecule, which suggests the predominance of molecular process in the system.

This molecule has also been investigated earlier in benzene by SMYTH *et al.* [4] who has obtained, using COLE-COLE plot [6], molecular and intramolecular group relaxation time, for  $-\text{CH}_2\text{CN}$  group as 26 ps. and 12 ps. respectively at 293 K. This is in good agreement with the present molecular relaxation time  $\tau_{(2)} = 23.2$  ps. and  $\tau_{(1)} (= 10.8$  ps.) associated with the group relaxation time at 296 K. Also the average relaxation time using Cole-Cole plot has been found to be 17.0 ps. which agrees well with  $\tau_0 = 15.8$  ps. being the average relaxation time of the molecule obtained using the present method of Higasi *et al.*

The observations favour the use of Higasi method for analysing the permittivity data without any serious error. This is supported by the results obtained from the earlier investigations of KRISHNAJI *et al.* [15] on some substituted ester molecules.

The  $-\text{CH}_2\text{CN}$  group relaxation time  $\tau_{(1)} = 10.8$  ps. in phenyl acetonitrile differs significantly with  $-\text{CH}_2\text{CN}$  group relaxation time as  $\approx 4$  ps. in some dicyano alkanes [16] in dilute solution of benzene. This behaviour is attributed to the attachment of

Table IV  
Free energy, enthalpy and entropy for Higasi Method, Gopala Krishna Method and viscous flow

Compound	Temperature deg. K	$\tau_{OH}$ ps.	$\tau_{GK}$ ps.	Higasi method			Gopalakrishna method			Viscous flow		
				$\Delta F_e$ kJ mol <sup>-1</sup>	$\Delta H_e$ kJ mol <sup>-1</sup>	$\Delta S_e$ J deg <sup>-1</sup> mol <sup>-1</sup>	$\Delta F_e$ kJ mol <sup>-1</sup>	$\Delta H_e$ kJ mol <sup>-1</sup>	$\Delta S_e$ J deg <sup>-1</sup> mol <sup>-1</sup>	$\Delta F_\eta$ kJ mol <sup>-1</sup>	$\Delta H_\eta$ kJ mol <sup>-1</sup>	$\Delta S_\eta$ J deg <sup>-1</sup> mol <sup>-1</sup>
(A) phenyl acetonitrile	296	15.5	23.7	11.2		-20.3	12.2		-16.5	12.1		-5.11
	304	13.9	22.1	11.3	5.8	-20.1	12.4	7.4	-16.8	12.2	10.5	-5.1
	312	13.0	19.5	11.5		-20.3	12.5		-16.7	12.2		-5.2
	320	11.8	18.4	11.6		-20.1	12.8		-17.0	12.3		-5.2
(B) <i>p</i> -chloro phenyl- acetonitrile	296	17.1	8.3	11.6		-8.4	9.7		-6.7	12.1		-5.1
	304	15.8	7.7	11.6	7.6	-8.2	9.8	7.6	-7.1	12.2	10.5	-5.1
	312	15.1	6.9	11.9		-8.9	9.9		-7.1	12.2		-5.2
	320	12.8	6.1	11.8		-8.4	9.9		-6.7	12.3		-5.2
(C) <i>p</i> -nitro phenyl acetonitrile	288	18.5	27.5	11.3		-5.9	12.2		-12.2	12.6		-5.0
	296	17.2	23.5	11.5		-6.2	12.3		-11.9	12.1		-5.1
	304	14.9	21.6	11.5	9.6	-6.4	12.7	8.7	-13.3	12.2	10.5	-5.1
	312	12.8	19.2	11.5		-6.1	12.8		-13.3	12.2		-5.2

aromatic group to  $-\text{CH}_2\text{CN}$  in phenyl acetonitrile. Similar conclusions have been drawn on intramolecular rotational behaviour of  $-\text{CH}_2\text{Br}$  group in aliphatic [17] and aromatic [18] molecules by earlier workers.

The relaxation processes have been further examined by evaluating the enthalpy of activation for different processes. The overlapped enthalpy  $\Delta H_{\tau_{\text{OH}}}$  evaluated, using most probable relaxation time  $\tau_{\text{OH}}$  has been found to be  $5.8 \text{ kJ mol}^{-1}$  which compares well with  $\Delta H_{\tau_{(2)}} = 5.3 \text{ kJ mol}^{-1}$ , the enthalpy of activation due to molecular process. This examination supports the dominance of molecular over intramolecular process in the system. The enthalpy of activation  $\Delta H_{\tau_{(1)}}$  associated with intramolecular group relaxation could not be estimated due to very small variation observed in the intramolecular relaxation time for the temperature range varying from 296 to 326 K. This shows almost a temperature independent behaviour of the group relaxation process. Similar behaviour in case of some esters were reported by PUROHIT *et al* [19].

