Temperature dependence of dielectric relaxation of rigid polar molecules acetophenone, pyridine and their mixtures in dilute solutions of benzene

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The dielectric absorption studies of acetophenone, pyridine and their binary mixtures, both consisting of rigid molecules, have been studied at 8.93 GHz in the dilute solutions of benzene at different temperatures. The relaxation times, dipole moments, thermodynamical parameters, viz. free energy, enthalpy and entropy of activation have been calculated from the dielectric data. The relaxation time (τ_0) of the single component agrees well with literature values. The experimental values of relaxation time (τ_0) of the dipolar mixture have been compared with the theoretical values obtained by employing different methods. The non-linear behaviour of μ^2 versus mole fraction is explained on the basis of solute-solute molecular association between these two-polar rigid molecules. The values of the molar entropy for the relaxation process indicate that, the cooperative orientation of the molecules in the single component system is retained in the mixture also.

1 Introduction

The knowledge of the relaxation times of a mixture of polar components under varying conditions of composition and temperature is of great importance because, it helps in formulating adequate models of liquid relaxation and also in obtaining information about the relaxation process in mixtures. Study of dielectric behaviour of mixtures of polar molecules[1-5], under varying conditions of composition and temperature, has evoked considerable interest. Dielectric measurements on aromatic ketones namely, acetophenone and its derivatives have been made by various workers[6,7]. Madan et al.[8] reported the dielectric absorption study of dilute solutions of rigid molecules pyridine, quinoline, isoquinoline and their mixtures in benzene. They found that, in the mixture, the degree of polarization order decays exponentially, just as it does for single component system. Several workers[1,8,9] studied dielectric relaxation behaviour of some polar molecules and their mixtures in the dilute solutions of benzene and found formation of complexes for mixtures of rigid polar molecules.

The existing literature shows that, elaborate

work has been done for pyridine and acetophenone. But, no work has been reported, so far, for their binary mixtures. It is, therefore, thought that an investigation of the mixture of two rigid polar liquids pyridine and acetophenone having significantly different values of the relaxation time could throw light on the molecular association in the mixture.

2 Experimental Details

A slotted section wave-guide and short circuiting plunger X-band setup was used to measure the wavelength, voltage standing wave ratio and the shift in the minima position in the dilute solutions of acetophenone, pyridine and their mixtures in benzene at temperatures 303, 313, 323 and 333 K using a temperature regulating system and a constant temperature water bath. The details of the apparatus used and the procedure are the same as described earlier by Bansal et al.[10]. The dielectric constant (ϵ') and the dielectric loss (ϵ'') were computed from these measurements by the method of Heston et al.[11]. The accuracy of measurements in the values of ϵ' and ϵ'' are of the order of ±1 and ± 5%, respectively. The dielectric constant ϵ_0 at 100 KHz. was measured using a dipole meter, by directly measuring the capacitance and calibrating it for standard liquids. The dielectric

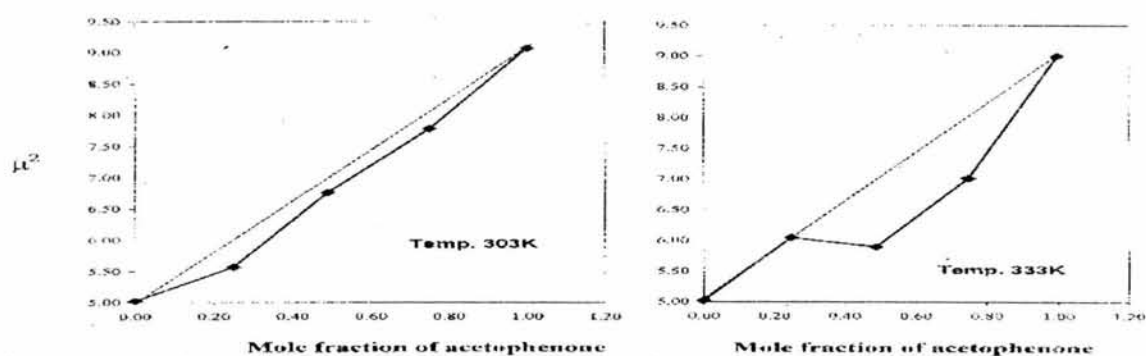*OSD Higher Education, Govt. of Rajasthan, Jaipur

