INTERNATIONAL JOURNAL OF RESEARCH IN PHARMACY AND CHEMISTRY

Available online at www.ijrpc.com

**Research Article** 

# DIELECTRIC RELAXATION STUDIES OF BENZAMIDE WITH CYCLOALCOHOLS USING FREQUENCY DOMAIN TECHNIQUE

# S. Kumar<sup>1\*</sup>, S. Sivakumar<sup>2</sup>, R. Premanand<sup>2</sup> and P. Jeevanandham<sup>1</sup>

<sup>1</sup>Department of Physics, Annamalai University, Annamalai Nagar, Tamilnadu, India.

<sup>2</sup>Department of Physics, Sri Sai Ram Engineering College, Chennai, Tamilnadu, India.

# ABSTRACT

The dielectric constants and dielectric losses of benzamide in dilute solutions of 1,4-dioxane have been measured at 303K using both J-band (7.22 GHz) and X-band (9.34 GHz) microwave benches. The relaxation time for overall rotation ( $\tau_1$ ) and for group rotation ( $\tau_2$ ) of the molecules was determined using Higasi's method. The activation energies for the process of dielectric relaxation ( $\Delta F_{\tau}$ ) and viscous flow ( $\Delta F_{\eta}$ ) were determined by using Eyring's rate theory. ( $\tau_1$ ) is found to be the function of the hydrogen bonding strength of the cycloalcoholic hydrogen, where as the group relaxation time ( $\tau_2$ ) is function of the steric interaction of the proton donor. The relaxation time is maximum at 1:1 mol % ratio.

Keywords: H-bonding, Complexation, Dielectric Relaxation, J-Band and X-Band Microwave Benches.

### 1. INTRODUCTION

Dielectric approach is a powerful tool for the determination of molecular structure. Recently dielectric relaxation behavior of mixtures of polar molecules under varying conditions complexation, temperature and environmental factors has evoked considerable interest. The influence of association through hydrogen bonds on the structure of liquids and their relaxation behavior has been studied for a long time<sup>1-4</sup>. Based on the results, models of relaxation process in liquid mixtures have been formulated. The study of association of two polar molecules due to hydrogen bonding from the dielectric measurements relaxation at microwave frequencies are scare<sup>5-8</sup>. Antony and Smyth<sup>9</sup> were the first to detect solute-solvent interaction through measurement of relaxation time. Being the simplest models for peptides, amides have been the subject of several structural studies. Cycloalcohols as proton donors occupy a particular position among the organic acids. By changing the type and number of substituents in

the cycloalcohol ring, one can regulate almost continuously their acidity. They form H-bonded adducts with amides. Sharma et al<sup>10</sup> studied the dielectric relaxation study of binary mixtures of ethyl alcohol and DMF in benzene solution from microwave absorbtion data. They showed that the relaxation time is maximum at equimolar concentration. The present work reports the dielectric relaxation behaviour of mixtures of benzamide with cycloalcohols like cvclopentanol, cvclohexanol and cvcloheptanol in benzene to obtain knowledge of the dynamic dielectric behavior of amides in cycloalcohol solutions. Many interesting effects which are of importance to biological systems were observed if cycloalcohols are used as solvents or cosolvents

### 2. EXPERIMENT

Sigma variety of benzamide E.merck variety of cyclopentanol, cyclohexanol and cycloheptanol were used. The mole ratio of the ternary mixtures of the amide:cycloalcohols were always

1

adjusted in the ratio of 3:1, 2:1, 1:1, 1:2 and 1:3, however keeping the solute concentration in benzene to be constant. The dielectric constant  $\epsilon'$  and dielectric loss  $\epsilon''$  have been measured using J-band (7.22GHz) and X-band (9.34GHz) microwave benches at 303K. The static dielectric constant  $\epsilon_0$  at 2MHz was measured by using a "WTW dipole meter DM01" based on the principle of heterodyne beat method. The refractive index n<sub>D</sub> of all the solutions have been measured by an Abbe's refractometer. The measurements for  $\epsilon'$  and  $\epsilon''$  are accurate to  $\pm$  1and  $\pm$  5 % respectively.

