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# MOLECULAR INTERACTION AND DIELECTRIC RELAXATION STUDIES OF CYCLOALCOHOLS WITH ACETAMIDE IN A NON-POLAR SOLVENT USING FREQUENCY DOMAIN TECHNIQUE

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## Abstract

The molecular interaction and dielectric relaxation studies were carried out between Cycloalcohols such as cyclopentanol, cyclohexanol and cycloheptanol with Acetamide in 1,4-dioxane. The experiment was carried out by using X-band (9.34GHz) and J-band (7.22GHz) microwave benches at 303K. The dielectric constants of the solutions were measured by using a Dipole meter DM01 operating at a frequency of 2 MHz. From the derived dielectric parameters like $\varepsilon_0$, $\varepsilon_\infty$, $\varepsilon'$, $\varepsilon''$, the dipole moment ($\mu$) by both Onsager and Higasi's methods are compared and the excess properties ($V^E$,$\eta^E$) were determined. The Kirkwood correlation factor (g') were also calculated. g' described something about the orientational ordering of molecules in a liquid through the angular correlations of neighboring dipoles and hence a measurement of g' would give useful information about the local structure of the liquid. The relaxation times ($\tau$) by Higasi's method for both binary and ternary liquid mixtures were calculated. From the ternary results it is observed that the relaxation time is found to be maximum at 1:1 complexes. Further it is evident from our data that the molar free energy of activation for viscous flow ($\Delta F_\eta$) is greater than that of the free energy activation for relaxation time ($\Delta F_\tau$).



***Key words***: Acetamide, Cycloalcohols, dielectric relaxation and molecular interaction.

## INTRODUCTION

Amides are the simplest molecule containing peptide linkage and study of their hydrogen bonding yields into the nature of the protein structure (Jeffrey *et al.*, 1991). Amides are used as synthetic reagents. Understanding the mutual interaction of amides with hydroxyl groups is important in relation to the conformational stability of proteins (Makhatadze *et al.*, 1992). Being the simplest models for peptides, amides have been the subject of several structural studies. In hydrogen bonded complexes a redistribution of electron density can occur due to three types of interactions namely, electrostatic, polarization and charge transfer interaction. Alcohols are excellent proton donors.

Alcohols play an important role in many chemical reactions due to their ability to undergo self-association with manifold internal structures and are in wide use in industry and as reagents, solvents and fuels (Bass *et al.*, 1964). Hydrogen bonds constitute a very interesting class of intermolecular interactions, which are of extreme importance in many fields of chemistry and molecular biology. Several researchers (Sabesan *et al.*, 2002; Thenappan *et al.*, 2001; Huyskens *et al.*, 1982; Singh *et al.*, 1983; Chelliah *et al.*, 1994; Ratajczak *et al.*, 1970 and Subramanian *et al.*, 2001) have studied the complex of alcohols and phenols with ketones, esters, piperidones, nitriles and amines in recent years using dielectric methods. Computer simulation studies of amides (Essex *et al.*, 1995) show that there are only marginal differences in the liquid structures of amides as represented by the radial distribution function but wide variations in the dielectric constant and almost the same dipole moment pose problems in establishing the proper potential function to account for the proton acceptor-donor properties of amides.

The dielectric investigation of hydrogen bonded compounds in non-polar solvent provides valuable information regarding molecular complex formation in solutions. The study of the H-bonds of the type O-H$^{\cdots}$O=C occupies a position of considerable importance as it relates to the study of biopolymers. Thus the study and knowledge of dielectric properties of the mixtures of Acetamide with three cycloalcohols such as

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cyclopentanol ($C_5H_9OH$), cyclohexanol ($C_6H_{12}O$) and cycloheptanol ($C_7H_{14}O$) in non-polar solvents is expected to provide useful and vital process parameters for industrial interest. Keeping both the industrial and scientific interests in mind, all attempts have been made in the present work to study the hydrogen bonding between free hydroxyl group of cycloalcohols and the carbonyl group of acetamide. This study is expected to provide better understanding of the nature of molecular interaction process. Further dielectric dispersion studies of polar liquids and their binary mixtures were carried out with a view for determining the electric dipole moment and relaxation time. The experiment was carried out using a cavity perturbation technique at 9.34GHz (X-band) and 7.22GHz (J-band).