Fig. 1 — Variaton of μ^2 versus mole fraction of acetophenone in the mixture at different temperatures

Table 1 — Values of a_0, a', a'' and a_∞ of single components as well as their mixtures in benzene solution at different temperatures

Substances	Temperature (K)	a_0	a'	a''	a_∞
Pyridine	303	6.79	6.27	1.66	0.48
	313	6.45	6.04	1.47	0.45
	323	6.11	5.79	1.26	0.44
	333	5.82	5.55	1.13	0.42
Pyridine (75%) + Acetophenone (25%)	303	7.27	6.55	1.98	0.58
	313	6.91	6.33	1.73	0.49
	323	6.74	6.29	1.74	0.47
	333	6.57	6.23	1.88	0.39
Pyridine (51%) + Acetophenone (49%)	303	7.70	6.63	2.32	0.46
	313	7.08	6.26	2.06	0.34
	323	6.23	5.60	1.71	0.27
	333	5.62	5.17	1.40	0.20
Pyridine (25%) + Acetophenone (75%)	303	8.05	6.69	2.48	0.45
	313	7.66	6.54	2.26	0.45
	323	7.12	6.25	2.00	0.44
	333	6.18	5.50	1.63	0.35
Acetophenone	303	8.48	6.71	2.75	0.44
	313	7.79	6.29	2.44	0.34
	323	7.41	6.08	2.26	0.22
	333	6.93	5.87	2.02	0.11

constant at optical frequency was obtained by squaring the refractive index for sodium D-lines, measured with the help of an Abbe's refractometer. The values of most probable relaxation time (τ_0), the distribution parameter (α) and the relaxation times $\tau(1)$ and $\tau(2)$ were computed by the method of Higasi et al[12]. The molecular dipole moment (μ) of the molecules under investigation were computed, using equation given by Koga et al[13]. The thermodynamical parameters viz. free energy (ΔF_ε), enthalpy (ΔH_ε) and entropy of activation (ΔS_ε) for the dielectric relaxation process were calculated

using Eyrings's equation[14]. Acetophenone, pyridine and benzene, all of AR grade, were procured from BDH, India. Benzene was distilled, twice, before use. Mixtures of three different concentrations of acetophenone and pyridine were prepared and treated as a single component in dilute solution of benzene.

3 Results and Discussion

The slopes a_0, a', a'' and a_∞ determined by plotting measured values of ϵ_0, ϵ', ϵ'' and ϵ_∞ against concentration of single components and their mixture in the dilute solutions of benzene at four

different temperatures are reported in Table 1. The values of most probable relaxation time τ_0, the relaxation times $\tau(1)$ and $\tau(2)$, the molecular dipole moment (μ) and distribution parameter (α) are reported in Table 2. The values of μ^2 are also listed in this Table along with their theoretically calculated values, obtained by the relation:

$$\mu^2 = x_1 \mu_1^2 + x_2 \mu_2^2$$

where x_1 and x_2 are the mole fractions of two constituents in the mixture.

τ_0, $\tau(1)$ and $\tau(2)$ values for pyridine molecule are almost same, at each temperature. This shows that, a single relaxation process exists in pyridine molecule i.e. no intra-molecular relaxation process exists in the pyridine molecule, because, the presence of this relaxation process might have caused significant difference between $\tau(1)$ and $\tau(2)$ values. The relaxation time for pyridine at 30 °C is 5 ps, which is comparable with 5.3 ps observed by Vyas *et al.*[9], at the same temperature. Table 2 shows that, the values of distribution parameter (α) for pyridine are very small. A very small value of α was reported by Khanna & Bhatnagar[6] and Vyas *et al.*[9] for pyridine,