The enthalpy of activation for viscous flow process has been found to be  $10.6 \text{ kJ mol}^{-1}$  and is greater than  $\Delta H_{\tau_{\text{OH}}}$ . This is because viscous flow involves translational motion also besides the rotational motion present in the dipolar relaxation process.

$\Delta F_a$  and  $\Delta S_a$ , the free energy of activation and the entropy of activation for the most probable relaxation processes  $\tau_{\text{OH}}$  have been found to be  $(11.2 - 11.6 \text{ kJ mol}^{-1})$  and  $(20.3 - 20.1 \text{ J deg}^{-1} \text{ mol}^{-1})$  respectively in the temperature range of  $(296 - 320 \text{ K})$ .

### B) *p*-Chlorophenyl acetonitrile

This molecule has again yielded high value of distribution parameter (0.31—0.29). The dielectric absorptions have further been resolved in terms of two independent Debye type mechanism characterised by the relaxation time  $\tau_{(1)}$  and  $\tau_{(2)}$ . The molecular relaxation time  $\tau_{(2)}$  and the intramolecular relaxation time  $\tau_{(1)}$  have been found to be 28.8 ps. and 10.2 ps. respectively at 296 K. The relaxation time  $\tau_{(0)}$  for the overlapped process estimated as geometrical mean of  $\tau_{(1)}$  and  $\tau_{(2)}$  has been found to be 17.1 ps. and compares well with the most probable relaxation time  $\tau_{\text{OH}} = 17.1 \text{ ps}$ .

The relaxation time  $\tau_{\text{GK}} (= 8.3 \text{ ps})$  for this molecule has been found to be 10.2 at 296 K. Contrary to molecule 'A' where  $\tau_{\text{GK}}$  agrees with  $\tau_{(2)}$  for molecule 'B',  $\tau_{\text{GK}}$  has been found to be nearer to  $\tau_{(1)}$ . These observations are in agreement with the earlier work of MISRA *et al.* [20] on tolualdehydes and VIZ and SRIVASTAVA [21] on some substituted anilines both experimentally and theoretically.

On comparing the relaxation behaviour of molecule 'A' with molecule 'B' it is found that  $\tau_{(2)} (= 28.8 \text{ ps})$  for 'B' is greater than  $\tau_{(2)} (= 23.0 \text{ ps.})$  for 'A'.  $\tau_{(1)}$  for both the molecules are in close agreement. This indicates that probably the addition of highly electronegative-chloro group at para-position of phenyl acetonitrile does not influence intramolecular relaxation behaviour to the extent it influences molecular relaxation process in the molecule 'B'.

The enthalpy of activation  $\Delta H_{\tau_{\text{OH}}}$  for the overlapped process has been found to be  $7.6 \text{ kJ mol}^{-1}$  and is greater than  $\Delta H_{\tau_{\text{OH}}} = 5.8 \text{ kJ mol}^{-1}$  for the molecule 'A'. The enthalpy of activation  $\Delta H_{\tau_{(1)}}$  associated with the intramolecular rotation has been estimated as  $1.6 \text{ kJ mol}^{-1}$  and is found to be smaller than  $\Delta H_{\tau_{(2)}}$  for molecule 'B'. The enthalpies  $\Delta H_{\tau_{\text{OH}}}$  and  $\Delta H_{\tau_{\text{GK}}}$  evaluated using  $\tau_{\text{OH}}$  and  $\tau_{\text{GK}}$  are in good agree-

ment. Further for this molecule  $\Delta H_{\eta} > \Delta H\tau_{OH}$ . This is similar to the observation for the molecule 'A'. The free energy of activation  $\Delta F_e$  and the entropy of activation  $\Delta S_e$  for the relaxation process have been found to vary from (11.6—11.8 deg<sup>-1</sup> kJ mol<sup>-1</sup>) and (8.2—8.9 Joules deg<sup>-1</sup> mol<sup>-1</sup>) respectively.

### (C) *p*-nitro phenyl acetonitrile

Having obtained high value of distribution parameter ranging from (0.41—0.37) for this molecule the dielectric absorptions, when further resolved gave rise to two relaxation time values,  $\tau_{(1)}$  (=8.8 ps.) and  $\tau_{(2)}$  (32.7 ps.) at 296 K. The 'average relaxation time estimated to be 17.0 ps. has been found to agree well with the most probable relaxation time  $\tau_{OH}$  (=17.2 ps.) indicating the presence of multiple relaxation in the system. The  $\tau_{GK}$  (=23.5 ps.) for the molecule has been found to be greater than  $\tau_{OH}$  and  $\tau_{(1)}$  but smaller than  $\tau_{(2)}$ . This indicates the predominance of molecular process in the system. It has been observed that relaxation time  $\tau_{OH}$ ,  $\tau_0$ ,  $\tau_{(2)}$  lengthens in the molecule in the order,  $C > B > A$ . It is observed from the Table II that the relaxation time  $\tau_{(1)}$  associated with the rotation of  $-\text{CH}_2\text{CN}$  group in the molecule *C*, *B* and *A* varies from 8.8 to 10.8 ps. at 296 K. This indicates the addition of a-chloro or a-nitro group at *p*-position in phenyl acetonitrile has hardly any influence on the intramolecular rotation process of  $-\text{CH}_2\text{CN}$  group. Similar results have been observed by Sengupta *et al.* in 1,2-dicyanoethane, 1,3-dicyanopropane and 1,4-dicyanobutane molecules.

