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Correlation of the Mutual Viscosity and the NMR Spin-Lattice Relaxation Time in Several Substituted Benzoic Acids

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The present communication reports on the experimental values of the mutual viscosity (η_{12}) and NMR spin-lattice time (T_1) of *o*-nitrobenzoic acid, *m*-nitrobenzoic acid, *p*-nitrobenzoic acid, *o*-hydroxybenzoic acid, *m*-hydroxybenzoic acid, *p*-hydroxybenzoic acid, and *m*-chlorobenzoic acid. The small difference between the values of η_{12} and η_1 suggests that the basic model of the dielectric relaxation process does not suffer any major changes even when η_{12} is used instead of η_1. The experimental values of the NMR spin-lattice relaxation time (T_1) have been correlated with the calculated values of T_1 obtained using various equations of the dielectric relaxation time (τ). It has been concluded that the equations of Writz and Murty are better representations of the dielectric relaxation phenomenon.

Structural studies of organic compounds using the dielectric relaxation mechanism and nuclear magnetic resonance have long been a subject of interest. A magnetic dipole experiences a force when placed in a magnetic field. The nuclear spin invariably interacts with its surrounding and undergoes violent thermal motion. The thermal motion of nuclei produces randomly oscillating magnetic fields with the precessional frequency of the relaxing nuclei, and permits the magnetic orientation energy to be converted into thermal energy. The rate of relaxation by this mechanism depends upon the temperature, the density of the magnetic nuclei and the viscosity of the medium in which they are embedded as well as the shape of the molecules.

Many workers[1–4] have evaluated the nuclear spin-lattice relaxation time from BPP theory, and have found that the calculated values range from 1/2 to 1/10 times the experimental values. The possibility of narrowing the gap between the experimental and calculated values stimulated the present work reported in this paper. We also wish to find out for these molecular systems whether the dipole orientation process is due to only the molecular rotations or by both the molecular and intramolecular rotations.

1. Theoretical

Bloembergen et al.[5] have derived an expression for the magnetic relaxation in terms of the correlation time (τ_c), which is closely related to Debye's theory[6] of the dielectric dispersion in polar liquids, according to which the dielectric relaxation time is given by

$$\tau = \frac{4\pi\eta a^3}{KT}, \tag{1}$$

where the symbols have their usual meaning.

In using BPP theory of nuclear magnetic resonance, the spin-lattice relaxation time of a molecule in the liquid state was calculated based on the assumption that the relaxation is produced by a dipole–dipole interaction between the nuclear spins.

Later Writz and co-workers,[7] elaborating Perrin's[8] idea, modified the Debye equation to the form given by

$$\tau = \frac{4\pi\eta a^3}{KT}\left[\frac{6a_1}{a_2} + \left(1 + \frac{a_1}{a_2}\right)^{-3}\right]^{-1}, \tag{2}$$

where

$$a_i = \left[0.556\left(\frac{M_i}{\pi d_i N}\right)\right]^{1/3}. \tag{3}$$

Here, M_i, d_i, and a_i are molecular weight, density, and radius of molecule, respectively, and N is Avagadro's Number.

Murty[9] has found a simple empirical equation for τ,

$$\tau = \frac{6\pi\eta\alpha}{(\varepsilon_1 + 2)KT}, \tag{4}$$

where α is the polarizability of the solute molecule and ε_1 is the dielectric constant of the solvent.

The spin-lattice relaxation of a single nuclear spin in a liquid is induced by the fluctuating local magnetic field of neighboring spins. If the spin that induces the relaxation is attached to the same molecule as the relaxing spin, the fluctuating field is produced by the molecular reorientational motion. The contribution of this mechanism to the overall T_1 is denoted by $(T_1)_{\text{rot}}$. If the relaxation that occurs when the relaxing spin and the spin that induces relaxation are attached to different molecules, is denoted by $(T_1)_{\text{trans}}$.

BPP have calculated the probability of the induced transition and thus obtained the expression

$$(T_1)^{-1} = (T_1)^{-1}_{\text{rot}} + (T_1)^{-1}_{\text{trans}}, \tag{5}$$

where

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

Here, γ is the gyromagnetic ratio, $\hbar = h/2\pi$, h is Planck's constant, τ_c is the correlation time and r_0 is the sum of the inter-proton distances within the molecule, and ω_0 is the resonance angular frequency.

