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Research Article

Correlation Of NMR Spin-Lattice Relaxation and Dielectric Relaxation Times of Binary and Tertiary Mixtures of Alcohols

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ABSTRACT

Experimental measurements of NMR spin-lattice relaxation time T_1 of binary mixtures of Methanol and Propanol with ratios 1:1, 1:2, 2:1 and 1:3 and tertiary mixtures of Methanol, Propanol and Butanol with ratios 1:1:1, 1:1:2, 1:2:1 and 2:1:1 have been reported. The experimental values of the NMR spin-lattice relaxation times have been correlated with the calculated values of the T_1 obtained using various equations for calculating dielectric relaxation time(τ). For calculation of NMR spin-lattice relaxation time, the absolute viscosity of binary and tertiary mixtures of alcohols have been obtained by using an Ostwald Viscometer and correlation time τ_c has also been reported by using the Debye theory of polar liquids.

Keywords- spin-lattice relaxation time, dielectric relaxation time, Viscosity, correlation time.

Introduction-

The NMR spin-lattice relaxation and dielectric relaxation studies of organic polar molecules having large dipole bearing groups put useful information about the structure of the molecules. Dielectric relaxation time is connected with molecular motion and intermolecular interaction in the molecular system and NMR spin-lattice relaxation time T_1 have been used to investigation the translational and rotational motions [1]. The measurement of mutual viscosity, spin-lattice relaxation time and dielectric relaxation time are very important to study of molecular structure and intramolecular forces. Many researchers [2-11] have worked, on the dielectric relaxation of polar molecules (alcohols) in non-polar solvents. S K vaish et.al [12-13] studied NMR spin lattice relaxation and correlation time for some methyl benzenes using Bloembergen [14] expression, which is closely related to Debye theory [15] of dielectric dispersion in polar liquids as $\tau_c = \tau/3$. In present studies dielectric constant (ε') and dielectric loss factor (ε") were reported with the help of Robert and Von Hippel method [16] and dielectric relaxation time have been calculated by Gopala Krishna's method [17]. The viscosities of the molecular system have been calculated by using an Ostwald Viscometer. With the help of BPP theory [14], relaxation times i.e. rotational and translational have been calculated and compared with experimental values of relaxation time for the mixtures of alcohols.

Theory

The local magnetic field is fluctuated due to neighboring spins. If the spin which induces relaxation is related to the molecule as relaxing spin, the fluctuating field is produced by molecular re-orientational motion. The overall relaxation time known as rotational relaxation time $(T_1)_{Rot}$ and if the spin which induces relaxation and relaxing spin are attached to different molecules, overall relaxation time known as translational relaxation time $(T_1)_{Trans}$. According to BPP theory spin-lattice relaxation time T_1 is expressed by the equation

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

Where modified form

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

$$\& \quad \frac{1}{(T_1)_{trans}} = \frac{2\pi^2\gamma^4\eta N}{10kT} \quad \ldots. \quad 3.$$

The authers have calculated dielectric relaxation time using Robert and Von Hippel method and Gopala-Krishana's method . Hence dielectric constant and dielectric loss tangent calculated by using equations as

$$\varepsilon' = \frac{\left(\frac{a}{\pi}\right)^2\left(\frac{X}{l_\varepsilon}\right)^2+1}{\left(\frac{2a}{\lambda_g}\right)+1} \quad \ldots. \quad 4.$$

$$\text{Tan } \varphi = \frac{(d_1-d_2)}{\varepsilon' l_\varepsilon}\left(\frac{\lambda_0}{\lambda_g}\right)^2 \quad \ldots. \quad 5.$$

Where a-Width of wave guide, λ_g – Guide wave length of a standing wave in the empty wave guide, λ_0 – free space wave-length, l_ε - length of the specimen, d_1 – distance between 3db points empty dielectric cell, d_2 – distance between 3db points with specimen.
Dielectric loss factor ε'' is determined as

$$\varepsilon'' = \varepsilon' \tan\varphi \quad \ldots. \quad 6.$$

dielectric relaxation times are calculated using the fixed frequency method of Gopala-Krishana for dilute solution of binary and tertiary mixture of alcohols using as non-polar solvents as

$$\tau = \frac{\lambda}{2\pi c}\left(\frac{dy}{dx}\right) \quad \ldots. \quad 7.$$

Where x & y defined as

$$X = \frac{\varepsilon'^2+\varepsilon''^2+\varepsilon'-2}{[(\varepsilon'+2)^2+\varepsilon''^2]} \;\&$$

$$Y = \frac{3\varepsilon''}{[(\varepsilon'+2)^2+\varepsilon''^2]}$$

And λ is free space wave-length and c is velocity of EM wave.
Viscosity of the samples calculated by an Ostwald Viscometer using the formula as

$$\eta_1 = \eta_2 \frac{d_1}{d_2}\frac{t_1}{t_2} \quad \ldots. \quad 8.$$

η_1- viscosity of sample, η_2- viscosity of pure water, d_1 & d_2 are the densities of sample and water respectively and t_1 & t_2 flow time of samples and water respectively.

