

Dielectric relaxation study and structural properties of acetophenone and its derivatives in dioxane at microwave frequency

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Abstract : Dielectric relaxation parameters of acetophenone, ortho-chloroacetophenone, para-chloroacetophenone, ortho-aminoacetophenone, meta-aminoacetophenone and para-aminoacetophenone in 1,4-dioxane solution have been determined at microwave frequency (10 GHz) using standing wave pattern technique. The values of dipole moment and relaxation time of acetophenone are in agreement with the values reported earlier. The thermodynamic parameters of the systems are also reported. Dielectric relaxation parameters of acetophenone and its amino derivatives in 1,4-dioxane suggests a hydrogen-bonding and intermolecular interaction in the system.

Keywords : Dielectric relaxation, dipole-moment, relaxation time, activation energy, acetophenone

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The dielectric relaxation study of acetophenone and its derivatives have been done to investigate its dipole moment and relaxation times in dilute solutions, which provides the structural informations along with its interaction with non-polar solvent [1–3]. The study has also been done in polar solvent [4] to investigate the influence of polar liquids on orientation of molecules. The influence of $-NH_2$ and $-Cl$ groups at different position on its orientations is of great significance because $-NH_2$ group may form hydrogen bond with dioxane whereas $-Cl$ group may interact with long-range forces. To study the influence of groups, ortho-, para-, chloro-acetophenone, ortho-, meta-, para-amino-acetophenone have been taken up for dielectric study. No dielectric relaxation measurement were reported for ortho-chloro-acetophenone, para-chloro-acetophenone, ortho-amino-acetophenone, meta-amino-acetophenone and para-amino-acetophenone in dioxane at microwave frequency.

The objective of the present paper is to report the dielectric relaxation study of acetophenone (ACT) in benzene and 1,4-dioxane, ortho-chloro-acetophenone (OCL), para-

chloro-acetophenone (PCL), ortho-amino-acetophenone (OAM), meta-amino-acetophenone (MAM) and para-amino-acetophenone (PAM) in 1,4-dioxane at various temperatures and concentrations using standing wave pattern technique.

Acetophenone, ortho-chloro-acetophenone, para-chloro-acetophenone, ortho-amino-acetophenone, meta-amino-acetophenone were obtained from MERK, Germany and para-amino-acetophenone was obtained from FERAC, Berlin. The benzene and 1,4-dioxane were supplied by M/S BDH of AnalaR grade. All chemical were used without purification.

Measurements were carried on X-band spectrograph [5,6]. The liquid sample were placed in the 6.0 cm long silvered waveguide cell with water circulation arrangement. The probe was adjusted to minima which lies closest to the liquid cell. In our experiment, the position of the shorting plunger inside the cell with liquid was moved up at regular intervals and each time the standing wave pattern (P), was recorded. This power profile of standing wave pattern consist of a set of 200 equally spaced experimental data points which were used for Least Squares fit to determine the values of propagation constant in the liquid. The values of permittivity, (ϵ') and (ϵ''), where (ϵ') is the real part and (ϵ'') is the imaginary part of the permittivity can be obtained from the propagation constant by using the following equation

$$\epsilon' = \lambda_0^2 + \left[\frac{1}{\lambda_c^2} + (\beta^2 - \alpha^2) / 4\pi^2 \right]$$

and
$$\epsilon'' = \lambda_0^2 \alpha \beta / (2\pi^2), \quad (1)$$

where λ_0 and λ_c are the free space and cutoff wavelength, respectively. Figure 1, shows the experimental profile of the standing wave pattern as obtained for dilute solutions of ACT in