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Later Kubo and Tomita[10] modified Eq. 6 and obtained

$$(T_1)^{-1}_{\mathrm{rot}} = \frac{3\gamma^4\hbar^2}{2r_0^6}\,\tau_c. \tag{7}$$

The correlation time (τ_c) required in Eq. 7 is closely related to the dielectric relaxation time (τ), of Debye's theory of dielectric dispersion in a polar liquids as

$$\tau_c = \frac{\tau}{3}. \tag{8}$$

The authors calculated the correlation time using Debye's equation, Perrin's modification of Debye's equation, Writz and Sperinol's equation, and Murty's equation.

In order to test the validity of these equations, different values of $(T_1)_{\mathrm{rot}}$ have been obtained using different values of τ_c.

Assuming that the BPP model is adequate to account for the translational contribution to the spin-lattice relaxation time (T_1), the expression for $(T_1)_{\mathrm{trans}}$ is given by

$$(T_1)^{-1}_{\mathrm{trans}} = \frac{9\pi^2\gamma^4\hbar^2\eta N_0}{10KT}, \tag{9}$$

where N_0 is the number of molecules per unit volume and η is the viscosity of the compound.

An investigation of the dielectric relaxation in a number of organic compounds showed a wide disagreement between the observed values of the dielectric relaxation time (τ) and those calculated using the Debye equation. This discrepancy can be explained if in the Debye equation we use a mutual viscosity parameter (η_{12}) as proposed by Hill,[11] representing the interaction between both the solute and solvent molecules, instead of the solvent viscosity (η_1). The expression for the coefficient of mutual viscosity (η_{12}) is given in our earlier papers.[12,13]

2. Experimental

All of the compounds used were of pure quality obtained from M/s British Drug House ltd., England. The percentage purity of the investigated compound ranged from 99.8 to 99.9%. The purest quality of deuterated dioxane obtained from M/s British Drug House was distilled before use.

The viscosities were measured to an accuracy of ±2% with a Hoppler precision viscometer. This method requires a determination of the time of fall of a glass or a metal ball between two marks in a glass tube filled with a liquid with known density. The viscosity of the liquid (η_m) is calculated using the relation $\eta_m = F(S_K - S_F)K$, where F is the time of the fall of the ball in seconds, S_K is the specific gravity of the ball, S_F is the specific gravity of the liquid, and K is the ball constant ($= 0.009495$).

For T_1 experiments, the inversion recovery method ($180°$–τ–$90°$) of Freeman and Hill[14] was used in each system to evaluate the spin-lattice relaxation time. The time was chosen initially for 10 seconds which varied in a graduated manner in order to obtain the correct phase modulation of the series of NMR spectrum in each system, so as to accurately calculate the spin-lattice relaxation time (T_1) values. The experiments were performed in an automation mode using the standard pulse programme from the Bruker software library.

3. Results

The chemical-shift positions and NMR spin-lattice relaxation time (T_1) of various protons of *o*-nitrobenzoic acid, *m*-nitrobenzoic acid, *p*-nitrobenzoic acid, *o*-hydroxybenzoic acid, *m*-hydroxybenzoic acid, *p*-hydroxybenzoic acid, and *m*-chlorobenzoic acid are given in Table 1. Table 2 gives the values of the mutual viscosity (η_{12}) and the ratio (τ/η_1), (τ/η_{12}). The experimental and calculated values of dielectric relaxation time (τ) and NMR spin-lattice relaxation time (T_1) of these compounds at 293 K are given in Tables 3 and 4, respectively.

