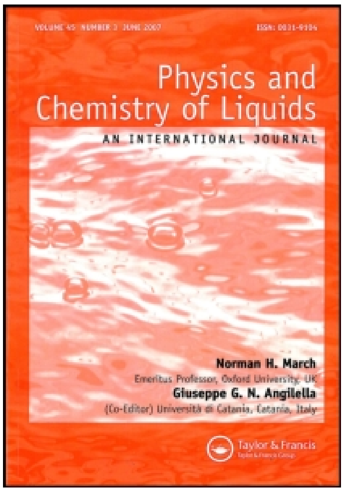

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Mutual viscosity and NMR spin-lattice relaxation time in some benzoic acids

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Experimental values of the NMR spin-lattice relaxation time (T_1) of *o*-aminobenzoic acid, *p*-aminobenzoic acid, *o*-chlorobenzoic acid, *p*-chlorobenzoic acid and 2,4-dinitrobenzoic acid and mutual viscosity (η_{12}) of *o*-chlorobenzoic acid, *m*-chlorobenzoic acid and *p*-chlorobenzoic acid have been reported. The experimental values of T_1 have been correlated with the calculated value of T_1 obtained using different equations of dielectric relaxation time (τ). It is concluded from this comparative study that Murty's equation is a better representation of the dielectric relaxation phenomenon. It is also concluded that the mutual viscosity (η_{12}) is a better substitute for the resistance to the rotation of the individual solute molecule.

Keywords: NMR spin-lattice relaxation time; Mutual viscosity; Dielectric relaxation time

1. Introduction

The dielectric investigation of relaxation and nuclear magnetic resonance studies of organic polar complexes having different dipole bearing groups provide useful information about the structure of the molecules. The dielectric relaxation time is very intimately connected with the molecular motion and intramolecular interaction in molecular species [1,2].

NMR spin-lattice relaxation time (T_1) has been used to investigate the rotational and translational motions and their relations to molecular structure, size, shape and intramolecular forces causing internal friction. The value of chemical shift of the proton depends on the various substituent groups at different positions and is affected when positions of the substituents are interchanged or one polar group is replaced by another. Therefore, the measurements of chemical shift, spin-lattice relaxation time (T_1) and dielectric relaxation time (τ) are of paramount importance for the study of molecular structure and intramolecular forces.

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Bloembergen *et al.* [3] have derived an expression for the magnetic relaxation in terms of the correlation time (τ_c), which is closely related to Debye's theory [4] of the dielectric dispersion in polar liquids, according to which the dielectric relaxation time is given by,

$$\tau = \frac{4\pi\eta_1 a^3}{KT} \tag{1}$$

where η_1 is the viscosity of solvent and a is the radius of solute molecule.

Many workers [5,6] have evaluated the nuclear spin-lattice relaxation time from Bloembergen, Purcell and Pound's (BPP) [3] theory and found that the calculated values of T_1 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 article.

2. Theory

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 to this mechanism to the overall T_1 is denoted by $(T_1)_{\text{rot}}$. 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 [3] have calculated the probability of the induced transition and thus obtained the expression

$$(T_1)^{-1} = (T_1)^{-1}_{\text{rot}} + (T_1)^{-1}_{\text{trans}} \tag{2}$$

where

$$(T_1)^{-1}_{\text{rot}} = \frac{3\gamma^4\hbar^2}{10r_0^6}\left[\frac{\tau_c}{1+w_0^2\tau_c^2} + \frac{2\tau_c}{1+4w_0^2\tau_c^2}\right]. \tag{3}$$

Here, γ is the gyromagnetic ratio, $\hbar = h/2\pi$, h is Planck's constant, r_0 is the sum of the interproton distances within the molecule, and w_0 is the resonance angular frequency.

Kubo and Tomita [7] modified equation (3) and obtained

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

The correlation time (τ_c) required in equation (4) is closely related to the dielectric relaxation time (τ), of Debye's theory of dielectric dispersion in a polar liquid as

$$\tau_c = \frac{\tau}{3}. \tag{5}$$

We calculated the correlation time using Debye's equation [4], Perrin's modification to Debye's equation [8], Writz and Sperinol's equation [9] and Murty's equation [10].

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 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

$$(T_1)^{-1}_{\mathrm{trans}} = \frac{9\pi^2\gamma^4\hbar^2\eta_2 N_0}{10KT} \tag{6}$$

where N_0 is the number of molecules per unit volume and η_2 is the viscosity of the compound.