suggesting a simple Debye-type relaxation behaviour of the system. This is a usual behaviour of rigid polar molecules, which generally exhibit a simple Debye relaxation pattern. The values of τ_0, reported by Khanna & Bhatnagar[6], for acetophenone in dilute solutions of benzene at temperatures 30, 40, 50 and 60°C are 7.94, 7.24, 6.56 and 5.75, respectively, which are quite comparable with observed values of the authors. There is a significant difference between $\tau(1)$ and $\tau(2)$ values of acetophenone, which shows that, intra-molecular relaxation process exists in addition to the overall molecular relaxation process. Acetophenone is of intermediate character between aromatic and aliphatic compounds[15]. It essentially behaves as rigid molecule and the acetyl group rotation makes a significant contribution to the dielectric relaxation and absorption of acetophenone[6,15]. The values of distribution parameter (α) are finite in the case of acetophenone. This again confirms the presence of more than one relaxation process in acetophenone. The values of dipole moment (μ) of acetophenone are presented in Table 2, which are comparable with the values reported by Khanna & Bhatnagar[6].

Table 2 — Values of relaxation times [$\tau(1)$, $\tau(2)$ and τ_0]/ps, distribution parameter (α), dipole moment μ/D of pyridine+acetophenone mixture in dilute solutions of benzene at different temperatures

Substances	Temperature (K)	$\tau(1)$	$\tau(2)$	τ_0	μ	α	μ^2	μ^2cal	% Deviation in μ^2
Pyridine	303	5.1	5.5	5.0	2.24	0.01	5.02	-	-
	313	4.7	5.1	4.6	2.24	0.01	5.02	-	-
	323	4.2	4.6	4.2	2.24	0.01	5.02	-	-
	333	3.9	4.2	3.9	2.24	0.01	5.02	-	-
Pyridine (75%) + Acetophenone (25%)	303	5.9	6.5	5.8	2.36	0.02	5.57	6.03	-7.62
	313	5.3	6.0	5.2	2.38	0.02	5.66	5.97	-5.19
	323	4.7	5.2	4.6	2.42	0.02	5.86	6.02	-2.66
	333	4.2	4.4	4.2	2.46	0.01	6.05	6.02	0.50
Pyridine (51%) + Acetophenone (49%)	303	6.7	8.2	6.6	2.60	0.03	6.76	7.00	-3.98
	313	6.2	7.1	6.1	2.57	0.03	6.60	6.88	-4.62
	323	5.7	6.6	5.6	2.49	0.03	6.20	6.97	-11.05
	333	5.0	5.7	4.9	2.43	0.03	5.90	6.97	-15.35
Pyridine (25%) + Acetophenone (75%)	303	7.1	9.8	7.0	2.79	0.08	7.78	8.05	-3.35
	313	6.6	8.8	6.5	2.80	0.07	7.84	7.87	-0.38
	323	6.1	7.8	6.0	2.77	0.05	7.67	8.00	-4.24
	333	5.5	7.3	5.2	2.65	0.06	7.02	8.01	-12.36
Acetophenone	303	7.8	11.5	7.8	3.01	0.10	9.06	-	-
	313	7.3	11.0	7.2	2.97	0.10	8.82	-	-
	323	6.9	11.4	6.7	3.00	0.10	9.00	-	-
	333	6.3	9.4	6.0	3.00	0.10	9.00	-	-

Table 3 — Experimental values of relaxation time (τ_0) and the theoretically calculated values τ_a for acetophenone+pyridine mixture at different temperatures

