

Structural studies of some organic polar compounds using nuclear magnetic resonance and microwave techniques

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The present communication reports the experimental measurements of dielectric relaxation times (τ) of methyl cyanide, methyl chloride, methylene chloride, chlorofluoro methane, dichlorofluoro methane, chlorodifluoro methane, 1,3,5 trifluorobenzene and toluene. The experimental values of nuclear spin-lattice relaxation time (T_1) found in the literature have been correlated with the calculated values of the NMR spin-lattice relaxation time, obtained using various equations for calculating the dielectric relaxation time. The calculated values of dielectric relaxation and spin-lattice relaxation time obtained using Murty equation are in better agreement with the experimental values. Therefore it has been concluded that the Murty equation is a better representation of the dielectric relaxation phenomenon.

1. INTRODUCTION

The study of dielectric relaxation time and nuclear magnetic relaxation time has long been a subject of interest for investigation of the molecular structure of liquids.

Bloembergen *et al* (B.P.P.) (1948) have derived an expression for the magnetic relaxation in terms of correlation time τ_c which is closely related to the Debye's theory (1929) of dielectric dispersion in polar liquids. To evaluate they used the value of dielectric relaxation time $\tau = \frac{4\pi\eta a^3}{kT}$. Many workers have calculated nuclear spin-lattice relaxation time from B.P.P. theory and found that the calculated values were ranging from $\frac{1}{3}$ to $1/10$ times the experimental values. In the present investigation the authors have modified B.P.P. equation using Murty's equation $\tau = \frac{6\pi\eta a}{(\epsilon' + 2)kT}$ for dielectric relaxation instead of Debye equation as used by B.P.P.

2. THEORY

Dielectric relaxation time (τ) and the dipole moment (μ) have been determined using the concentration variation method of Gopala Krishna (1957) discussed in an earlier paper of the authors (1967). The free energies of activation have been calculated using the same procedure as discussed in our paper (Somevanshi & Mehrotra 1976).

The spin-lattice relaxation of a single nuclear spin in a liquid is induced by the fluctuating local magnetic field of neighbouring spins. If the spin which induces the relaxation is attached to the same molecule as the relaxing spin, the fluctuating field is produced by molecular reorientational motion. The contribution of this mechanism to the overall T_1 is denoted by $(T_1)_{rot}$. If the relaxation which occurs when the relaxing spin and spin which induces relaxation are attached to different molecules is denoted by $(T_1)_{trans}$. B.P.P. have calculated the probability of transition induced and the equation as thus obtained is

$$\left(\frac{1}{T_1} \right) = \left(\frac{1}{T_1} \right)_{rot.} + \left(\frac{1}{T_1} \right)_{trans.} \quad \dots (1)$$

and

$$\left(\frac{1}{T_1} \right)_{rot} = \frac{3\gamma^4 \hbar^2}{10r_0^6} \left[\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{2\tau_c^2}{1 + 4\omega_0^2 \tau_c^2} \right] \quad \dots (2)$$

where γ is gyromagnetic ratio, $\hbar = \frac{h}{2\pi}$, h is Planck's constant, τ_c is the correlation time and r_0 is sum of interproton distances within the molecule, $\omega_0 = 2\pi\nu_0$ where ν_0 is resonance frequency.

Later on above equation was modified by Kubo & Tomita (1954) and they obtained

$$\left(\frac{1}{T_1} \right)_{rot.} = \frac{3\gamma^4 \hbar^2}{2r_0^6} \tau_c \quad \dots (3)$$

The correlation time τ_c required in the above equation is closely related to the dielectric relaxation time τ of Debye's (1929) theory of dielectric dispersion in polar liquids as

$$\tau_c = \tau/3 \quad \dots (4)$$

The authors have calculated correlation time using Debye's equation (1929). Perin's (1934) modification of Debye's equation. Wirtz & Coworkers' equation (1953), Eyring's equation (1941), and Murty's (1958) equation is discussed in our earlier papers (1976). Using these values of τ_c in equation (4) we get different values of $(1/T_1)_{rot}$.