#### 3. RESULTS

The dielectric relaxation times ( $\tau$ ) were calculated by using Higasi's method. Assuming  $\epsilon'$ ,  $\epsilon_0$ ,  $\epsilon_{\infty}$  and  $\epsilon''$  vary linearly with the concentration of the solute. We have,

$$\begin{array}{c} \varepsilon_{0} = \varepsilon_{1} + a_{0}W_{2} \\ \varepsilon^{'} = \varepsilon_{1} + a^{'}W_{2} \\ \varepsilon^{''} = a^{''}W_{2} \\ \varepsilon_{a} = \varepsilon_{1a} + a_{a}W_{2} \end{array} \right\} \longrightarrow (1)$$

The Debye equation in terms of  $a_0$ , a', a" and  $a_{\alpha}$  yields two independent equations<sup>11</sup>

$$\tau_{(1)} = \frac{a}{\omega(a'-a_{\alpha})} \rightarrow (2)$$

and

$$\tau_{(2)} = \frac{\mathbf{a}_0 - \mathbf{a}'}{\boldsymbol{\omega} \mathbf{a}''} \longrightarrow (3)$$

 $\tau_{(1)}$  Stands for the molecular relaxation time of the complex as a whole and  $\tau_{(2)}$  indicates the relaxation of the base molecule of amides.

$$\tau_{(0)} = \sqrt{\tau_{(1)} \times \tau_{(2)}} \rightarrow (4)$$

 $τ_0$  may be called the mean relaxation time. The free energy of activation for rotation (ΔFτ) is obtained from Eyring's theory of rate processes<sup>12</sup>. The results are shown in Tables I (a), I (b), II (a), II (b), III (a) and III (b).

#### 4. DISCUSSION

Our results show that the relaxation time is larger at 1:1 mole ratio of amides with cycloalcohols. The relaxation time decreases continuously for the other mole ratios but are higher than either of the components. Kumar et

 $al^{13}$ studied the interaction behaviour of acetamide with cycloalcohols in different molar composition ratios. They also observed that the relaxation time of tertiary mixtures (two polar solutes in an inert solvent) is always much greater than either of the polar solutes in the inert solvent. Further if the complex is rigid, the distribution parameter is larger, the two relaxation times are well separated, one representing the rotation of the complex as a whole, while the other representing the rotation of one of the interacting polar solute molecules. The relaxation time for dilute solution of cyclopentanol, cyclohexanol and cyloheptanol, observed in the present study ranges between 4 and 16ps. With excess of cycloalcohols, the relaxation time of benzamide+cycloalcohol systems show slight increase. This result is in agreement with the earlier investigation of Tucker et al<sup>14</sup>. The result also shows that the molecular association between amides and cycloalcohols is maximum at 50:50 mol% ratio and then decreases at other mol%. From this we conclude that the 1:1 complex is dominant in amide cvcloalcohol svstems. Further t values get increases as the chain length of the cvcloalcohol increases. It indicates that T depends upon viscosity also. The average relaxation time  $(\tau_0)$  is 16ps at 1:1 molar ratio for J-band frequency of 7.22 GHz and is 21ps for Xband frequency of 9.34 GHz. Similar trend was observed for cyclohexanol and cycloheptanol also. For cyclohexanol with benzamide system T<sub>0</sub> value is 20 ps at 1:1 molar ratio for 7.22 GHz (J-band) and is 23 ps for 7.34 GHz (X-band). Similarly for cycloheptanol with benzamide  $\tau_0$ value is 25 ps at 1:1 molar ratio for J-band and 37 ps for X-band. Hence T is frequency dependent as well as viscosity dependent and also chain length of the proton donor molecules (cycloalcohols). This result was supported by srivastava and vij<sup>15</sup>. From NMR studies<sup>16</sup>, the enthalpy activation energy for the internal group rotation of amides have been estimated to be greater than 40 KJmol<sup>-1</sup>. Our present study of microwave dialectic relaxation  $\Delta F_{\tau}$  showed in tables I (b), II (b) and III (b) a very low value indicating that there is no group rotation in these Smyth<sup>17</sup> pointed out that the complexes. relaxation time of proton donor increases as the acceptor ability of the solvent environment increases. Similarly for a given proton acceptor the relaxation time must increase with the proton donor ability of the donor solute. Our results are in accordance with this conclusion. From the measurement of free energy of activation for