The molar volume V_{m} of molecules was determined from equation

$$V_{\mathrm{m}} = \frac{M}{D}. \tag{7}$$

Debye's volume (V_{D}) has been calculated using Debye's equation and the experimental values of relaxation time (τ) given by equation (1) which yields

$$V_{\mathrm{D}} = \frac{\tau KT}{3\eta_1}. \tag{8}$$

The calculated values of ΔF_τ are nearly equal to ΔF_η. So we can assume approximately, $\Delta F_\tau = \Delta F_\eta$ in Eyring's equations [11]

$$\tau = \frac{A}{T}\exp\left(\frac{\Delta F_\tau}{RT}\right) \tag{9}$$

and

$$\eta_1 = B\exp\left(\frac{\Delta F_\eta}{RT}\right) \tag{10}$$

simplifying equations (9) and (10) we get

$$\frac{\tau}{\eta_1} = \frac{A}{BT}$$

where

$$B = \frac{hN}{V_x}.$$

Therefore

$$V_x = \frac{hNT\tau}{\eta_1 A}. \tag{11}$$

From equation (11) V_x has been calculated.

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's equation. This discrepancy can be explained if in the Debye's equation we use a mutual viscosity parameter (η_{12}) as proposed by Hill [12] 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 is given in our earlier paper [13].

3. Experimental

All the compounds used were of the pure quality LR grade and were obtained from M/s British Drug House, England. They were used after distillation. The solvent, deuterated benzene, was obtained from M/s British Drug House, England and was reported to be of the purest quality. It was distilled before use.

All the NMR experiments were performed on Bruker Avance DRX 200 MHz FT-NMR spectrometer, equipped with 5 mm multinuclear inverse probe head with Z-shielded gradient. For normal proton experiments typical experimental conditions are as follows.

Flip angle 90°, spectral width 4139.073 Hz; data size 32k; relaxation delay 5 s; number of transients 8. The FIDs were line broadended by 0.3 Hz prior to Fourier transformation. The sample concentration were kept in the range of 32–50 m molar.

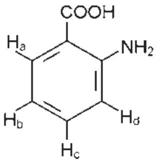
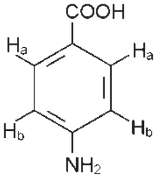
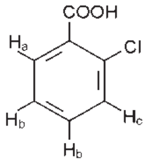
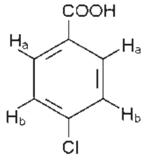
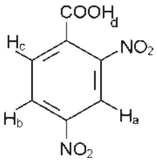
For T_1 experiments inversion recovery method (180–90°) of Becker *et al.* [14] was used in each system for evaluation of spin-lattice relaxation time. The time was chosen initially for 10 s which varied in a graduated manner in order to obtain correct phase modulation of the series of NMR spectrum in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

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 of 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 is seconds, S_K and S_F are specific gravities of the ball and the liquid respectively, and K is the ball constant (=0.009495).

4. Results

The chemical shift position and NMR spin-lattice relaxation time (T_1) of various protons of *o*-aminobenzoic acid, *p*-aminobenzoic acid, *o*-chlorobenzoic acid, *p*-chlorobenzoic acid and 2,4-dinitrobenzoic acid are given in table 1. The experimental and calculated values of dielectric relaxation time (τ) and statistical average of T_1 of these compounds at 300 K are given in tables 2 and 5 respectively. Molar volume, Debye's volume and Eyring's volume of these compounds are given in table 4. Table 3 shows the values of mutual viscosity (η_{12}) and the ratio (τ/η_1, τ/η_{12}) of *o*-chlorobenzoicacid, *m*-chlorobenzoic acid and *p*-chlorobenzoic acid.

Table 1. Chemical shift and NMR spin-lattice relaxation time (T_1) of various protons at 300 K.