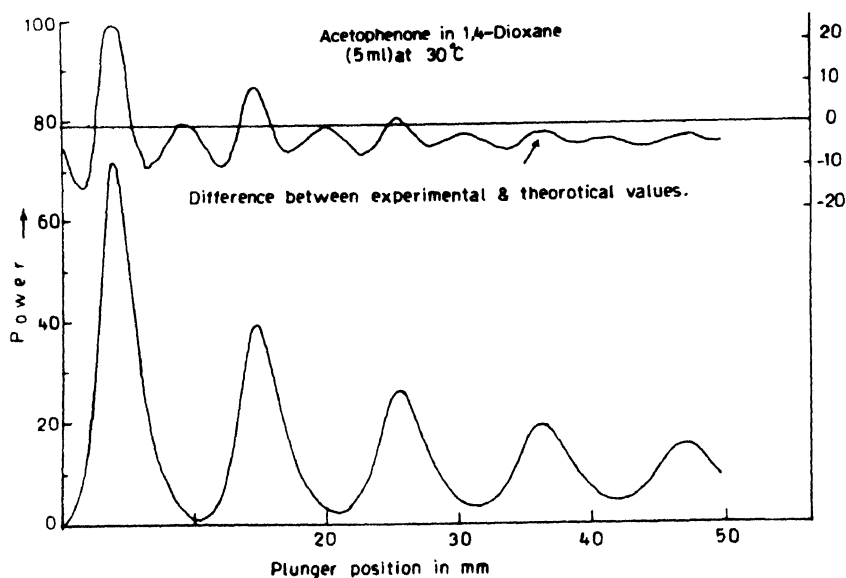


Figure 1. The standing wave pattern for weight fraction of ACT (0.02573) in 1,4-dioxane at 30°C, along with the difference between experimental and theoretical values.

1,4-dioxane along with theoretical values at 30°C. The typical example of correlation matrix is given in Table 1. The correlation matrix shows that the power at infinite thickness (P_0) is very much dependent on attenuation constant (α) but less dependent on phase constant (β) and phase change (δ).

Table 1. Correlation matrix for OCT in 1,4-dioxane solution at 30°C

	P_0	β	α	δ
P_0	1	0.14	0.76	0.20
β		1	0.09	0.73
α			1	0.14
δ				1

The values of (ϵ') and (ϵ'') can be obtained for ACT in benzene, OCL, PCL, OAM, MAM, PAM, in 1,4-dioxane solution using the propagation constant [5] at different concentrations and temperatures. The dipole moment of polar molecules can be obtained by using the Debye equation in the straight forward manner [7]. However, we have determined the values by using the Least Squares fit method. In the method, the experimental values of [$\epsilon^* = (\epsilon' - j\epsilon'')$] were fitted with Debye equation [7,8] as follows

$$\frac{(\epsilon^* - 1)}{(\epsilon^* + 2)} = \frac{(\epsilon - 1)}{(\epsilon + 2)} + \frac{4 \pi n \mu^2}{9 k T (1 + i\omega\tau)}, \tag{2}$$

with μ , τ and ϵ as fitting parameters. In the above equation, n is the number density of solute molecule, μ is the dipole moment, τ is the relaxation time, T is the temperature in ° Kelvin and ω is the angular frequency. The values of dipole moment and relaxation time are given in Table 2 at different temperatures. It is observed from Table 2 that the relaxation time decreases with rise in temperature whereas the dipole moment does not depend upon the

Table 2. Relaxation time τ and dipole moment μ for acetophenone and its derivatives in 1,4-dioxane solutions

Temperature	τ (ps)		μ (Debye)		
	a	b	a	b	c
Acetophenone					
15°C	13.90 (26)	11.53 (15)	2.27 (28)	3.56 (14)	
30°C	13.45 (17)	12.80 (19)	2.78 (65)	3.01 (14)	
50°C	12.21 (19)	11.24 (17)	2.86 (72)	3.29 (15)	
ortho-chloro-acetophenone					
20°C	29.29 (60)	21.05 (55)	3.33 (12)	3.96 (18)	
40°C	16.32 (44)	14.32 (45)	3.49 (12)	4.15 (25)	
50°C	10.83 (33)	7.80 (23)	3.76 (14)	5.47 (34)	

Table 2. (Cont'd)

