Dielectric Dispersion Studies of Some Intramolecular Hydrogen Bonded Molecules at Microwave Frequencies

H. D. Purohit, S. Kumar, and A. D. Vyas

Microwave Laboratory, Department of Physics, University of Jodhpur, Jodhpur, India

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The permittivity and dielectric loss of acetyl acetone, benzoyl acetone and dibenzoyl methane have been measured at four microwave frequencies viz., 30.20, 24.50, 18.26, and 9.83 GHz and also at 1 MHz and optical frequency at 35 °C. The permittivity and dielectric loss at different frequencies have been plotted against concentration (wt. fraction). The slopes of these straight lines have been used for the complex plane plots (a'' vs. a'). The complex plane plots for these compounds are Cole-Cole arcs. The dielectric relaxation time (τ_0) and distribution parameter (α) have been calculated from these plots. Data have been analysed in terms of two relaxation processes i. e., corresponding to overall rotation and group rotation. The dipole moments of these molecules are reported.

Infrared and NMR studies are powerful tools of studying intramolecular hydrogen bonding. Intramolecular hydrogen bonding has a marked effect on infrared O–H absorption frequencies, these frequencies being lowered by several wave numbers. NMR spectrascopy offers an advantage for the study of H-bonding because the infrared bands sometimes overlap with C–H bands. The dielectric dispersion studies can also be profitably used to study intramolecular motions, complex formation and extent of hydrogen bonding. These studies can be carried out in dilute solutions as intramolecular hydrogen bonding is practically unaffected by dilution. Such studies have been carried out earlier by Meakins[1] in substituted quinols and Magee et al.[2] in substituted phenols. The dielectric dispersion studies in solution containing a specified mole fraction of a powerful electron donor molecule can be used to study complex formation and the extent of hydrogen bonding which may lead to a classification of intramolecular hydrogen bonding, viz., weak, medium and strong. β-diketones form an intramolecular hydrogen bond and have been found to exist predominantly in enolic form in dilute solutions of nonpolar solvents. In the present investigation dielectric dispersion studies of three β-diketones namely acetyl acetone, benzoyl acetone and dibenzoyl methane have been carried out at different microwave frequencies in benzene with a view to study molecular and intramolecular rotations and their contribution to the average relaxation time. The dipole moment of acetyl acetone has been reported earlier[3] but no systematic dielectric dispersion studies of these molecules have been done so far. The dipole moments of benzoyl acetone and dibenzoyl methane have been determined and reported for the first time. These studies further include the calculation of the molar polarization of these solutes in benzene for different concentrations.

Method of Measurement and Analysis of Data

The permittivity ε' and dielectric loss ε'' at the microwave frequencies 9.83, 18.26, 24.50, and 30.20 GHz were determined by measurements of the wavelength and the standing wave ratio using a short circuited movable plunger applying the method suggested by Heston et al.[4] adapted for short circuited termination. The heterodyne beat method was used for the determination of static permittivity ε_0. ε_∞ was taken as the square of the refractive index which was measured by Abbe's refractometer. The density was found out by using a pycnometer. All measurements were made at 35 °C and the temperature was controlled within ±0.5 °C by a thermostat.

Benzoyl acetone and dibenzoyl methane (Purum grade) were obtained from Messrs Fluka, A.G. (Switzerland) while acetyl acetone G.R. was procured from E. Merck, Germany. These compounds were used without further purification. Benzene Analar (B.D.H., India) was distilled twice over sodium and used as solvent.

