

## NMR spin-lattice relaxation time and activation energy in some molecular systems

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The experimental values of NMR spin-lattice relaxation time ( $T_1$ ) of N-butylamine, di-isopropylamine, N, N, N-tributylamine, N, N- dimethylformamide, N, N- dimethylacetamide have been reported. The experimental values of  $T_1$  have been correlated with the calculated values of  $T_1$  obtained using various equations of the dielectric relaxation time ( $\tau$ ). It has been concluded that Murty's equation is a better representations of the dielectric relaxation phenomenon. The values of activation energy ( $\Delta E_A$ ) obtained using dielectric relaxation time have been correlated with calculated values obtained using Arrhenius equation of NMR spin-lattice relaxation time ( $T_1$ ) for these compounds.

**Keywords:** NMR, Spin-lattice relaxation time, Activation energy

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### 1 Introduction

The dielectric investigation of relaxation and nuclear magnetic resonance studies of organic polar complexes having different dipole bearing groups provides useful information about the structure of the molecules<sup>1</sup>. The dielectric relaxation time is very intimately connected with the molecular motion and intramolecular interaction in molecular species<sup>2,3</sup>.

NMR spin-lattice relaxation time ( $T_1$ ) has been used to investigate the rotational and transnational 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 ( $\tau$ ) are of paramount importance to study the molecular structure and intramolecular forces.

Bloembergen *et al*<sup>4</sup>. have derived an expression for the magnetic relaxation in terms of the correlation time ( $\tau_c$ ), which is closely related to Debye's theory<sup>5</sup> of the dielectric dispersion in polar liquids, according to which the dielectric relaxation time is given by:

$$\tau = \frac{4\pi\eta_1 a_1^3}{kT} \quad \dots (1)$$

where  $\eta_1$  is the viscosity of solvent and  $a_1$  is the radius of solute molecule.

Many researchers<sup>6-8</sup> have evaluated the spin-lattice relaxation time ( $T_1$ ) from Bloembergen, Purcell and Pound<sup>4</sup> (BPP) theory and found that the calculated values of  $T_1$  range from 1/2 to 1/10 times the experimental values. For narrowing the gap between the experimental and calculated values of  $T_1$ , we have used different models of dielectric relaxation.

Writz and Sperinol<sup>10</sup>, elaborating Perrin's<sup>9</sup> idea, modified the Debye equation to the form given by:

$$\tau = \frac{4\pi\eta_1 a_1^3}{kT} \left[ 6 \frac{a_1}{a_2} + \left( 1 + \frac{a_1}{a_2} \right)^{-3} \right]^{-1} \quad \dots (2)$$

where

$$a_i = \left[ 0.556 \left( \frac{M_i}{\pi d_i N} \right) \right]^{1/3} \quad i=1,2 \quad \dots (3)$$

where  $M_i$  are molecular weight and  $d_i$  are density of molecules and  $a_1$  and  $a_2$  are radius of solute and solvent molecules, respectively.

Murty<sup>11</sup> has found a simple empirical equation for  $\tau$  as :

$$\tau = \frac{6\pi\eta_1\alpha}{(\epsilon_1 + 2)kT} \quad \dots (4)$$

where  $\alpha$  is the polarizability of the solute molecule and  $\epsilon_1$  is the dielectric constant of the solvent.

## 2 Theory

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 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  $(T_1)_{\text{rot}}$ . If the relaxation occurs when the relaxing spin and the spin that induce relaxation are attached to different molecules, are denoted by  $(T_1)_{\text{trans}}$ . BPP<sup>4</sup> have calculated the probability of the induced transition and thus, obtained the expression.

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

where

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

where  $\gamma$  is the gyromagnetic ratio,  $\eta = \frac{h}{2\pi}$ ,  $h$  is Planck's constant,  $r_0$  the sum of the interproton distances within the molecule, and  $\omega_0$  is the resonance angular frequency.

Kubo and Tomita<sup>12</sup> modified Eq.( 6) and obtained :

$$(T_1)_{\text{rot}}^{-1} = \frac{3\gamma^4\eta^2}{2r_0^6} \tau_c \quad \dots (7)$$

The correlation time ( $\tau_c$ ) required in Eq. (7) is closely related to the dielectric relaxation time ( $\tau$ ), of Debye's theory of dielectric dispersion in a polar liquid as :

$$\tau_c = \frac{\tau}{3} \quad \dots (8)$$

We have calculated the correlation time using Debye's equation<sup>5</sup>, Perrin's modification to Debye's equation<sup>9</sup>, Writz and Sperinol equation<sup>10</sup> and Murty's

equation<sup>11</sup>. In order to test the validity of Eqs (5,9,10,11), different values of  $(T_1)_{\text{rot}}$  have been obtained using different values of  $\tau_c$ .