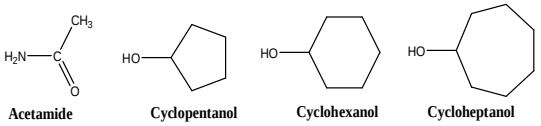


Fig. 1. Structure of Acetamide, cyclopentanol, cyclohexanol and cycloheptanol

## Experimental

According to Higasi's method (Higasi *et al.*, 1996), $\tau_{(1)}$ stands for molecular relaxation time of the complex as a whole and is given by,

$$\tau_{(1)} = \frac{1}{\omega}\left[\frac{a''}{a' - a_\infty}\right] \qquad (1)$$

And $\tau_{(2)}$ indicates the relaxation time of the individual or base molecule of amides.

$$\tau_{(2)} = \frac{1}{\omega}\left[\frac{a_0 \quad a'}{a''}\right] \qquad (2)$$

Higasi parameters such as $a_0$, a', a" and $a_\infty$ are defined by the equation (3)

$$\varepsilon_0 = \varepsilon_1 + a_0 w_2 \qquad \ldots(3a)$$

$$\varepsilon' = \varepsilon_1 + a' w_2 \qquad \ldots(3b)$$

$$\varepsilon'' = a'' w_2 \qquad \ldots(3c)$$

$$\varepsilon_\infty = \varepsilon_{1\infty} + a_\infty w_2 \qquad \ldots(3d)$$

The mean relaxation time is given by,

$$\tau_{(0)} = \sqrt{\tau_{(1)}\tau_{(2)}} \qquad \ldots(4)$$

The free energy of activation for dielectric relaxation ($\Delta F_\tau$) and viscous flow ($\Delta F_\eta$) has been calculated by using Eyring's equation (Eyring *et al.*, 1963)

$$\tau = \left[\frac{h}{kT}\right]\exp\left(\frac{\Delta F_\tau}{RT}\right) \qquad \ldots(5)$$

$$\eta = \left[\frac{N_A h}{V}\right]\exp\left(\frac{\Delta F_\eta}{RT}\right) \qquad \ldots(6)$$

The values of relaxation time and activation energies are given in Table II, III and IV. Kirkwood correlation factor g' is given by

$$g' = \frac{9KTM_2}{4\pi N_A \mu_2^2 W_2 (\varepsilon_\infty + 2)^2}\left[\left(\frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_{2\infty})}{\varepsilon_0 d}\right)\left(\frac{W_1(\varepsilon_1 - \varepsilon_{1\infty})(2\varepsilon_1 - \varepsilon_{1\infty})}{\varepsilon_1 d1}\right)\right] \ldots(7)$$

## RESULT

Table 1 shows the variation of dielectric parameters ($\varepsilon_0$) and ($\varepsilon_\infty$) with mole fraction of the acetamide. The dipole moment by both Onsager and Higasi's were calculated and are reported. Excess properties such as excess molar volume ($V^E$) and excess viscosity ($\eta^E$) were also calculated and are presented in Table I. Depends upon the values of ($V^E$) and ($\eta^E$) the nature of molecular interactions were discussed. The concentration of the Acetamide increases the dipole moment values were also increases. The excess molar volumes ($V^E$) were found to be negative (Fig.4). It means that the contractive factors dominate over the expansion factors. The negative ($V^E$) arises due to dominance of the following two factors. They are

- Chemical interaction between constituent molecules such as hetero molecular association through the formation of H – bond, often termed as strong specific interaction and
- Association through weaker physical force or any other force of this kind.