Temperature	τ (ps)		μ (Debye)		
	a	b	a	b	c
para-chloro-acetophenone					
20°C	15.31 (34)	13.72 (31)	1.93 (59)	2.88 (13)	
30°C	14.57 (24)	12.37 (13)	1.99 (53)	2.55 (97)	
40°C	13.00 (23)	10.83 (92)	2.03 (56)	2.09 (54)	
ortho-amino-acetophenone					
20°C	14.09 (26)	13.93 (32)	1.74 (10)	1.79 (22)	
40°C	12.58 (23)	11.97 (28)	1.87 (55)	2.07 (12)	
50°C	12.50 (28)	11.66 (32)	1.98 (62)	2.00 (14)	
meta-amino-acetophenone					
20°C	12.31 (18)	11.55 (21)	3.02 (79)	3.36 (16)	
30°C	10.92 (14)	11.36 (16)	3.11 (77)	3.46 (16)	
50°C	10.50 (16)	8.90 (12)	3.28 (94)	4.13 (18)	
para-amino-acetophenone					
20°C	23.93 (81)	18.74 (44)	3.14 (13)	4.09 (17)	4.94
30°C	22.20 (66)	17.32 (42)	3.27 (13)	4.12 (18)	
40°C	18.11 (33)	15.73 (24)	3.33 (96)	4.04 (16)	
50°C	16.48 (33)	13.47 (20)	3.44 (10)	4.47 (17)	

Error are given in brackets e.g. 13.90 (26) means 13.90 + 0.26.

a Keeping density as a constant in fitting procedure.

b Keeping density as a variable with respect to solute in fitting procedure

c The value of μ is taken from ref. [18].

temperature under experimental error. The thermodynamic properties of ACT, OCL, PCL, OMA, MAM and PAM in 1,4-dioxane solutions were obtained by using the eq. [9].

$$\tau = \frac{h}{kT} \exp\left[\frac{\Delta H - T\Delta S}{RT}\right]. \quad (3)$$

The values of activation energies (ΔH) in kcal/mol are given in Table 3.

Table 3. Thermodynamic parameters for acetophenone in benzene and 1,4-dioxane and OCL, PCL, OAM, MAM, PAM in dioxane solutions.

Compound	Solvent	ΔH kcal/mol
ACT	benzene	1.37 (31)
ACT	dioxane	8.63 (15)
OCT	dioxane	3.93 (11)
PCT	dioxane	0.88 (36)
OAM	dioxane	0.18 (22)
MAM	dioxane	0.30 (40)
PAM	dioxane	1.87 (33)

The dipole moment and relaxation time of ACT in benzene solution shown in Table 4 are in good agreement with literature [10–12] values within the experimental error at 30°C whereas no literature values are available for the systems.

Table 4. Relaxation time τ and dipole moment μ of acetophenone in benzene and 1,4-dioxane solutions.

Temperature	τ (ps)		μ (Debye)		
	a	b	a	b	c
Acetophenone in benzene					
20°C	8.59 (82)	8.44 (88)	2.43 (33)	2.58 (11)	7.8 2.6
30°C	7.33 (86)	6.55 (38)	2.51 (60)	3.12 (55)	7.9 2.5
50°C	6.21 (55)	6.18 (65)	2.69 (56)	2.73 (11)	6.5 2.6
Acetophenone in 1,4-dioxane					
15°C	13.90 (26)	11.53 (15)	2.27 (15)	3.56 (14)	
30°C	13.45 (17)	12.80 (15)	2.28 (16)	3.01 (14)	
50°C	12.21 (17)	11.24 (17)	2.86 (72)	3.29 (13)	

a Keeping density as a constant in fitting procedure

b Keeping density as a variable with respect to solute in fitting procedure

c The values of relaxation time and dipole moment are taken from Refs. [11], [12] and [10] respectively.

It can be seen from Table 4 that the mean relaxation time of ACT in dioxane at 30°C is 13.45 ps and the corresponding values in benzene is 7.33 ps. At 50°C they are 12.21 ps and 6.21 ps, in dioxane, respectively. It indicates that the mean values of relaxation time in dioxane are higher than the corresponding values of benzene. The higher values of relaxation time in dioxane may be either due to a viscosity effect [10] or hydrogen-bonding [10] between the hydrogen atom of $-\text{COCH}_3$ group of ACT and the oxygen atom of the 1,4-dioxane (shown in Figure 2). This suggests the presence of solute-solvent interaction [10] particularly in case of 1,4-dioxane. It is also seen from Table 3 that decrease of relaxation time with rise of temperature may be due to the fact that the cluster of molecules breaks slowly with rise in temperature [10].

The dipole moments of PCL is 42% smaller than the corresponding value of OCL whereas the relaxation time of PCL is 34% smaller than the corresponding values of OCL at 20°C (see Table 2). This can be explained on the basis of the fact that the former molecule experiences greater steric hindrance to the free rotation than the latter [13].