0.1467

0.1289

dielectric relaxation  $\Delta F_{\tau}$  and the free energy of activation for viscous flow  $\Delta F_{\eta}$  for all systems studied it is clear that the free energy of activation for dielectric relaxation  $\Delta F_{\tau}$  in lesser then the free energy of a activation flow  $\Delta F_{\eta}$  since the relaxation time involves rotation motion only. Whereas the viscosity involves both rational and translational motion for cycloalcohols with benzamide. A graph is drawn

1:2

1:3

between the relaxation time  $\tau_0$  and volume percentage of benzamide for both J-band and X-band. In both the bands the trend was the same (i.e.). As the chain length of cycloalcohols increases the average relaxation time gets increase which was shown in fig (1) and fig (2) respectively.

2.3860

2.4189

System: Benzamide with Cyclopentanol									
Band	Ratio	Static dielectric constant	Dielectric constant at optical frequency	Dielectric constant at an angular frequency	Dielectric loss				
	Amide: Alcohol	<b>6</b> 0	ε	ε'	3				
	3:1	2.4325	2.0164	2.3989	0.0562				
J - band	2:1	2.4974	2.0192	2.4437	0.0621				
	1:1	2.5456	2.0192	2.4467	0.0607				
	1:2	2.5814	2.0220	2.4901	0.0840				
	1:3	2.6050	2.0235	2.5411	0.1219				
	3:1	2.4325	2.0164	2.3486	0.1289				
	2:1	2.4974	2.0192	2.3752	0.1467				
X -band	1:1	2.5456	2.0192	2.3486	0.1805				

Table I (a): Values of Dielectric	parameters	for	various	molar	ratios
System: Benzamic	de with Cyc	lope	entanol		

Table I (b): Values of Dielectric Relaxation time and activation Energies
System: Benzamide with Cyclopentanol

2.0220

2.0235

2.5814

2.6050

Band	Ratio	Relaxat	ion time by Method (ps)	Higasi's	α	$\Delta F_{\tau}$	$\Delta F_{\eta}$
	Amide: Alcohol	$ au_1$	$ au_2$	$ au_{0}$		KJ/mol	KJ/mol
	3:1	08.580	18.540	12.612	0.0038	11.027	13.657
	2:1	07.327	23.848	13.219	0.0022	11.146	13.665
J -band	1:1	07.056	40.705	16.947	0.0021	11.772	13.590
	1:2	08.032	27.438	14.845	0.004	11.438	13.709
	1:3	09.575	13.992	11.575	0.0044	10.811	13.726
	3:1	19.253	10.420	14.164	0.0075	11.320	13.657
	2:1	17.948	13.324	15.464	0.0070	11.541	13.665
X-band	1:1	15.593	31.037	21.999	0.0059	12.429	13.590
	1:2	15.121	23.848	18.989	0.0078	12.058	13.709
	1:3	16.967	16.496	16.730	0.0061	11.739	13.726

Table II (a): Values of Dielectric parameter	s for various molar ratios
System: Benzamide with Cy	vclohexanol