Mole fraction. of acetophenone	$\tau_0 \times 10^{12}$ in sec	$\tau_{acal} \times 10^{12}$ in sec (SM)	$\tau_{acal} \times 10^{12}$ in sec (RM)	$\tau_{acal} \times 10^{12}$ in sec (Madan)	% deviation of τ_{acal} (SM)	% deviation of τ_{acal} (RM)	% deviation of τ_{acal} (Madan)
Temperature 303 K							
0.00	5.0	-	-	-	-	-	-
0.25	5.8	5.7	5.5	5.8	-1.7	-5.1	0.0
0.49	6.6	6.4	6.1	6.5	-3.0	-7.6	-1.5
0.75	7.0	7.1	6.8	7.2	1.4	-2.9	2.9
1.00	7.8	-	-	-	-	-	-
Temperature 313 K							
0.00	4.6	-	-	-	-	-	-
0.25	5.2	5.3	5.1	5.4	1.9	-1.9	3.8
0.49	6.1	5.9	5.6	6.0	-3.3	-8.1	-1.6
0.75	6.5	6.6	6.3	6.6	1.5	-3.1	1.5
1.00	7.2	-	-	-	-	-	-
Temperature 323 K							
0.00	4.2	-	-	-	-	-	-
0.25	4.6	4.8	4.6	5.5	4.3	0.0	19.6
0.49	5.6	5.4	5.1	6.6	-3.6	-8.9	17.9
0.75	6.0	6.1	5.8	6.1	1.6	-3.3	1.7
1.00	6.7	-	-	-	-	-	-
Temperature 333 K							
0.00	3.9	-	-	-	-	-	-
0.25	4.2	4.4	4.3	4.5	4.8	2.4	7.1
0.49	4.9	4.9	4.7	5.0	0.0	-4.1	2.0
0.75	5.2	5.6	5.3	5.5	7.7	1.9	5.8
1.00	6.0	-	-	-	-	-	-

The dielectric data of polar mixtures were analyzed in a similar manner, as for the single component system. The values of τ_0, $\tau(1)$, $\tau(2)$, α and μ for mixtures of acetophenone + pyridine in the dilute solution of benzene at different temperatures are given in Table 2. It is evident from Table 2 that, the values of distribution parameter (α) for all the three mixtures investigated, are finite at all temperatures, indicating the presence of more than one relaxation process in the mixtures.

Further, the observed values of relaxation time for all the mixtures lie between those for individual molecules. This suggests that, there is an overlap of two individual Debye regions. The degree of overlap varies with the concentration ratio of the two components of the mixtures. This is consistent with Davidson's analysis[16] that, for the resolution of two distinct relaxation processes, the relaxation time of individual components should be six-times that of the other. These results are in agreement with those of Hill et al.[17], who suggested that, larger liquid regions are involved in mixtures in relaxation

process in comparison to single molecule. The values of relaxation times of the mixtures increase with the increase of concentration of acetophenone in them. This may be due to the fact that, relaxation time of acetophenone is higher than the relaxation time of pyridine.
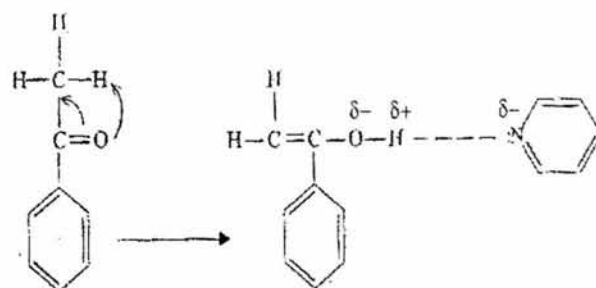

Fig. 2 — Solute-solute molecular association due to hydrogen bonding

The values of dipole moment (μ) of pyridine acetophenone and their mixtures in benzene at different temperatures calculated using the method