If it is assumed that the B.P.P. model is adequate to account for the translational contribution to the spin-lattice relaxation time, and if modification of Kubo & Tomita (1954) is also applied, then expression for $(1/T_1)_{trans}$ is given by

$$\left(\frac{1}{T_1} \right)_{trans.} = \frac{3\pi^2 \hbar \gamma n N}{kT} \quad \dots (5)$$

where N is the number of molecules per unit volume.

3. EXPERIMENTAL PROCEDURE

The samples of compounds in our study were supplied by M/s L. Light & Co. London and were reported to be of high standard of purity. The solvent benzene was B.D.H., A.R. grade of purity and was distilled before use.

A microwave bench of 3.13 cm wavelength region has been used for measuring the dielectric constant ϵ' and the loss factor ϵ'' of dilute solutions of compounds in benzene. The microwaves were generated by a C. V. 129 Klystron and dielectric constant ϵ' and losses ϵ'' were determined using standing wave technique of Roberts & Von Hippel (1946) and its subsequent simplification by Dakin & Works (1947). The accuracy in measurements of dielectric constants and loss tangents were within $\pm 2\%$ and $\pm 5\%$ respectively. Consequently the dielectric relaxation times τ were found to be accurate to $\pm 0.5\%$.

4. RESULTS

The experimental data for calculation of dielectric relaxation time and dipole moment are given in table 1. Table 2 shows the experimental and calculated values of τ . Experimental and calculated values to T_1 are reported in table 4. The calculated and literature values of dipole moment μ are mentioned in table 3.

5. DISCUSSION

(1) Dielectric Relaxation time : It is evident from the table 2 that the dielectric relaxation time τ of methyl chloride is larger than that of methyl cyanide which is in accordance with the larger size of the former molecule. Methylene chloride has higher values of τ than methyl chloride which may be explained due to more steric hinderance between the chlorine atoms in former molecule. It is evident from table 2 that the relaxation time of chlorofluoro methane is smaller than that of dichlorofluoromethane which is due to the smaller volume swept out by the former molecule for dipole orientation. The higher value of relaxation time for toluene than 1,3,5 trifluorobenzene may be explained on the basis of higher electronegativity of fluorine which decreases the electron density on benzene ring and thus decreases the shielding with consequent lowering of the τ value. It is also evident from the table 2 that the values of τ obtained using Murty's equation are in better agreement with the experimentally obtained values. Similar results were obtained by the authors in case of some substituted benzenes, benzoic acids and esters.

The values of dipole moments of the compounds as given in table 3 are found to be in good agreement with values obtained from literature. The activation energies for the process of dipole orientation are found to be smaller than that for viscous flow of the solvent benzene, since the former involves only the rotation of the molecule, while the latter involves both rotation and translation.

Table 1. Experimental data for evaluation of relaxation time (τ) and dipole moments at 20°C