Compound	Proton	Chemical (ppm)	NMR spin-lattice relaxation time T_1 (s)
1. *o*-Aminobenzoic acid 	H_a	8.18	2.90
	H_d	7.10	3.27
	H_b	6.58	2.60
	H_c	6.24	2.81
2. *p*-Aminobenzoic acid 	H_a	8.18	2.83
	H_b	6.16	2.41
3. *o*-Chlorobenzoic acid 	H_a	7.86	2.67
	H_c	7.14	4.68
	H_b	6.81	3.33
4. *p*-Chlorobenzoic acid 	H_a	7.87	1.76
	H_b	7.06	2.67
5. 3,4-Dinitrobenzoic acid 	H_a	4.06	1.23
	H_b	7.56	2.45
	H_c	8.37	3.68
	H_d	8.85	6.29

5. Discussion

5.1. *Chemical shift*

From table 1 it is observed that in the ^{1}H NMR spectrum of *o*-aminobenzoic acid H_a and H_d protons give doublet at 8.18 and 7.10 ppm respectively. H_b and H_c protons give multiplet due to orthocoupling of neighboring protons (H_a, H_c and H_b, H_d respectively). In *p*-aminobenzoic acid, H_a and H_b protons give doublet, the H_b proton resonates at a slightly higher field region due to domination of the –COOH group. In *o*-chlorobenzoic acid H_a and H_c protons give a doublet at 7.86 and 7.14 ppm respectively. H_b proton gives a multiplet at 6.81 ppm due to orthocoupling

Table 2. Values of dielectric relaxation time (τ) (in 10^{-12} s) at 300 K for compounds studied.

Polar compound	$\tau_{\text{Exp.}}$	τ_{Debye}	τ_{Perin}	τ_{Writz}	τ_{Murty}
o-Aminobenzoic acid	16.64[b]	89.19	32.11	10.11	16.07
p-Aminobenzoic acid	15.50[b]	72.21	25.99	12.20	15.23
o-Chlorobenzoic acid	12.60[a]	73.68	26.53	12.70	12.53
p-Chlorobenzoic acid	18.20[a]	76.68	27.49	13.32	17.50
3,4-Dinitrobenzoic acid	20.30[c]	136.57	49.16	22.73	21.29

[a]Ref. [15]; [b]Ref. [16]; [c]Ref. [17].

Table 3. Values of molar volume (V_m), Debye's volume (V_D) and volume (V_x) calculated from Eyring's equations.

Compound	$\tau \times 10^{12}$ (s)	$V_m \times 10^{24}$ (cc)	$V_D \times 10^{24}$ (cc)	$V_x \times 10^{24}$ (cc)
o-Aminobenzoic acid	16.64	122.73	58.88	69.96
p-Aminobenzoic acid	15.50	99.37	54.84	65.17
o-Chlorobenzoic acid	12.60	101.41	44.58	52.97
p-Chlorobenzoic acid	18.20	105.08	64.40	76.53
3,4-Dinitrobenzoic acid	20.30	126.03	71.83	85.36

of H_a and H_c protons. In *p*-chlorobenzoic acid H_a and H_b protons give doublet at 7.87 and 7.06 ppm respectively. In 2,4-dinitrobenzoic acid the H_b and H_c protons of the ring, which are orthocoupled to each other show resonance signals at 7.56 and 8.37 ppm respectively. The H_a proton, surrounded by two –NO_2 groups gives a singlet at 4.06 ppm.

5.2. *Dielectric relaxation time*

It is observed from table 2 that the relaxation time of *o*-chlorobenzoic acid is smaller than that of *p*-chlorobenzoic acid, although the size of the two molecules is the same. This can be attributed to the greater steric hindrance experienced by the latter molecule to the free rotation.

The relaxation time of *o*-aminobenzoic acid is smaller than that of *o*-chlorobenzoic acid. This is due to the intramolecular rotation of the –NH_2 group round its bond with the ring in the former molecule.

The experimental values of the dielectric relaxation time have been correlated with the calculated values obtained using Debye's equation, Perrrin's modification to Debye's equation, Writz's equation and Murty's equation. We have observed that the Murty's equation gives better correlation between the calculated and experimental values of the dielectric relaxation time.

5.3. *Volumes*

It is observed from table 3 that the molar volumes are nearly 2–3 times of the Debye's volume. This discrepancy can be explained by considering the ratio (V_D/V_m) which will be same as that of the microscopic to macroscopic viscosity. The volumes V_x calculated using the rate process equation of Eyring are found to be in better agreement with the values of molar volumes.

Table 4. Values of mutual viscosity (η_{12}) and the ratio τ/η_1, τ/η_{12}, for the investigated compounds. Viscosity of benzene at 300 K (η_1) = 0.593 cps.