by Koga *et al.*[13] which are given in Table 2. It shows that, μ values of the mixture lie between the μ values of its constituents, at each temperature. The μ^2 values of the mixture versus mole fraction of acetophenone (X) in the mixture and are plotted in Fig. 1.
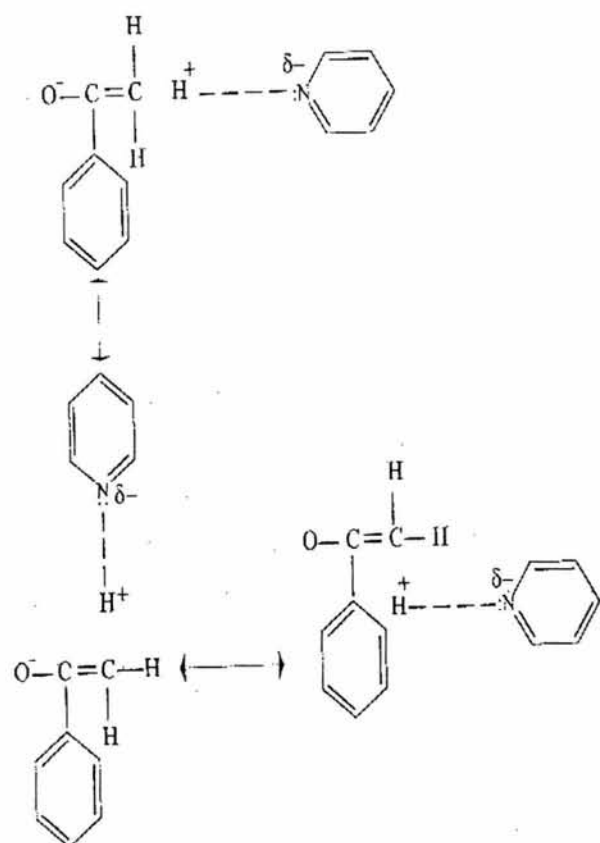

Fig. 3— Solute-solute molecular association through resonating structure

It is noticed that, μ^2 versus X curves are non-linear at each temperature. The deviation from linearity are higher than the permissible error (0.5%). This deviation may be attributed to the presence of solute-solute molecular association through hydrogen bonding between pyridine and acetophenone, as shown in Figs 2 and 3. Similar results have been reported by Singh & Sharma[1] for para-methyl acetophenone and dimethyl sulphoxide and their mixtures in dilute solutions of benzene. Moreover, the deviation from linearity is found to be temperature-dependent. The deviation is maximum at temperature 333 K, which indicates that, solute-solute interaction predominates at higher temperatures.

The experimental values of τ_0 of the mixture of acetophenone + pyridine at different temperatures are compared with the values obtained by various theoretical methods. The simplest method for theoretical estimation of relaxation time (τ_a) of a mixture using linear mixing rule is:

$$\tau_a = \sum_{i=1}^{n} x_i \tau_i \qquad \ldots(1)$$

where τ_i is the relaxation time of the ith component of mole fraction x_i in the mixture. Another simple formula for finding out values of τ_a is by reciprocal mixing rule, given by:

$$\frac{1}{\tau_a} = \sum_{i=1}^{n} \frac{x_i}{\tau_i} \qquad \ldots(2)$$

Madan[18] proposed an ingenious method for estimating the relaxation behaviour of the system of Debye-type polar compounds in a non-polar solvent. For a system consisting of a number of rigid polar molecules in dilute solutions with a non-polar solvent, the apparent relaxation time (τ_a) can be represented by:

$$\frac{1}{\tau_a} = \sum_{i=1}^{n} \frac{A_i}{\tau_i} \qquad \ldots(3)$$

where A_i are the parameters representing the effect of molecular environment, shape, size, viscosity, fractional volume, solute-solute interaction and other factors affecting the dipole reorientation. Taking into consideration that, weight of a particular relaxation process depends on the square of the associated dipole moment, the parameter A of the ith constituent, as given by Madan[18] is:

$$A_i = C_i \, \mu_i^2 / \left(\sum C_i \, \mu_i^2 \right) \qquad \ldots(4)$$

where C_i are the parameters involving effects other than those due to dipole moments μ_i for a binary system. Eq. (3) takes the form as given by Madan[18]:

$$\frac{1}{\tau_a} = \left[\frac{C \mu_1^2}{\left(C \mu_1^2 + \mu_2^2 \right) \tau_1} + \frac{\mu_2^2}{\left(C \mu_1^2 + \mu_2^2 \right) \tau_2} \right] \qquad \ldots(5)$$

where $C = C_1 / C_2$. The value of C in dilute solution can be estimated by considering it to be roughly equal to the volume fraction V_1 / V_2. Thus, C_i can be estimated from the molar volume. Using the molar volumes and dipole moments, the computed values of τ_a for the mixture are given in Table 3. The