Compounds	Concentration	Dielectric Constant (ϵ')	Loss Factor (ϵ'')
1. Methyl Cyanide	0.0074	2.2264	0.0441
	0.0161	2.2304	0.0605
	0.0192	2.2534	0.0691
	0.0213	2.2662	0.0739
	0.0326	2.2791	0.0893
2. Methyl Chloride	0.0293	2.2223	0.0312
	0.0401	2.2449	0.0409
	0.0423	2.2519	0.0442
	0.0621	2.2678	0.0631
	0.0728	2.2730	0.0728
3. Methylene Chloride	0.0231	2.2291	0.0418
	0.0298	2.2363	0.0532
	0.0346	2.2415	0.0619
	0.0432	2.2561	0.0714
	0.0517	2.2643	0.0825
4. Chlorofluoro methane	0.0079	2.2318	0.0541
	0.0132	2.2397	0.0648
	0.0169	2.2419	0.0752
	0.0219	2.2492	0.0799
	0.0298	2.2561	0.0814
5. Dichlorofluoro methane	0.0131	2.2219	0.0256
	0.0192	2.2283	0.0279
	0.0263	2.2313	0.0341
	0.0299	2.2387	0.0399
	0.0342	2.2409	0.0651
6. Chlorodifluoro methane	0.0219	2.2145	0.0284
	0.0283	2.2193	0.0319
	0.0316	2.2243	0.0443
	0.0424	2.2398	0.0512
	0.0498	2.2459	0.0683
7. 1. 3. 5 trifluoro benzene	0.0116	2.2581	0.0661
	0.0162	2.2792	0.0835
	0.0207	2.2938	0.0985
	0.0221	2.2982	0.0997
	0.0259	2.3057	0.1079
8. Toluene	0.0099	2.2536	0.0684
	0.0132	2.2733	0.0721
	0.0192	2.2879	0.0792
	0.0276	2.2924	0.0856
	0.0345	2.3041	0.0932

Table 2. Experimental and calculated values of dielectric relaxation time (τ)

Compounds	τ exp. $\times 10^{12}$ sec.	τ Pebye $\times 10^{12}$ sec.	τ Perin $\times 10^{12}$ sec.	τ Eyring $\times 10^{12}$ sec.	τ Wirtz $\times 10^{12}$ sec.	τ Murty $\times 10^{12}$ sec.
1. Methyl Cyanide	5.31	22.23	7.90	7.41	6.39	4.71
2. Methyl Chloride	7.29	11.43	4.11	3.82	9.21	6.23
3. Methylene Chloride	8.34	33.44	12.13	11.14	11.34	7.91
4. Chlorofluoro Methane	8.13	62.61	22.60	22.87	12.16	7.21
5. Dichlorofluoro Methane	11.46	66.23	23.83	22.07	14.29	10.52
6. Chlorodifluoro Methane	10.91	70.31	25.36	23.43	10.31	9.34
7. 1.3.5 trifluoro benzene	14.36	71.36	25.67	23.78	16.21	18.99
8. Toluene	16.28	72.61	26.13	24.20	19.23	19.23

Table 3. The activation energies and dipole moments (μ)

Compounds	ΔH_r K Cal/mole	ΔH_r K Cal/mole	μ_{obs} $\times 10^{18}$ Debye	μ_{calc} $\times 10^{18}$ Debye
1. Methyl Cyanide	0.896	2.90	2.93	3.11(a)
2. Methyl Chloride	0.956	2.90	1.72	1.86(b)
3. Methylene Chloride	0.990	2.90	1.53	1.61(c)
4. Chlorofluoro Methane	0.984	2.90	1.18	$\times \times$
5. Dichlorofluoro Methane	1.071	2.90	1.21	1.29(d)
6. Chlorodifluoro Methane	1.116	2.90	1.32	1.40(d)
7. 1.3.5 trifluoro benzene	1.127	2.90	1.73	\times
8. Toluene	1.186	2.90	0.76	0.52(e)

Note :—The values of dipole moments have been obtained from following references :
(a) Werner (1929), (b) Sanger (1929), (c) Mahanti (1929), (d) Smyth (1933), (e) Williams (1927).

It is evident from table 4 that the values of spin-lattice relaxation time calculated using B.P.P. equation are smaller than the experimental values. When Perin & Eyring modifications are used in calculating (T_1) these give better correlation than the B.P.P. theory. The calculated values of T_1 using Wirtz &

Coworkers equation are nearer to the experimental values. The values of spin-lattice relaxation time (T_1) calculated using Murty's equation are in quantitative agreement with the experimental values. Therefore it is concluded that the Murty's equation is a better substitute for the correlation time in B.P.P. equation for spin-lattice relaxation than the Debye equation. Similar results have also been obtained by Moniz *et al* (1963).