Band	Ratio Amide: Alcohol	Static dielectric constant ε <sub>0</sub>	Dielectric constant at optical frequency &	Dielectric constant at an angular frequency ε'	Dielectric loss ε"
	3:1	2.4885	2.0206	2.4291	0.0658
J-band	2:1	2.5224	2.0178	2.4437	0.0444
	1:1	2.5784	2.0178	2.4379	0.1126
	1:2	2.6190	2.0192	2.4885	0.1308
	1:3	2.6212	2.0220	2.5332	0.1488
	3:1	2.4886	2.0206	2.3842	0.1243
X-band	2:1	2.6212	2.0178	2.3557	0.1119
	1:1	2.5225	2.0178	2.3072	0.0832
	1:2	2.4886	2.0192	2.3645	0.1137
	1:3	2.4886	2.0220	2.4301	0.1422

Band	Ratio	Relaxation time by Higasi's Method (ps)			α	$\Delta F_{\tau}$	$\Delta F_{\eta}$		
	Amide: Alcohol	$ au_1$	$ au_2$	$ au_{0}$		KJ/mol	KJ/mol		
J–band	3:1	08.50	24.41	14.41	0.074	11.363	13.661		
	2:1	05.19	45.75	15.42	0.076	11.533	13.710		
	1:1	13.62	30.04	20.22	0.045	12.217	13.718		
	1:2	12.43	24.17	17.33	0.037	11.828	13.700		
	1:3	11.96	15.00	13.39	0.054	11.179	13.682		
	3:1	14.37	13.43	13.89	0.020	11.271	13.661		
X-band	2:1	18.89	48.18	27.98	0.006	12.121	13.710		
	1:1	20.71	52.17	32.86	0.006	13.441	13.718		
	1:2	15.14	35.83	23.29	0.004	12.573	13.700		
	1:3	12.45	21.51	16.36	0.065	11.683	13.682		

## Table II (b): Values of Dielectric Relaxation time and activation Energies System: Benzamide with Cyclohexanol

Table III (a): Values of Dielectric parameters for various molar ratio	s
System: Benzamide with Cycloheptanol	

Band	Ratio Amide: Alcohol	Static dielectric constant	Dielectric constant at optical frequency	Dielectric constant at an angular frequency	Dielectric loss
		ε0	€∞	8'	ε"
	3:1	2.4982	2.0207	2.4320	0.0990
J - band	2:1	2.5383	2.0150	2.3975	0.1108
	1:1	2.5836	2.0121	2.4003	0.1100
	1:2	2.6223	2.0164	2.4452	0.1325
	1:3	2.6249	2.0192	2.5007	0.1531
	3:1	2.4981	2.0206	2.3123	0.1014
X -band	2:1	2.5383	2.0149	2.3072	0.1187
	1:1	2.5836	2.0121	2.2904	0.1005
	1:2	2.6223	2.0164	2.3174	0.1223
	1:3	2.6249	2.0192	2.3522	0.1508

Table III (b): Values of Dielectric Relaxation time and activation Energies
System: Benzamide with Cycloheptanol

Band	Ratio	Relaxation	n time Higa (ps)	si's method	~	$\Delta F_{\tau}$	$\Delta F_{\eta}$	
	Amide: Alcohol	$ au_1$	$ au_2$	$ au_{_0}$	ŭ	KJ/mol	KJ/mol	
	3:1	12.567	17.716	14.921	0.0092	11.451	13.711	
l bond	2:1	16.903	30.575	22.734	0.0087	12.512	13.750	
J – band	1:1	16.145	39.237	25.169	0.0087	12.769	13.823	
	1:2	15.275	31.570	21.960	0.0086	12.425	13.784	
	1:3	13.824	19.741	16.520	0.0086	11.708	13.713	
	3:1	24.370	29.337	26.738	0.0073	12.921	13.711	
	2:1	28.291	31.157	29.690	0.0073	13.185	13.750	
X –band	1:1	30.282	46.685	37.599	0.0076	13.780	13.823	
	1:2	25.778	39.885	32.065	0.0073	13.379	13.784	
	1:3	22.395	28.940	25.458	0.0069	12.797	13.713	



Fig. 1: Relaxation time Vs volume % of amides with cycloalcohols in 1,4-dioxane (J-band)



