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Research Paper

To investigate Dielectric Relaxation Time by Absorption of Microwave and NMR Spin Lattice Relaxation Time for Mixtures of Aldehydes and Ketones

PHYSICS

KEYWORDS : Dielectric relaxation time, NMR Spin Lattice Relaxation Time, resonance

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ABSTRACT

The molecular rotations and group orientations studied by Dielectric relaxation times (τ) through Microwave Absorption Technique and NMR Spin Lattice Relaxation Times (T1) values through inversion recovery method 180°-τ-90° pulse sequence are investigated of dilute solutions of mixtures. Mixtures are carried three Hetero- atomic Aldehydes (-CHO) and Ketones (-CO-) polar solutes namely Formaldehyde (HCHO), Benzaldehyde (C6H5CHO) & Acetone (CH3COCH3) at various concentration ratios [1:2:3, 2:3:1 and 3:1:2] and studied at ascending temperatures [35°, 40° and 45°C] in non- polar solvent of Benzene. The quantitative information such as steric hindrance, Dielectric relaxation times and nmr Spin Lattice Relaxation Times explored the characters of molecular motions in the non polar liquid. On the basis of the experimental observations it is noticed that the variation in the Dielectric relaxation times (τ) and NMR Spin Lattice Relaxation Times (T1) values are associated with the contribution amount of Benzaldehyde solute in the mixtures.

1 Introduction

The dielectric relaxation studies of individual or the binary mixtures of polar molecules in non-polar solvents have been attempted by many researchers [1-9]. Author obtained the experimental values of Dielectric relaxation times (DRT) and NMR Spin Lattice Relaxation Times (SLRT) (T_1) for mixtures of three organic polar solutes at a time. The DRT (τ) is a parameter which depends upon the mechanisms of energy hindrance in dielectric medium. Also it used to investigate the molecular and intramolecular motions and their relations to molecular structures, such as steric hindrance, resonance of π-electrons & the hydrogen bonding which are the cause of potential barriers to such rotations and internal friction. It also provided an idea about conductive or inductive nature of the specimen material response with E-M waves. In the presented research Standard Microwave Standing Wave Technique & single frequency (9.567GHz) with concentration variation method of Gopala Krishna [10] used for the measurement of dielectric constant ε' and loss factor ε″ of dilute solution. The DRT (τ) depends upon the presence of different polar groups at various positions in the molecule and upon the capability of polar group to rotate independently of the rest molecule [11-13,28].

Nuclear Magnetic Resonance (NMR) spectroscopy is the most important physical tool for the characterization of organic solutions and disclosure of molecular structure and stereochemistry. NMR depends upon the presence of different polar groups at various positions in the molecule & it is sharply affected when one polar group is replaced by the other or the position of the group is changed with respect to other. The analysis of the NMR spin lattice relaxation behavior provides instantly recognizable proof of the molecular rotation, group orientations and phase transitions in the sample molecule. Fourier Transformation NMR Spectrometer, Model- (AVANCE 500) [Make: Ultrashield Bruker Bio Spin International AG, Switzerland.] instrument is used. The Structural revelation of Small Organic Molecules studied by 1D, 2D and Multi Dimensional-Solution NMR Spectroscopy [14-15]. Simple aqueous solutions investigate by a range of techniques including neutron diffraction [16], NMR [17,18], Raman spectroscopy [19,20], infrared spectroscopy [21,22], dielectric spectroscopy [23], and mass spectrometry [24], as well as numerical and computational studies.

2 MATERIAL & METHODS

Benzene, Aldehydes and Ketones (A R Grade) from Sisco Research Laboratories, Mumbai (India) were reported to be a high standard of purity about 99%. The method of Robert and Von Hippel used to measure the dielectric constant (ε') and the loss factor (ε") [12].

The microwave is propagating through the rectangular waveguide then the dielectric constant and the loss tangent can be calculated from the relations:

$$\varepsilon' = \left[(a/\pi)^2 (X/l_\varepsilon)^2 + 1\right] / \left[(2a/\lambda_g)^2 + 1\right] \quad \ldots (1)$$

and $$\tan\delta = \left[(d_1 - d_2)/\varepsilon' l_\varepsilon\right](\lambda_0/\lambda_e)^2 \quad \ldots (2)$$

where a - width of wave guide, λ_g - Guide wave length of standing wave in the empty waveguide,

λ_0 - free space wave length, lε – length of specimen, d_1 – distance between 3db points empty dielectric cell and d_2 - distance between 3db points with specimen.