Enthalpy of activation for molecular rotation  $\Delta H_{\tau_{(2)}}$  and for overlapped process  $\Delta H_{\tau_{OH}}$  has been estimated for this molecule and has been found to be 6.0 kJ mol<sup>-1</sup> and 9.3 kJ mol<sup>-1</sup> respectively. The observed enthalpy of molecule 'C' being the highest in the series is attributed to the largest molecular size of the system. The enthalpy of activation  $\Delta H_{\tau_{(1)}}$  associated with the intramolecular rotation of  $-\text{CH}_2\text{CN}$  group could not be ascertained due to the small change observed in  $\tau_{(1)}$  values with temperature.

Free energy of activation  $\Delta F_e$  for this molecule has been found in the range (11.3—11.5 kJ mol<sup>-1</sup>) and is almost the same for the molecule 'A' and 'B' and the entropy of activation  $\Delta S_e$  for the molecule is found to be (5.9—6.4 J. deg<sup>-1</sup> mol<sup>-1</sup>) in the temperature range of 288 K to 312 K and is highest in the series.  $\Delta S_e$  has been found to be negative for all the molecules *A*, *B* and *C* indicating the presence of cooperative orientations [22] in the system.

### Conclusion

The flexibility of phenyl acetonitrile molecules has been indicated by the observed high values of distribution parameter ' $\alpha$ ' for all the three systems. The two distinct relaxation time  $\tau_{(1)}$  and  $\tau_{(2)}$  observed for all the three molecules are appreciably different from one another; thus establishing two separate processes occurring in the observed dispersion. It has been observed by HIGASI *et al.* [9, 13] and several other workers [23, 24] that  $\tau_{(2)}$  corresponds to molecular rotation process where as  $\tau_{(1)}$  is an implicit function of  $\tau_1$ ,  $\tau_2$  and weight factor  $C_1$ , and would be associated with some other process. Thus, in the present set of molecules, the process other than the mole-



cular one, which gives rise to dielectric absorption would be probably due to internal rotation of  $-\text{CH}_2\text{CN}$  group. The observed relaxation time  $\tau_{(1)}$  at 296 K for *p*-nitrophenyl acetonitrile, *p*-chloro phenyl acetonitrile and phenyl acetonitrile have been found to be 8.8 ps., 10.2 ps. and 10.8 ps., respectively; whereas the relaxation times  $\tau_{(2)}$  for the other process, presumably the molecular one for the same set of molecules at 296 K has been found to be 32.7 ps., 28.8 ps. 23.2 ps. respectively. The observed relaxation time  $\tau_{(1)}$  indicates no significant variation whereas there exists an appreciable change in the values obtained for  $\tau_{(2)}$ , which stands for the molecular process. The only common rotating unit present in all the three molecules is  $-\text{CH}_2\text{CN}$  group, and therefore, the observed  $\tau_{(1)}$  parameter, which is almost unchanged within the limits of experimental error, could be assigned to the internal rotation of  $-\text{CH}_2\text{CN}$  group. This behaviour has been found true at all the observed temperatures.

Further, the present investigations have been carried out using Higasi, Koga and Nakamura method for resolving the two processes. A comparison of the data for phenyl acetonitrile molecule, earlier analyses using Cole-Cole method shows good agreement with the present results for both  $\tau_{(1)}$  and  $\tau_{(2)}$ , establishing the validity of Higasi, Koga and Nakamura method for resolving the relaxation behaviour of simple molecules at a given frequency and temperature.

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ИССЛЕДОВАНИЕ ДИЭЛЕКТРИЧЕСКОЙ РЕЛАКСАЦИИ У НЕКОТОРЫХ  
ПРОИЗВОДНЫХ ФЕНИЛАЦЕТОНИТРИЛА

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Изучена диэлектрическая релаксация в разбавленных бензольных растворах фенилацетонитрила, *н*-хлорфенилацетонитрила и *н*-нитрофенилацетонитрила в интервале температур 228—320 К, при частоте 9,86 Нз. Полученные диэлектрические постоянные оценивались с помощью метода Гопала Кришны для расчета  $\tau_{GK}$ , а для расчета наиболее вероятной релаксации  $\tau_{OH}$  и параметра распределения  $\alpha$  использовали метод Хигаши.