The relaxation time of OAM is about 14% larger than the corresponding value of MAM at 20°C, whereas it is found that the value of dipole moment is 42% smaller than the corresponding value of MAM at 20°C. Qualitatively as observed [14], the lowering in relaxation time from ortho- to meta- positions of the compound occur due to a tendency of bond formation [14–17] between the hydrogen atom of $-\text{COCH}_3$ group and the oxygen atom

of the 1,4-dioxane. Since the oxygen atom of the carbonyl group has greater affinity of forming bond with substituted amine group at the adjacent position and intramolecular hydrogen-bonding is expected to be formed preferably in the case of ortho-substituted amino group (see Figure 3).

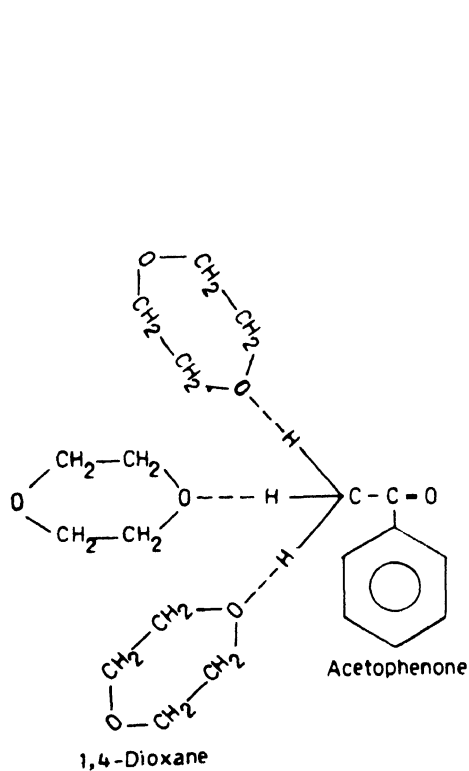


Figure 2. A suggested model for hydrogen-bonding of acetophenone in the mixture of 1,4-dioxane. (---) line shows the hydrogen-bonding.

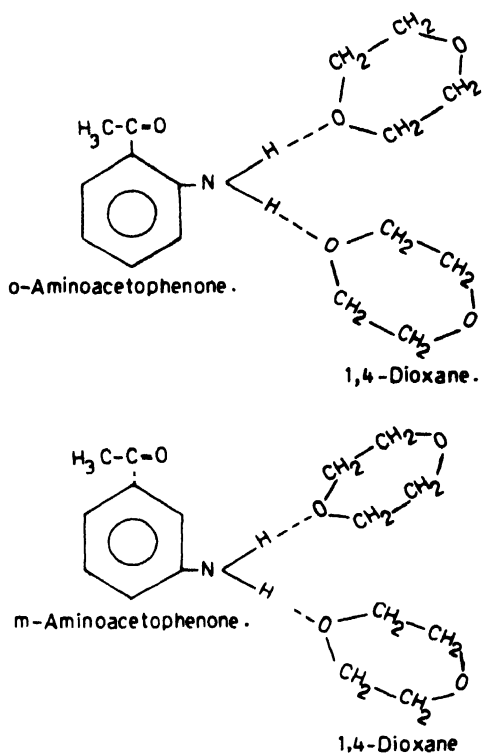


Figure 3. A suggested model for hydrogen-bonding of polar molecule in the mixture of 1,4-dioxane. (---) line shows the hydrogen-bonding.

The dipole moment of PAM [18] in benzene is 4.48 D and in 1,4-dioxane is 4.94 D, respectively at 25°C. The larger value of dipole moment in dioxane solution shows that the moment vector of higher polar structure is in-line with the moment of the compound. Also it is observed [18] that PAM has a greater molar refraction and absorbs at a longer wavelength (in the ultraviolet region) in a mixture of dioxane. The relaxation time of PAM is about 49% higher than the corresponding values of MAM at 20°C, whereas the dipole moment is only 4% higher than the corresponding value of MAM.

In this paper, a systematic study of dielectric relaxation and thermodynamic properties of ACT, OCL, PCL, OAM, MAM and PAM in 1,4-dioxane solutions have been carried out. The structural information have also given (Figures 2 and 3) in case of ACT, OAM and MAM in 1,4-dioxane solutions. The study has provided the values of dipole moments, relaxation time and activation energies for the systems.

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