The value of dielectric loss factor ε″ can be determine as:

$$\varepsilon'' = \varepsilon' \tan\delta \quad \ldots (3)$$

The DRTs are determined using the fixed frequency method of Gopala Krishna for the dilute solutions of polar molecules in non-polar solvents as followings:

$$\tau = (\lambda/2\pi C)(dy/dx) \quad \ldots (4)$$

In equation (4), factors X and Y are:

$$x = \left(\varepsilon'^2 + \varepsilon''^2 + \varepsilon' - 2\right) / \left[(\varepsilon' + 2)^2 + \varepsilon''^2\right]$$

&

$$y = 3\varepsilon'' / \left[(\varepsilon' + 2)^2 + \varepsilon''^2\right]$$

Where λ is free space wavelength, C is the velocity of electromagnetic waves and ε′ & ε″ are dielectric constant and loss factor respectively.

The slope of line drawn between X and Y was used to resolve the value of dy/dx and then relaxation time τ (see eqn. 4).

NMR SLRT (T_1) results of the mixtures are established from NMR spectrometer. The inversion recovery method [25] (180°-τ-90° pulse sequence) is used. The 180° pulse inverse the spin population and rotates the equilibrium magnetization on to z- axis. Following this pulse the magnetisation relaxes back towards its equilibrium value by an exponential process with a rate constant T_1. After some time τ, the sample is subjected to a 90° pulse which rotates the residual longitudinal magnetisation on to the Y′ axis. A free induction decay result which is transformed to produce spectrum. This spectrum is a snapshot of the spin system τ seconds after the spin population has been inverted. The experiments were performed in automation mode using standard pulse programme from the Bruker Pulse programme [25].

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Benzene used as a non- polar solvent in Standing Microwave Absorption Techniques. Three solutes got from aldehydes & ketones functional groups as Benzaldehyde, Acetone and Butanone and mixed together to obtained three mixtures of different conc. ratios at 1:2:3, 2:3:1 and 3:1:2. Here ratio 1:2:3 stands for Benzaldehyde is 17%, Acetone is 33% and Butanone is 50% in non-polar solvent.

The complete experiment repeated with carried another combination of three aldehyde and ketone solutes i.e Formaldehyde, Benzaldehyde and Acetone so as to ensure the more understandable results.

3 RESULT AND DISCUSSION

3.1 Analysis under Microwave Absorption Technique- Values ε′ and ε″ required to obtain the factors X and Y as per equations. The slope of the line drawn by the values of factors X and Y are essential to calculate the DRT (τ) were obtained from 2-D graphs. Here TABLES- 1 & 2 accounted the computed values of relaxation times (τ) for the mixtures of Aldehydes and Ketones at different conc. ratios and ascending temperatures.

According to the experimental values of DRTs (τ) from Table-1 & 2, it is observed that the values of relaxation time τ are decreased gradually with increase in temperature. Due to the decreasing viscosity of the mixtures i.e. viscosity is decreased with increase in temperature and the increased thermal agitation at higher temperature, would increase the energy loss, and got the large number of collisions among the molecules and hence the time taken to reach from activated state to the normal state is decreased [30,33]. The study of DRT values (From tables 1- 2), it is found that the variation in the values of relaxation time, are accordance with the contribution amount of solute- Benzaldehyde in the mixtures. It is observed that Benzaldehyde has larger molecular size and molecular weight. Thus the molecules of Benzaldehyde experienced more rotational friction than other molecules of solutes in the same solvent environment. In Table 1&2, the value of relaxation time τ has maximum (i.e. 11.066 x 10^{-12} Sec) for the mixture (2:3:1) in which Formaldehyde (HCHO) is 33%, Benzaldehyde (C_6H_5CHO) is 50%, and Acetone (CH_3C-OCH_3) is 17% in solvent. And the values of relaxation times τ of other mixtures varied in accordance with the conc. of effective molecules of solute Benzaldehyde. It is noticed that Benzaldehyde has maximum number of carbon atoms, maximum molecular weight, B. P. and density in compare to formaldehyde and Acetone. According to Debye's equation [26,27], this is fact that the molecules having large size show large relaxation time. CHO group of Benzaldehyde (C_6H_5CHO) may also constitute an additional mode of orientation, i.e. the intramolecular rotation of polar group round its bond with benzene ring, increase the hindrance of molecule [29]. It is seen that the effect of Formaldehyde and Acetone on the values of relaxation time τ are not sufficiently remarkable, because of there smaller molecular size and weight. It is also observed that for all experimental solutions the minima (in VSWR meter of experiment) is shifted towards liquid cell w.r.t. reference minima. Thus all solutions had conductive nature with relative to E-M waves.