Experimental details-

NMR spin-lattice relaxations have been observed experimentally by NMR Spectroscopy. For this inversion recovery method [18](180^o-τ-90^o pulse sequence) have been used. The 180^o pulse inverse the spin population and rotates the equilibrium magnetization on to z-axis. Following this pulse, the magnetization relaxes back towards its equilibrium value by an exponential process with a rate constant T_1. After time τ the sample is subjected to a 90^o pulse which rotes the residual longitudinal magnetization on to the y-axis. As a result we find the spectrums. These spectrums are the snapshots of the spin system τ seconds after the spin population have been inverted. The experiments were performed in automation mode using standard pulse programmed from the Bruker pulse programme [18]. For dielectric relaxation time microwave absorption technique has been used.

Experimental values of dielectric relaxation time, spin-lattice relaxation time and viscosity of binary mixtures of Methanol & Propanol

Ratios	Dielectric relaxation time τ(ps)	Experimental Spin-lattice relaxation time T_1 (s)	Theoretical Spin-lattice relaxation Time T_1 (s)	Viscosity η(Centipoise)
1:1	15.1	5.24	6.02	1.1782
1:2	21.3	4.79	5.41	1.0279
1:3	28.3	4.98	5.96	1.1403
2:1	26.3	4.81	5.43	1.0293

Table-1

Experimental values of Dielectric relaxation time (τ) and spin-lattice relaxation time (T_1) and viscosity (η) of tertiary mixture of Methanol, Propanol and Butanol

Ratios	Dielectric relaxation time τ (ps)	Experimental Spin-lattice relaxation time T_1(s)	Theoretical spin-lattice relaxation time T_1(s)	Viscosity η (centipoise)
1:1:1	35.4	5.15	5.75	1.1617
1:1:2	11.5	4.91	5.32	1.3325
1:2:1	6	4.81	5.54	1.2807
2:1:1	11.8	4.96	5.30	1.0489

Table-2

Result and discussion-

Table-1 represents the experimental value of dielectric relaxation time and experimental & theoretical value of spin-lattice relaxation time as a function of viscosity in binary mixture of Methanol and Propanol at different concentrations. Table-2 shows the experimental value of τ and experimental & theoretical values of T_1 as a function of viscosity in tertiary mixture of Methanol, Propanol and Butanol in different concentrations. It is observed that as the one of propanol increases, dielectric relaxation time goes on increasing but the spin-lattice relaxation time first decreases then increases which is in according with the Debye theory of polar molecules, which says that the molecular motion play an important role in the determination of dielectric relaxation time as the molecular size increases, dielectric relaxation time also increases. While the spin-lattice relaxation time changes in according with the viscosity of the mixture. In tertiary mixtures of Methanol, Propanol and Butanol we observe a high dielectric relaxation time when all the three are taken in equal concentration. The spin-lattice relaxation time value is also very high, when the concentration of Butanol is doubled the DRT & SLRT both decrease. Similar trend is obtained when concentration of Propanol is doubled keeping other two in equal ratio. As the concentration of Methanol is doubled keeping Propanol and Butanol in equal ratio of 1:1, there is an increase in the values of DRT & SLRT. Since the viscosity decreases in tertiary mixture of Methanol, Propanol and Butanol from concentration ratio 1:1:2 to 2:1:1 , the DRT Changes from 11.5 ps to 11.8 ps while SLRT changes fron 4.91s to 4.96s which shows that the intramolecular interaction increases.

Conclusion-

From above results it is concluded that in binary mixtures as concentration of large molecule is increased, the DRT increases while SLRT decreases which is in accordance with BPP Theory. When Butanol is added to this mixture, intramolecular interactions play a dominant role in molecular rotation rather then intramolecular interactions. The theoretical value of SLRT obtained by using the correlation time τ_c using experimental values of τ are in accordance with the experimental values of SLRT.

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