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

$$(T_1)_{\text{trans}}^{-1} = \frac{9\pi^2\gamma^4\eta^2\eta_2N_0}{10kT} \quad \dots (9)$$

where  $N_0$  is the number of molecules per unit volume and  $\eta_2$  is the viscosity of the compound.

The molar volume  $V_m$  of molecules was determined from equation:

$$V_m = \frac{M}{D} \quad \dots (10)$$

where  $M$  and  $D$  are molecular weight and density of molecules, respectively.

Debye's volume ( $V_D$ ) has been calculated using the Debye equation and the experimental values of relaxation time ( $\tau$ ):

$$\tau = \frac{4\pi\eta_1 a_1^3}{kT}$$

where  $\eta_1$  is the viscosity of the solvent molecule, which gives

$$V_D = \frac{\tau kT}{3\eta_1} \quad \dots (11)$$

The calculated values of free energy of activation for dielectric relaxation ( $\Delta F_\tau$ ) are nearly equal to free energy of activation for viscous process ( $\Delta F_\eta$ ). So we can assume approximately,  $\Delta F_\tau = \Delta F_\eta$  in Eyring's equations<sup>13</sup>.

$$\tau = \frac{A}{T} \exp\left(\frac{\Delta F_\tau}{RT}\right) \quad \dots (12)$$

and

$$\eta_1 = B \exp\left(\frac{\Delta F_\eta}{RT}\right) \quad \dots (13)$$

Simplifying Eqs (12) and (13), we get:

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

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

Therefore

$$V_x = \frac{hNT\tau}{\eta_1 A} \quad \dots (14)$$

From Eq.(14),  $V_x$  has been calculated. In order to collect information about the volumes taking part in dipole orientation, the molar volume  $V$ , the volume  $V_D$  calculated from the Debye's equation and the volume  $V_x$  which occurs in the expression of constant  $B$  in the equation of rate process have been calculated for some of the investigated compounds.

Dielectric relaxation mechanism can be explained in terms of absolute rate theory<sup>13</sup> by treating dipole orientation as a rate process in which the polar molecules rotate from one equilibrium position to another. This process of rotation requires an activation energy ( $\Delta E_A$ ) sufficient to overcome the potential barrier and separating the two mean equilibrium position and is given by

$$\tau = \frac{A}{T} \exp(\Delta E_A / RT) \quad \dots (15)$$

where  $A = \frac{h}{k}$  is frequency factor. The energy of activation ( $\Delta E_A$ ) is calculated from the slope of the plot of  $\log T\tau$  against  $(1/T)$ .

The activation energy ( $\Delta E_A$ ) has also been evaluated using Arrhenius theory of rate process. The correlation time ( $\tau_c$ ) for the molecular motion can be written in terms of activation energy ( $\Delta E_A$ ) which is given as :

$$\tau_c = \tau_0 \exp\left[\frac{\Delta E_A}{RT}\right] \quad \dots (16)$$

where  $\tau_0$  is frequency factor.

The NMR theory developed by BPP shows a relation between the spin-lattice relaxation time ( $T_1$ ) and correlation time ( $\tau_c$ ) as :

$$T_1 = C \tau_c \text{ for } \omega_0 \tau_c \ll 1 \quad \dots (17)$$

where  $C$  is a constant factor,  $\omega_0 = 2\pi\nu_0$  and  $\nu_0$  is the resonant frequency.

The energy of activation ( $\Delta E_A$ ) can be obtained from the temperature variation of  $\log T_1$  and is given by<sup>14</sup> :

$$\Delta E_A = 2.303R \left[ \frac{\partial \log T_1}{\partial (1/T)} \right] \quad \dots (18)$$

On substituting value of  $T_1$  using Eqs (4,5 and 7) in Eq. (18), we get:

$$\Delta E_A = \frac{2.303R}{T_1} \cdot \frac{3\pi\gamma^4\eta^2}{k} \left[ \frac{\alpha\eta_1}{(\epsilon_1 + 2)r_0^6} + \frac{\pi N_0 \eta_2}{5} \right] \quad \dots (19)$$

### 3 Experimental Details

All the compounds used are of the pure quality LR grade and have been obtained from M/s British Drug House, England. They have been used after distillation. The solvent; deuterated benzene has been obtained from M/s British Drug House; England and are reported to be of the purest quality. They have been distilled before use. All the NMR experiments were performed on Bruker Avance DRX 200 MHz FT-NMR spectrometer, equipped with 5mm multinuclear inverse probe head with Z-shielded gradient. For normal proton experiments typical experimental conditions are follows:

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

For  $T_1$  experiments inversion recovery method ( $180^\circ - \tau - 90^\circ$ ) of Becker *et al*<sup>15</sup> . was used in each system for evaluation of spin-lattice relaxation time. The time was chosen initially for 10s, which varied in 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.