3.2 Analysis under NMR spin lattice relaxation time- The analysis of the NMR spin lattice relaxation behavior provides instantly recognizable proof values of the molecular rotation, group orientations, relaxation times and phase transitions in the sample molecules [31,32]. As most of the theories of dielectric relaxation phenomenon are either empirical or semi –empirical, hence to test validity of these theories, author has therefore undertaken investigation of the experimental values of DRTs of several organic polar complexes and correlate it with the SLRTs (T_1) obtained from NMR spectroscopy.

NMR studied for one Hetero- atomic functional group of aldehydes & ketones out of organic functional groups. We accepted three aldehydes- ketones as Benzaldehyde, Acetone and Butanone, are mixed together to obtained three mixtures of conc. ratios as 1:2:3, 2:3:1 and 3:1:2. Here the ratio 1:2:3 stands for Benzaldehyde is 17%, Acetone is 33% and Butanone is 50% in non-polar solvent. The deutreated Chloroform ($CDCl_3$) has been used as non-polar solvent under NMR investigations.

To explore NMR SLRT of the dilute mixtures of conc. ratios (1:2:3), (2:3:1) & (3:1:2), Fig.-1(a, b & c) represented the NMR spectral peaks vs. chemical shift positions. Computer programmers are installed in the instrument of NMR System, which directly provide NMR spectrums, related contour plot graphs and NMR SLRT T_1 values of the specimen.

The spectrum of mixture is complex in signals having nine to ten peaks at various chemical shifts as shown. After the suspicious study of the chemical shift positions, intensity of the complex spectrums and compare with the individual nmr spectrum of three solutes (Benzaldehyde, Acetone and butanone) [14,15]. Then the observed signals could be explained and correlate with other nmr spectrums of samples. It is became aware of the range of chemical shifts from δ 7.349 ppm to δ 10.024 ppm signals in the nmr spectrums of mixtures, are represented due to present of the protons of Benzaldehyde. The signals of range from chemical shift δ 1.028 ppm to δ 2.172 ppm showed due to the protons of Butanone while the signals of Acetone solute are always obtained about chemical shift δ 2.424 ppm to δ 2.484 ppm in the NMR spectrums of all three mixtures.

Table-3 contained the experimental values of NMR SLRTs T_1 (i.e. the statistical average all T_1 values of peaks for each specimen) and DRT (τ) values (by Microwave Absorption Technique) of substituted Benzaldehyde, Acetone, Butanone and their three mixtures. The conc. amount of solutes in mixtures and their NMR relaxation times provide adequate information to correlate each other. It is originated that the mixture of conc. ratio (3:1:2) showed larger NMR T_1 of 8.501 secs. The T_1 value of mixtures of conc. ratio (1:2:3) showed short time 5.945 secs to relax till equilibrium. While the mixture of ratio (2:3:1) relaxed within intermediate relaxation time of 7.852 secs. Thus NMR T_1 values of mixtures are varied in accordance with the conc. amount of Benzaldehyde solute in the mixtures.

The DRT (τ) of mixture of conc. ratio (3:1:2) showed maximum value of 21.492 psecs (See Table-3), where the conc. amount of Benzaldehyde is 50% mixed. While the DRT (τ) of mixture of conc. ratio (1:2:3) is relaxed quicker in time 5.360 psecs. Mixture of conc. ratio (2:3:1) showed an intermediate time 9.229 psecs. Hence conc. ratios of solutes of mixtures and correlation of DRTs & nmr SLRTs results, it came to know that the relaxation times of mixtures are varied according to the conc. amount of Benzaldehyde in the mixtures. Similar results may be very constructive for investigations under Forensic Sciences and further scientific research.