It has been observed that the permittivity and dielectric loss in dilute solution are linear functions of concentration. Thus one can represent the per-

Reprint requests to Dr. H. D. Purohit, Department of Physics the University of Jodhpur, *Jodhpur/India.*

mittivity and dielectric loss by the following equations[5]

$$\mathcal{E}_0 = \mathcal{E}_{10} + a_0 W_2 , \quad (1)$$

$$\mathcal{E}' = \mathcal{E}_1' + a' W_2 , \quad (2)$$

$$\mathcal{E}'' = a'' W_2 , \quad (3)$$

$$\mathcal{E}_\infty = \mathcal{E}_{1\infty} + a_\infty W_2 \quad (4)$$

where subscript 1 refers to the pure solvent, W_2 is the concentration of the polar solute in wt. fraction and the a's are the slopes of the straight lines obtained by plotting the dielectric quantity against concentration. The slopes thus obtained are recorded in Table 1.

Complex plane plots a'' vs a' have been used for finding the relaxation time τ_0 and distribution parameter α. These plots are shown in Figures 1, 2 and 3. The calculated values of τ_0 and α are recorded in Table 2. The dielectric data have been analysed in terms of two relaxation processes using Kastha's[6] method and the value of relaxation time for overall rotation τ_1 and for group rotation τ_2 and their weight factors have been calculated. These are given in Table 2.

The dipole moments were calculated by Halverstadt and Kumler's method[7]. The calculated values of the dipole moments are given in Table 2.

The molar polarization P_2 of the solute was calculated by the equation[8, 9]

$$P_2 = P_1 + (P_{12} - P_1)/f_2 \quad (5)$$

where P_1 is the molar polarization of the solvent, which is given by $P_1 = (\mathcal{E}_1 - 1)/(\mathcal{E}_1 + 2) \cdot M_1/d_1$,

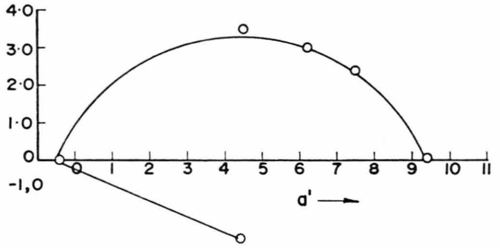

Fig. 1. a' vs. a'' plot of acetyl acetone.

Table 1. Values of the Slopes of $\mathcal{E}'$ and $\mathcal{E}''$ vs. Concentration for β-diketones.

Frequency	a'	a''
Acetyl Acetone		
1 MHz	9.33	—
18.26 GHz	7.50	2.40
24.50 GHz	6.20	3.00
30.20 GHz	4.50	3.50
Optical	−0.35	—
Benzoyl Acetone		
1 MHz	7.54	—
9.83 GHz	5.00	2.50
18.26 GHz	2.10	2.10
24.5 GHz	1.78	1.70
30.2 GHz	1.40	1.65
Optical	0.28	—
Dibenzoyl Methane		
1 MHz	5.56	—
9.83 GHz	3.43	2.17
18.26 GHz	1.39	1.47
24.5 GHz	1.33	1.38
30.2 GHz	0.90	1.05
Optical	0.62	—

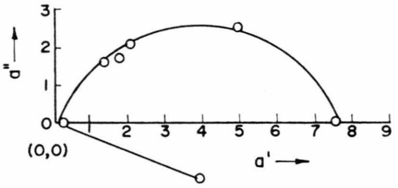

Fig. 2. a' vs. a'' plot of benzoyl acetone.

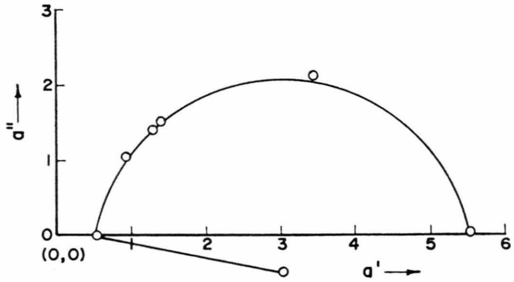

Fig. 3. a' vs. a'' plot of dibenzoyl methane.

Table 2. Values of Relaxation time τ_0, distribution parameter α, Relaxation time for overall rotation τ_1, Group Roxation τ_2, Weight factors C_1 and C_2 and dipole moment μ for β-diketones in benzene at 35 °C.