Table 1—Dielectric relaxation time, NMR spin-lattice relaxation time and molecular volumes at 298 K

		N-butylamine	Di-isopropyl amine	NNN tributyl amine	NNdimethyl formamide	NNdimethyl acetamide
Dielectric relaxation time ( $\tau$ )( $10^{-12}$ sec)	Expt.	3.8 <sup>+</sup>	10.4 <sup>+</sup>	18.1 <sup>+</sup>	14.5 <sup>*</sup>	153
	Debye	58.8	92.1	147.7	56.2	67.6
	Perrin	21.1	33.1	53.2	20.2	24.3
	Writz	9.9	15.7	32.7	9.6	10.8
	Murty	4.9	11.2	17.4	13.3	14.4
Spin-lattice time ( $T_1$ )(sec)	Expt.	3.59	2.95	3.06	5.64	537
	Debye	0.63	0.41	0.26	0.14	0.12
	Perrin	1.73	0.96	0.87	3.19	2.23
	Writz	3.04	2.16	1.14	4.73	4.12
	Murty	3.60	2.89	2.08	5.63	5.33
Molecular volumes ( $10^{-24}$ cc)	Molar	122.73	99.37	101.41	105.08	126.03
	Debye	58.88	54.84	44.58	64.40	71.83
	Calculated ( $V_x$ )	69.96	65.17	52.97	76.53	85.36

+ Ref. 16, \* Ref. 17

Table 2—Values of activation energy for investigated compounds

Compounds	$\Delta E_A$ (lit)(Kcal/mol)	$\Delta E_A$ (kcal/mol) Author's work
N – butylamine	7.83 <sup>+</sup>	9.34
Di – isopropyl amine	10.32 <sup>+</sup>	11.87
N,N,N-tributylamine	11.69 <sup>+</sup>	12.45
N, N – dimethyl formamide	14.50 <sup>*</sup>	15.32
N, N – dimethyl acetamide	15.30 <sup>*</sup>	16.50

+ Ref 16, \* Ref 17

## 4 Results

The experimental and calculated values of NMR spin-lattice relaxation time ( $T_1$ ) and dielectric relaxation time ( $\tau$ ) of N-butylamine, Di-isopropylamine, N,N,N- tributylamine, N,N - dimethylformamide, N,N - dimethylacetamide are given in Table 1 at 298K. Molar volume, Debye Volume and Eyring's volume of these compounds are given in Table 3. Table 4 presents the values of activation energy of these compounds.

## 5 Discussion

### 5.1 Dielectric relaxation time

From Table 1, it is clear that dielectric relaxation time of amines increases from N-butylamine to N,N,N-tributylamine via Di-isopropylamine. This can be explained on the basis of greater hindrance experienced by the secondary amine molecule as compared to primary amine molecule. This interaction is still greater in the case of a tertiary amine molecule as it contains three interacting alkyl groups resulting in the highest relaxation time of the molecule.

The dielectric relaxation time of N, N-dimethylacetamide is greater than dimethylformamide which is in conformity with Debye theory as former molecule has greater size than the later. The values of  $\tau$  calculated using Debye equation are found to be much greater than the experimental values. When Perrin's modification is used, a better correlation has been obtained. The calculated values of  $\tau$  using Writz and Sperinol equation are more nearer to observed values of  $\tau$ . The values of  $\tau$  calculated using Murty's equation are found to be in quantitative agreement with the experimental values. It is, therefore, concluded that Murty equation is a better representation to the process of dipole orientation.

### 5.2 NMR spin-lattice relaxation time

The values of NMR spin-lattice relaxation time, calculated using BPP equation are smaller than the experimental values (Table1). The discrepancy in the theoretical and experimental values of the spin-lattice relaxation time ( $T_1$ ) is due to Debye's value of  $\tau$  used in the BPP equation, which is valid only for the spherical molecules. The main source of the shortcoming of BPP formula lies in the evaluation of the rotational contribution to the spin-lattice of the relaxation time, which is much smaller than the experimental relaxation time. Moniz<sup>8</sup> also agree with the view that the BPP treatment gives much smaller value of  $T_1$ . However, according to them the discrepancy in the results is due to 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 can be explained due to the polarizability of the molecules used to calculate the dielectric relaxation time ( $\tau$ ).

### 5.3 Volumes

The molar volumes are nearly 2-3 times of the Debye volume (Table 1). The discrepancy between the two values of the volumes may be due to the fact that the molar volumes are different from the volumes for dipole orientation. 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. However, the volumes  $V_x$  calculated using the rate process equations of Eyring are found to be in better agreement with the values of molar volumes.

### 5.4 Activation energy

From Table 2, it is clear that the values of activation energy obtained using NMR spin-lattice relaxation time are found to be in good agreement with the values obtained using absolute rate theory. This shows that Murty's equation for dielectric relaxation time is the appropriate substitute for correlation time  $\tau_c$  in BPP equation for NMR spin-lattice relaxation time.

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