4. Discussion

4.1 Chemical Shift. Table 1 represents the NMR spin-lattice relaxation time (T_1) of various protons present in *o*-nitrobenzoic acid, *m*-nitrobenzoic acid, *p*-nitrobenzoic acid, *o*-hydroxybenzoic acid, *m*-hydroxybenzoic acid, *p*-hydroxybenzoic acid, and *m*-chlorobenzoic acid. In the ^{1}H NMR spectrum, because the –COOH group of *o*-nitrobenzoic acid is meta directing, it increases the electron density at the meta position. The two H_b protons are ortho coupled with neighboring H_a and H_c, though the chemical environment of the H_a and H_b protons are not the same. Hence, we obtain a double doublet at a higher field region. The peak multiplicities of the H_a and H_c protons are triplet in the lower field region. The H_a proton resonates at slightly lower field region due to hydrogen bonding of the –COOH group. The spin-lattice relaxation time of *o*-nitrobenzoic acid indicates the statistical average of the overall relaxation time. In the ^{1}H spectrum of *m*-nitrobenzoic acid five peaks are observed, which correspond to five different protons having different chemical environments. The H_d proton of the –COOH group is attached to the oxygen atom, which is electronegative in nature. Due to its presence, deshielding takes place at a lower field region, giving a double doublet, which is orthocoupled with neighboring protons. The proton H_a is influenced by the –NO_2 group, which is less electronegative with respect to –COOH. Hence, a singlet of the H_a proton resonates at a slightly higher field region. Similarly, the double doublet of the H_b proton resonates at a higher field region. The peak multiplicity of H_c is a triplet at 7.55 ppm, which is orthocoupled with neighboring protons. This is the reason that the NMR spin-lattice relaxation time (T_1) of *m*-nitrobenzoic acid is the statistical average of the overall relaxation time. In *p*-nitrobenzoic acid, the H_a and H_b protons are represented by a double doublet; the H_b proton resonates at a slightly higher field region due to domination of the –COOH group. This also confirms the statistical average of the overall relaxation time. The H_d proton of *o*-hydroxybenzoic acid resonates at a lower field region, which is influenced by the ortho directing –OH group. The peak multiplicity is a double doublet due to ortho coupling with neighboring protons. The triplet of H_c also resonates at a lower field region, due to the ortho-coupling of two neighboring protons. The H_b protons resonate at a higher field region, due to the presence of the meta directing –COOH group. The doublet of the H_a proton resonates at a slightly lower field region, due to hydrogen bonding with the oxygen atom of the –COOH group. The statistical average of the overall relaxation time for obtaining the NMR relaxation time for *o*-, *m*-, *p*-hydroxybenzoic acids and *m*-chlorobenzoic acid can be explained similarly.

4.2 Mutual Viscosity. The results tabulated in Table 2 show that the dielectric relaxation time (τ) of the three nitrobenzoic acids decrease from ortho via meta to para compounds. The ratio τ/η_1 for these compounds also decreases in the same

Table 1. Chemical Shift Position (δ) and NMR Spin-Lattice Relaxation Time (T_1) of Various Protons

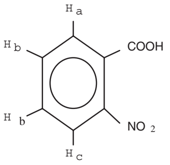
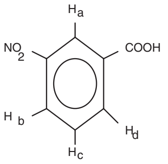
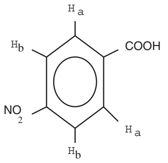
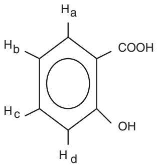
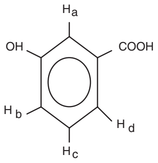
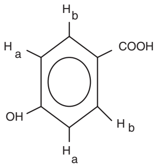
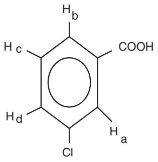
S. No	Polar compound	Proton	Chemical shift (δ) /ppm	The statistical average of NMR spin-lattice relaxation time T_1 /sec
1	*o*-Nitrobenzoic acid 	H_a H_b H_c	7.83 7.79 7.70	3.65
2	*m*-Nitrobenzoic acid 	H_a H_b H_c H_d	7.03 6.96 7.55 7.94	3.77
3	*p*-Nitrobenzoic acid 	H_a H_b	8.31 8.21	3.89
4	*o*-Hydroxybenzoic acid 	H_a H_b H_c H_d	6.91 6.85 7.43 7.86	4.19
5	*m*-Hydroxybenzoic acid 	H_a H_b H_c H_d	7.43 7.00 7.26 7.49	4.38
6	*p*-Hydroxybenzoic acid 	H_a H_b	7.82 7.44	4.61
7	*m*-Chlorobenzoic acid 	H_a H_b H_c H_d	7.91 7.57 7.43 7.95	3.45

Table 2. Values of Mutual Viscosity η_{12} and the Ratio (τ/η_1), (τ/η_{12}) for the Investigated Compounds