Table 4 — Thermodynamical parameters of single components as well as their mixtures
in benzene solution at different temperatures

Substances	Temp. (K)	τ_0	ΔF_ε kcal/ mole	ΔH_ε kcal/ mole	ΔS_ε cal/ mole/deg
Pyridine	303	5.0	2.08	1.14	-3.10
	313	4.6	2.12		-3.11
	323	4.2	2.14		-3.07
	333	3.9	2.18		-3.11
Pyridine (75%) + Acetophenone (25%)	303	5.8	2.17	1.61	-1.85
	313	5.2	2.19		-1.85
	323	4.6	2.21		-1.85
	333	4.2	2.23		-1.85
Pyridine (51%) + Acetophenone (49%)	303	6.6	2.24	1.29	-3.16
	313	6.1	2.29		-3.37
	323	5.6	2.33		-3.39
	333	4.9	2.34		-3.30
Pyridine (25%) + Acetophenone (75%)	303	7.0	2.28	1.22	-3.48
	313	6.5	2.33		-3.52
	323	6.0	2.37		-3.56
	333	5.2	2.38		-3.47
Acetophenone	303	7.8	2.35	1.10	-4.12
	313	7.2	2.39		-4.14
	323	6.7	2.44		-4.17
	333	6.0	2.47		-4.11

computed values of τ_a by the three different methods compare well among themselves at each temperature and mole fraction of acetophenone. It is evident from Table 3 that, for the mixture under investigation, the calculated values of τ_a by different methods are almost in agreement with experimental values. However, there is some deviation noticed in τ_a values calculated by Eq. (5) at temperature 323 K and at 0.25 and 0.49 mole fraction of acetophenone. The deviation observed in τ_a values by various methods may reduce, if more appropriate values could be assigned to C, to include the effect of the variety of conditions encountered in the rotations of polar molecules in solutions. Perusal of Eq. (5) reveals that, the agreement between observed and calculated values of relaxation times of the mixture depends upon the ratio of dipole moments of its components. Best results are obtained when, two polar compounds have equal dipole moments. In the present investigation, since the μ values of pyridine and acetophenone have almost equal dipole moments, theoretically calculated values of τ_a by different methods are in good agreement with experimental values.

The various thermodynamical parameters ΔF_r, ΔH_ε and ΔS_ε for the dielectric relaxation processes can be obtained, using rate process Eq. 14. These thermodynamical parameters are presented in Table 4, both for single component as well as for two component solutions. The ΔF_ε values for the three mixtures are greater than ΔF_ε values of pyridine and are lesser than the corresponding values of acetophenone. This indicates that, the presence of acetophenone molecule in the mixture dominates over the pyridine molecule. It can be seen from Table 4 that, ΔF_ε values for acetophenone, pyridine and their mixture in dilute solution for the dipole relaxation increases with temperature. This may be attributed to the decreasing viscosity of the medium with rising temperature. Also, as the temperature increases, thermal agitation increases and their molecules require more energy to come to the activated state. It is also evident that, for the individual compound and their mixture, the molar enthalpy of activation (ΔH_ε) values are less than corresponding ΔF_ε values, resulting in the negative molar entropy of activation ΔS_ε. These negative values of ΔS_ε suggest that, the existence of

cooperative orientation, resulting from dipole-dipole interaction in the molecule of pyridine and acetophenone, is retained by their mixture also. Thus, a large number of molecules, surrounding the one which rotates, are involved in the process of dipole orientation and the activated state is more in order than the normal state.

Acknowledgement

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