Table 4. Experimental and calculated values of N.M.R. spin-lattice relaxation time (T_1)

Compounds	Temp °K	(T_1) exp. (Sec.)	(T_1) Debye (Sec.)	(T_1) Perin (Sec.)	(T_1) Eyring (Sec.)	(T_1) Wirtz (Sec.)	(T_1) Murty (Sec.)
1. Methyl Cyanide	298	15.3*	2.31	6.42	6.93	16.17	17.56
2. Methyl Chloride	293	18.6*	2.01	5.59	6.03	14.07	19.21
3. Methylene Chloride	293	28.6*	6.91	19.20	20.73	48.37	22.78
4. Chlorofluoro Methane	293	34.6+	7.15	19.86	21.45	50.05	31.29
5. Dichlorofluoro Methane	293	46.9+	8.21	22.80	24.63	57.47	41.43
6. Chlorodifluoro Methane	293	6.30+	2.14	5.94	6.42	14.98	7.28
7. 1,3,5 trifluoro benzene	293	24.0+	5.13	14.25	15.39	35.91	24.39
8. Toluene	298	16.0*	4.73	13.14	14.19	33.11	16.12

Note : The references of experimental data of spin-lattice relaxation time are follows :
*Moniz (1963). + Gutowsky (1956)

The discrepancy between the calculated and experimental values of T_1 also arises due to the fact that the dielectric relaxation equations are valid for dilute solutions, where major contribution to the spin-lattice relaxation phenomenon arises from intramolecular interactions which are less important and intermolecular interactions are dominant.

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REFERENCE

- Bloembergen N., Purcell E. M. & Pound R. V. 1948 *Phys Rev.* **73**. 673.
- Debye P. 1929 *Polar Molecules*. Chem. Catalogue Company. p. 90.
- Dakin T. W. & Works C. N. 1947 *J. Appl. Phys.* **18**. 789.
- Eyring H., Glasstone S. & Laidler K. J. 1941 *The theory of rate process*. Mc-Grall Hill Book Co., Inc. New York. p 458
- Gopala Krishna K. V. 1957 *Trans. Faraday Society* **53**. 767.
- Gutowaky H. S. & Woessner D. E. 1956 *Phys. Rev.* **104**. 843.
- Kubo R. & Tomita K. 1954 *J. Phys. Soc. Japan* **9**. 888.
- Mahanti & Das Gupta 1929 *J. Ind. Chem. Soc.* **6**. 411.
- Mehrotra N. K., Shukla J. P. & Saxena M. C. 1967 *Ind. J. Pure & Appl. Phys.* **5**. 61.
- Mehrotra N. K. & Somevanshi S. K. S. 1976 *Current Sci. (Ind.)* **45**. 254.
- Moniz W. B. *et al* 1963 *J. Chem. Physik* **38**. 2418.
- Murty S. R. K. 1958 *Ind. J. Phys.* **32**. 580.
- Nederbraght G. W. & Reilly C. A. 1956 *J. Chem. Phys.* **24**. 1110.
- Perin F. 1934 *J. of Phys. Radium* **5**. 497.
- Roberts S. & Von Hippel A. 1946 *J. of Appl. Phys.* **17**. 610.
- Sanger R. & Steiger O. 1929. *Helv. Physic. Acta.* **2**. 411.
- Smyth C. P. & MacAlpine K. B. 1933 *J. Chem. Phys.* **1**. 190.
- Somevanshi S. K. S. & Mehrotraz N. K. under publicaton in *Ind. J. Pure & Appl. Phys.* Proof no 2703.
- Werner O. 1929 *Z. Physik. Chem.* **B4**. 371.
- Wilson C. W. & Pake G. E. 1957 *J. Chem. Phys.* **27**. 115.
- Williams J. W. & Krehma I. 1927 *J. Am. Chem. Soc.* **49**. 1676.
- Wirtz K. & Spornol A. 1953 *Z. Naturforsch* **8A**. 522.