S. No	Polar compounds	τ_{Exp} $/10^{-12}$ sec	τ/η_1	η_{12} /cps	τ/η_{12}
1	*o*-Nitrobenzoic acid	15.2[a)]	10.73	1.509	10.07
2	*m*-Nitrobenzoic acid	14.2[a)]	10.02	1.505	9.44
3	*p*-Nitrobenzoic acid	12.3[a)]	8.68	1.503	8.18
4	*o*-Hydroxybenzoic acid	11.10[b)]	7.84	1.499	7.40
5	*m*-Hydroxybenzoic acid	10.79[b)]	7.62	1.495	7.22
6	*p*-Hydroxybenzoic acid	9.96[b)]	7.03	1.490	6.68
7	*m*-Chlorobenzoic acid	10.0[a)]	7.06	1.429	7.00

Viscosity of dioxane at 293 K $(\eta_1) = 1.4165$ cps. a) Ref. 16. b) Ref. 17.

Table 3. Values of Dielectric Relaxation Time (τ) (in 10^{-12} sec) at 293 K for Compound Studies

S. No	Polar compounds	Molecular radius (a) $/10^{-8}$ cm	τ_{Exp}	τ_{Debye}	τ_{Perrin}	τ_{Writz}	τ_{Murty}
1	*o*-Nitrobenzoic acid	3.02	15.2[a)]	121.40	43.74	21.09	17.97
2	*m*-Nitrobenzoic acid	3.14	14.2[a)]	136.92	49.29	20.32	15.37
3	*p*-Nitrobenzoic acid	2.93	12.3[a)]	110.40	39.74	18.46	11.92
4	*o*-Hydroxybenzoic acid	2.90	11.10[b)]	107.76	38.79	13.87	13.93
5	*m*-Hydroxybenzoic acid	2.89	10.79[b)]	104.27	37.53	13.32	12.19
6	*p*-Hydroxybenzoic acid	2.85	9.96[b)]	102.41	36.86	12.42	8.18
7	*m*-Chlorobenzoic acid	2.82	10.0[a)]	98.74	35.56	14.19	11.23

a) Ref. 16. b) Ref. 17.

Table 4. Values of NMR Spin-Lattice Relaxation Time T_1 (in sec) at 293 K

S. No	Polar compounds	$T_{1\mathrm{Exp}}$	$T_{1\mathrm{Debye}}$	$T_{1\mathrm{Perrin}}$	$T_{1\mathrm{Writz}}$	$T_{1\mathrm{Murty}}$
1	*o*-Nitrobenzoic acid	3.65	1.82	2.88	3.46	3.56
2	*m*-Nitrobenzoic acid	3.77	1.73	2.85	3.61	3.79
3	*p*-Nitrobenzoic acid	3.89	1.96	3.06	3.68	3.94
4	*o*-Hydroxybenzoic acid	4.19	2.09	3.31	4.20	4.20
5	*m*-Hydroxybenzoic acid	4.38	2.14	3.38	4.29	4.35
6	*p*-Hydroxybenzoic acid	4.61	2.15	3.39	4.29	4.51
7	*m*-Chlorobenzoic acid	3.45	2.00	2.97	3.56	3.66

order as τ. The result also shows that the values of τ/η_1 and τ/η_{12} for *m*-nitrobenzoic acid, which has greater size, are greater than those for *m*-chlorobenzoic acid, as expected. However, the difference between the ratio τ/η_{12} for these two compounds is less than that between the ratio τ/η_1 for the same. This can be explained as being due to the great hindrance experienced by the carboxylic group in intramolecular rotation around its bond by the neighboring nitro-group. A similar argument can be given in the case of *o*-, *m*-, and *p*-hydroxybenzoic acids.

However according to the Debye theory, this ratio (τ/η_1) should remain constant for molecules of similar size. This anomaly can be explained if η_{12}, the mutual viscosity of the solute and solvent is used in place of the solvent viscosity (η_1). Because η_{12} also decreases from ortho via meta to para compounds, the ratio (τ/η_{12}) is almost constant. Mehrotra[15] has also obtained similar results in the case of some substituted benzaldehydes. However, the small difference between the values of η_{12} and η_1 suggests that the basic model of dielectric relaxation process does not suffer any major changes even when η_{12} is used instead of η_1.