4 Conclusions

The present study that the variation of DRTs (τ) and nmr SLRTs (T_1) values of these the mixtures of aldehydes and ketones at conc. ratios (1:2:3), (2:3:1) and (3:1:2) in agreement that the contribution amount of Benzaldehyde is most effective solute to responsible in the relaxation times of the mixtures as per its structural characteristics of molecule in compare to other solutes. NMR results are also verified the used equations and relaxation time results of "Microwave Absorption Method". It has been found that Debye relations of DRT and viscosity of the medium holds good. On the basis of minima shift (Microwave Bench Apparatus), all the experimental used solutions had conductive nature relevant to E-M waves. Since dielectric relaxation techniques for the study of molecular behaviour and structure

are applicable only to the polar molecules, while another technique, namely NMR, is applicable to polar as well as non-polar solutions.

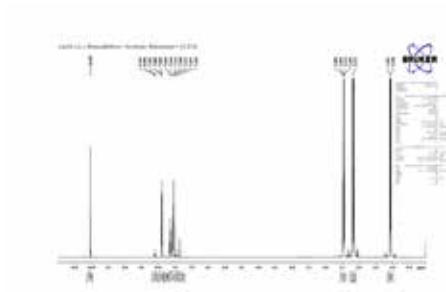

Figure-1 (a) NMR Spectra of Mixture at conc. ratio (1:2:3)

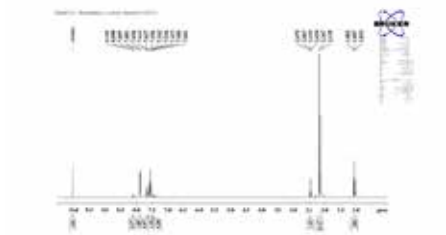

Figure-1 (b) NMR Spectra of Mixture at conc. ratio (2:3:1)

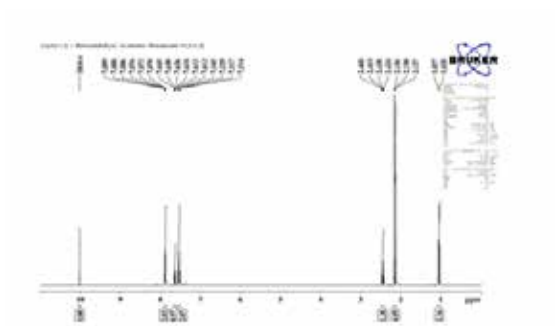

Figure-1 (c) NMR Spectra of Mixture at conc. ratio (3:1:2)

Table-1 Relaxation Times for Mixtures of (Benzaldehyde: Acetone: 2-Butanone)

Temp. T°C	Relaxation Times (τ) x 10^{-12} sec. (±0.5%)		
	(1 : 2 : 3)#	(2 : 3 : 1)	(3 : 1 : 2)
35°C	5.360	9.229	21.492
40°C	3.685	7.470	18.841
45°C	2.227	4.248	15.015

#[The conc. ratio (1:2:3) means (16.66% of Benzaldehyde + 33.33% of Acetone + 50% of Butanone) and so on]

Table-2 Relaxation Times for Mixtures of (Formaldehyde: Benzaldehyde: Acetone)

Temp. T°C	Relaxation Times (τ) x 10^{-12} sec. (±0.5%)		
	(1 : 2 : 3)	(2 : 3 : 1)	(3 : 1 : 2)
35°C	7.566	11.066	4.013
40°C	6.130	7.897	3.685
45°C	5.583	6.732	3.335

Table-3 Dielectric relaxation time (τ) and H-NMR Spin Lattice Relaxation Times (T_1) at 298°K (±0.1%)

S. No.	Solution	(τ) 10^{-12} sec.	(T_1) sec.
1.	Benzaldehyde	10.2	3.524
2.	Acetone	11.08	2.601
3.	Butanone	9.11	4.927
4.	Mixture (1:2:3)*	5.360	5.945
5.	Mixture (2:3:1)	9.229	7.852
6.	Mixture (3:1:2)	21.492	8.501

*[The conc. ratio (1:2:3) shows (16.66% of Benzaldehyde + 33.33% of Acetone + 50% of Butanone) and so on]

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