Fig. 2: Relaxation time Vs volume % of amides with cycloalcohols in 1,4-dioxane (X-band)

#### REFERENCES

- 1. Thenappan T and Sankar U. Dielectric Studies of Hydrogen Bonded Complexes of Alcohols with N, N-Dimethyl Formamide. J Mol Liq. 2006;126:38-42.
- Chaudhari A More NM and Mehrotra SC. Static Dielectric Constant and Relaxation time for the binary mixture of water, Ethanol, N, N-Dimethylformamide, Dimethylsulphoxide, and N, N-

Dimethylacetamide with 2-Methoxyethanol, Bull Korean Chem Soc. 2001;22:257-361.

- Chaudhari A Chaudhari H and Mehrotra SC. Dielectric Properties for the Binary Mixture of Dimethylsulphoxide and Dimethylacetamide with 2-Nitrotoluene at Microwave Frequencies. Fluid Phase Equil. 2002;201:107.
- Pawar VP and Mehrotra SC. Dielectric Relaxation Study of Chlorobenzene– Dimethylformamide Mixtures Using Time Domain Reflectometry. J Mol Liq. 2002;95:63-74.
- Guo YQ Liang XH. Phase transition properties of polyethylene glycolcellulose blends and their miscibility in mixed solvents. J Micro molecular Sci B. 1999;38:449-459.
- Sengwa RJ and Rakhee Chaudhary. Microwave dielectric relaxation and molecular dynamics in binary mixtures of poly (propylene glycol) 2000 and poly (ethylene glycol)s of varying molecular weight in dilute solution. Polymer Int. 2001;50:433-441.
- Rachocki A Mickiewicz E and Tritt-Goc J. Dielectric Relaxation in Cellulose and its Derivatives. Acta Physica Polon. A. 2005;108:137-145.
- 8. Malathi M Sebasen R and Krishnan S. Dielectric relaxation studies of *N*,*N*dimethyl formamide and *N*,*N*-dimethyl acetamide on complexation with phenols. Mater. Sci. Eng. B. 2003;100:318-322.
- Antony A Smyth CP. Microwave absorption and molecular structure in liquids. LIII. Hydrogen bonding and dielectric properties in chloroform mixtures. J Am Chem. Soc. 1996;386(2):152-156.
- Sharma V Thakur N Sharma DR Negi NS and Rangra VS. Dielectric relaxation study of binary mixtures of ethyl alcohol and DMF in benzene solution from microwave absorbtion data. Ind J Pure &Applied Phys. 2007;45:163-167.
- S. M. Khameshara, M. L. Sisodia. Dielectric relaxation study of some substituted anilines in various non-polar solvents. Adv Mol Relax Int Processes. 1980;16(3):195-207.
- 12. Eyring H and Cernuschi F. Elementary theory of condensation. J Chem Phys. 1939;7:547-551.

- 13. Kumar S Sivakumar S and Jeevanandham P. Molecular interaction and dielectric relaxation studies of cycloalcohols with acetamide in a nonpolar solvent using frequency domain technique. International Journal of Recent Scientific Research. 2010;7:177-181.
- 14. Tucker SW and Walker S. Dielectric studies. Part 10. Relaxation of two intermolecularly hydrogen bonded complexes. Trans Faraday Soc. 1966;62:2690-2694.
- 15. Srivastava KK Vij JK. Dielectric relaxation and molecular structure. I. Dielectric relaxation in substituted anilines. Bull. Chem. Soc., Japan, 1970;43:2307-2312.
- Reeves LW Sheddick RC and Shaw KN. Nuclear Magnetic Resonance Studies of Multi-site Chemical Exchange. III. Hindered Rotation in Dimethylacetamide, Dimethyl Trifluoroacetamide, and Dimethyl Benzamide. Can J Chem. 1971;49(22):3683-3691.
- 17. Smyth CP Ratajczak H Orville-Thomas WJ. Molecular interactions. Vol II, Wiley, New York, 1981.