4.3 Dielectric Relaxation Time. It can be observed from the Table 3 that the dielectric relaxation times of the three nitrobenzoic acids decrease from ortho via meta to para compounds. This can be explained based on steric hindrance offered by the $-NO_2$ group to the rotation of the –COOH group. The steric hindrance is maximum at the ortho position, and is least at the para position. Similar results were obtained earlier by one of the authors in the case of benzaldehydes. The smaller values of the relaxation time of hydroxybenzoic acids compared to nitrobenzoic acids can be explained based on the intra molecular rotation of the –OH group around its bond with a ring. The dielectric relaxation time (τ) of *m*-chlorobenzoic acid is less than that of *m*-nitrobenzoic acid, which is in accordance with the smaller size of the former molecule. The hydrogen-bonding association between the solute and solvent molecules would be present in the case of all benzoic acid, and would result in an additional hindrance of the rotational orientation.

It is concluded from an investigation of the relaxation time of these molecular species, that the process of the dipole orientation is contributed by both molecular as well as intra-molecular rotations. The experimental values of the dielectic relaxation time have been correlated with the calculated values obtained using the Debye equation, Perrin's modification to the Debye equation, Writz's equation, and Murty's equation. We have observed that the equations of Murty and Writz give better correlations between the calculated and experimental values of the dielectric relaxation time.

4.4 NMR Spin Lattice Relaxation Time. It can be observed from Table 4 that the relaxation rate ($T_1{}^{-1}$) of *o*-nitrobenzoic acid is larger than those of the meta and para isomers. This may be explained based on hydrogen bonding, which is maximum at the ortho-position and minimum at the para-position, resulting in an increase of the steric hindrance to the process of the dipole orientation from the para position to the ortho position. The explanation for *o*-hydroxybenzoic acid would be similar. It is evident from Table 4 that the values of the spin-lattice relaxation time, calculated using BPP equation, are smaller than the experimental values. Moniz et al. also agree with the view that the BPP treatment gives a much smaller value of (T_1). However according to them the discrepancy in the results is due to the time dependence of the rotational angular auto-correlation function of these molecules. They suggested that this time dependence is dominated by the dynamical coherence, rather than by frictional forces, as used in the BPP theory. When the equation of Writz and Sperinol is used, a better correlation is obtained. This is probably due to the introduction of a microfriction factor in the equation.

However, the values of T_1 calculated using Murty's equation are in close agreement with the experimental values. This is probably due to the polarizability of the molecules used to calculate the dielectric relaxation time (τ). This leads to the conclusion that the models of Writz and Murty are comparable in performance.

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References

1 W. B. Moniz, *J. Chem. Phys.*, **38**, 2418 (1963).

2 M. Poschi and H. G. Hertz, *J. Phys. Chem.*, **98**, 8195 (1994).

3 E. B. Feldman and A. K. Khitrin, *Phys. Solid State*, **37**, 1383 (1995).

4 A. Singh and N. K. Mehrotra, *Asian J. Phys.*, **12**, 13 (2003).

5 N. Bloembergen, B. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73**, 973 (1948).

6 P. Debye, *Polar Molecules (Chemical Catalogue)*, **1929**, 90.

7 K. Writz and A. Sperinol, *Z. Naturforsch.*, **8A**, 522 (1953).

8 F. Perrin, *J. Phys. Radium*, **5**, 497 (1934).

9 C. R. K. Murty, *Indian J. Phys.*, **32**, 580 (1958).

10 R. Kubo and K. Tomita, *J. Phys. Soc. Jpn.*, **9**, 888 (1954).

11 N. E. Hill, *Proc. Phys. Soc., London*, **67**, 149 (1954).

12 N. K. Mehrotra, T. C. Pant, and M. C. Saxena, *Bull. Chem. Soc. Jpn.*, **45**, 356 (1972).

13 N. K. Mehrotra and M. C. Saxena, *Indian J. Pure Appl. Phys.*, **11**, 438 (1966).

14 R. Freeman and H. D. W. Hill, *J. Chem. Phys.*, **54**, 3367 (1971).

15 N. K. Mehrotra, *Indian J. Phys.*, **45**, 83 (1971).

16 S. I. Ahmad, "Study of Dielectric Relaxation in Dilute Solutions of Organic Polar Molecules in Non Polar Solvents Using Microwave Techniques" Ph.D. Thesis, Lucknow University (1966).

17 N. K. Mehrotra, "Study of Dielectric Relaxation in Dilute Solutions of Organic Polar Molecules in Polar Solvents Using Microwave Techniques," Ph.D. Thesis, Lucknow University (1966).