Compound	τ_0 (p. sec.)	α	τ_1 (p. sec.)	τ_2 (p. sec.)	C_1	C_2	μ (Debye)
Acetyl acetone	5.3	0.25	8.0	0.7	0.54	0.46	3.00
Benzoyl acetone	14.0	0.22	—	—	—	—	3.34
Dibenzoyl methane	18.1	0.12	36.5	8.5	0.72	0.28	3.56

and P_{12} is the molar polarization of the solution which is given by

$$P_{12}=\frac{\mathcal{E}_0-1}{\mathcal{E}_0+2}\cdot\frac{M_1 f_1+M_2 f_2}{d_{12}} \qquad (6)$$

where $\mathcal{E}_0$ and $\mathcal{E}_1$ are the static dielectric constants of the solution and solvent, respectively, d_{12} is the density of the solution, and f_1 and f_2 are the mole fractions of the solvent and solute, respectively. The molar polarization has been plotted against concentration and the plots are shown in Figure 4.

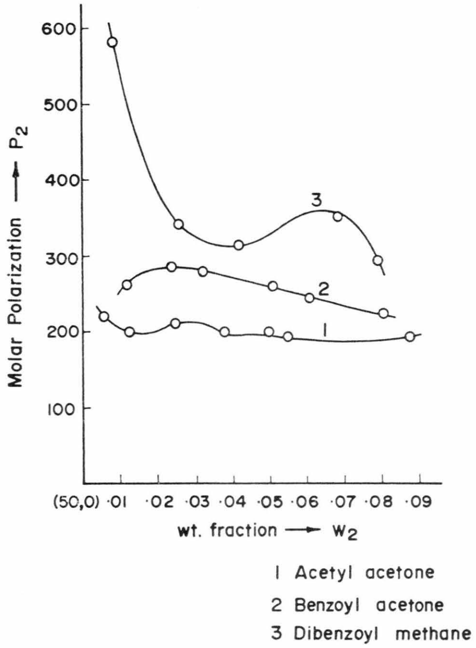

Fig. 4. Molar polarization vs. concentration plots of β-diketones.

Results and Discussion

The molar polarization of an unassociated solute in a non-polar solvent usually decreases with increase of concentration. In the case of acetyl acetone, benzoyl acetone and dibenzoyl methane the molar polarization concentration curves show anomalous behaviour i. e., the curves show maxima and minima. This leads to the conclusion that the molecules are essentially in the enolic form. The extent of hydrogen bonding decreases from dibenzoyl methane to acetyl acetone (Figure 4). This type of behaviour of these compounds has also been concluded earlier from infrared absorption data [10] and their chemical properties [11].

The complex plane plots a'' vs a' for acetyl acetone, benzoyl acetone and dibenzoyl methane are Cole-Cole arcs which show symmetrical distribution of relaxation time. The average relaxation time τ_0 increases with molecular size which is the normal behaviour of polar solutes in non-polar solvents. The distribution parameter α is comparatively large which indicates the presence of more than one relaxation process in these molecules. In the case of acetyl acetone and dibenzoyl methane it is possible to resolve the curve into two Debye type dispersions using Kastha's method [6] but it is not possible to resolve the curve for benzoyl acetone because in it there are two different rotating polar groups. The two different relaxation times obtained as a result of resolution in acetyl acetone may be assigned to overall rotation $\tau_1=8.0$ p.sec. and to a group rotation $\tau_2=0.7$ p.sec. Similarly $\tau_1=36.8$ p.sec. in case of dibenzoyl methane may be attributed to the overall rotation while $\tau_2=8.5$ p.sec may be assigned to a group rotation. The weight factors corresponding to overall rotation and group rotation indicate the relative possibility of these two relaxation processes. Although the molecules exist predominantly in enolic form, a small fraction of the molecules may also exist in keto form in case of acetyl acetone and may contribute to the average relaxation time.

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