Compounds	$\tau_{\text{Exp.}}$	$(\tau/\eta_1) \times 10^{10}$	η_{12} (cps)	$(\tau/\eta_{12}) \times 10^{10}$
o-Chlorobenzoic acid	12.6[a]	21.24	0.85	14.82
m-Chlorobenzoic acid	16.1[a]	27.11	1.06	15.10
p-Chlorobenzoic acid	18.2[a]	30.69	1.17	15.53

[a] Ref [15].

Table 5. Values of NMR spin-lattice relaxation time T_1 (in seconds) at 300 K.

Polar compound	$T_{1\text{Exp.}}$	$T_{1\text{Debye}}$	$T_{1\text{Perin}}$	$T_{1\text{Writz}}$	$T_{1\text{Murty}}$
o-Aminobenzoic acid	2.89	0.43	0.95	1.89	2.30
p-Aminobenzoic acid	2.62	0.18	1.31	1.53	2.02
o-Chlorobenzoic acid	3.50	0.29	1.83	2.54	3.13
p-Chlorobenzoic acid	2.21	0.20	1.01	1.75	2.12
2,4-Dinitrobenzoic acid	3.41	0.22	0.65	2.43	3.03

5.4. *Mutual viscosity*

It is observed from table 4 that the ratio (τ/η_1) increases in the order of the increase of the relaxation times of ortho-, meta- and para-chlorobenzoic acid. This is not in conformity with Debye's theory. But if the solvent viscosity (η_1) is replaced by (η_{12}) mutual viscosity of both solvent and solute, then the variation in the ratio (τ/η_{12}) becomes less marked. The results show that the mutual viscosities of the ortho-, meta- and para-compounds increase in the order of the increase of their relaxation times, which accounts for the different relaxation times for the ortho-, meta- and para-compounds. This leads to the conclusion that η_{12} is a better representation of the resistance to the rotation of the individual solute molecules.

5.5. *NMR spin-lattice relaxation time*

From table 5 it can be observed that the relaxation rate (T_1^{-1}) of *p*-aminobenzoic acid is smaller than that of the *o*-aminobenzoic acid. This may be explained on the basis of intra-molecular hydrogen bonding in later molecule. The values of NMR spin-lattice relaxation time, calculated using BPP equation, are smaller than the experimental values. Moniz *et al.* [18] also agree with the view that the BPP equation 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 model of Murty is comparable in performance.

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References

[1] K. Dutta, S.K. Sit, S. Acharya. *Parmana*, **57**, 5285 (2001).
[2] A.D. Vyas, V.A. Rana. *Indian J. Pure & Appl. Phys.*, **40**, 69 (2002).
[3] M. Bloembergen, E.M. Purcell, R.V. Pound. *Phys. Rev.(USA)*, **73**, 679 (1948).
[4] P. Debye. *Polar Molecules (Chemical Catalogue)*, 90 (1929).
[5] A. Singh, N.K. Mehrotra. *Asian J. Phys.*, **12**, 13 (2003).
[6] A. Singh, A.K. Singh, N.K. Mehrotra. *Bull. Chem. Soc. Jpn.*, **77**, 1 (2004).
[7] R. Kubo, K. Tomita. *J. Phys. Soc. Jpn.*, **9**, 888 (1954).
[8] F. Perrin. *J. Phys. Radium*, 5, 497 (1934).
[9] K. Writz, A. Sperinol. *Z. Naturforsch.*, **8A**, 522 (1953).
[10] C.R.K. Murty. *Indian J. Phys.*, **31**, 580 (1958).
[11] H. Eyring, S. Glasstone, K.J. Laider. The Theory of Rate Processes, p. 149, Mc Graw Hill Co. Inc, New York (1941).
[12] N.E. Hill. *Proc. Phys. Soc. London*, **67**, 149 (1954).
[13] N.K. Mehrota, T.C. Pant, M.C. Saxena. *Bull. Chem. Soc. Jpn.*, **45**, 356 (1972).
[14] E.D. Becker, J.A. Ferreti, R.K. Gupta, G.H. Waiss. *J. Magn. Reson.*, **37**, 381 (1980).
[15] S.I. Ahmad. PhD thesis, Lucknow University (1963).
[16] N.K. Mehrotra. *Indian J. Pure & Appl. Phys.*, **5**, 61 (1967).
[17] S.K.S. Somevanshi, S.B.L. Mishra. *Proc. Indian Acad. Sci. (Chem. Sci.)*, **89**, 43 (1980).
[18] W.B. Moniz, W.A. Steele, J.A. Dixon. *J. Chem. Phys.*, **38**, 2418 (1963).