The excess viscosities ($\eta^E$) were also found to be negative. It means the dispersion forces are dominant. It is confirmed from our data that the molar free energy of activation for viscous flow ($\Delta F_\eta$) is greater than that of, the free energy of activation for dielectric relaxation ($\Delta F_\tau$). The Kirkwood correlation factor g′ were also calculated and are reported. As the concentration of Acetamide increases the g′ values get decreases. The obtained values are greater than unity. It indicates that parallel orientation of dipoles takes place. The linear correlation factor is a shape dependent parameter that helps in a qualitative interpretation of the liquid structure. (Fig.2)

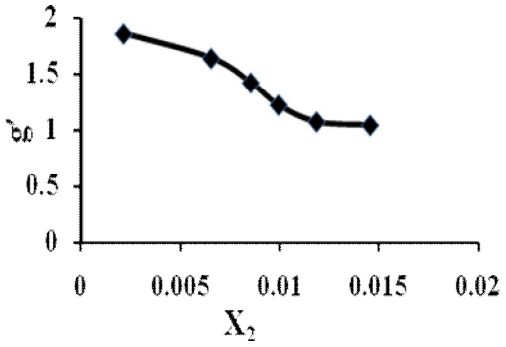


**Fig. 2. Variation of g' with mole fraction of Acetamide**

**Table 1. Variation of $\varepsilon_0$, $\varepsilon_\infty$, $\mu$, $V^E$, $\eta^E$ and g' with mole fraction of Acetamide**

| Mole fraction $X_2$ | $\varepsilon_0$ | $\varepsilon_\infty$ | Dipole moment ($\mu$) Onsager (D) | Higasi (D) | $V^E$ $x10^{-6}$ $m^3$ $mol^{-1}$ | $\eta^E$ $x10^{-3}NSm^{-2}$ | g' |
|---|---|---|---|---|---|---|---|
| 0.0021 | 2.3885 | 1.9824 | 3.33 | 3.61 | -0.3278 | -0.7625 | 1.86 |
| 0.0065 | 2.4227 | 1.9852 | 3.40 | 3.62 | -3.5144 | -0.7550 | 1.64 |
| 0.0085 | 2.4408 | 1.9881 | 3.57 | 3.65 | -6.1372 | -0.7481 | 1.42 |
| 0.0099 | 2.5108 | 1.9909 | 3.71 | 3.67 | -7.8226 | -0.7450 | 1.22 |
| 0.0118 | 2.6370 | 1.9937 | 3.79 | 3.72 | -9.3800 | -0.7407 | 1.07 |
| 0.0145 | 2.7521 | 1.9965 | 3.86 | 3.86 | -12.153 | -0.7344 | 1.04 |

**Table 2. Dielectric data, relaxation parameter and activation energies for Acetamide + 1,4-dioxane system at 303K**

| Band | $X_2$ | ε' | ε '' | Relaxation time (ps) $\tau_1$ | $\tau_2$ | $\tau_0$ | Activation energy KJ/mol $\Delta F\tau$ | $\Delta F\eta$ |
|---|---|---|---|---|---|---|---|---|
| X-band | 0.0021 | 2.2433 | 0.1387 | 28.86 | 18.06 | 22.83 | 12.37 | 13.30 |
| | 0.0065 | 2.2483 | 0.1750 | 30.70 | 19.95 | 24.75 | 12.57 | 13.44 |
| | 0.0085 | 2.2500 | 0.2217 | 30.83 | 22.62 | 26.41 | 12.73 | 13.49 |
| | 0.0099 | 2.2528 | 0.2778 | 35.00 | 28.05 | 31.33 | 13.16 | 13.50 |
| | 0.0118 | 2.2546 | 0.2920 | 37.78 | 35.49 | 36.62 | 13.24 | 13.53 |
| | 0.0145 | 2.2556 | 0.3395 | 43.30 | 41.12 | 42.20 | 13.30 | 13.55 |
| J-band | 0.0021 | 2.2838 | 0.1587 | 22.72 | 16.06 | 19.10 | 11.93 | 13.30 |
| | 0.0065 | 2.2875 | 0.1956 | 24.59 | 15.51 | 19.40 | 11.96 | 13.44 |
| | 0.0085 | 2.2915 | 0.2402 | 41.51 | 09.41 | 19.83 | 12.02 | 13.49 |
| | 0.0099 | 2.2974 | 0.2956 | 71.61 | 07.81 | 23.48 | 12.44 | 13.50 |
| | 0.0118 | 2.3035 | 0.3161 | 101.18 | 05.92 | 24.56 | 12.55 | 13.53 |
| | 0.0145 | 2.3095 | 0.3638 | 172.51 | 03.96 | 26.14 | 12.71 | 13.55 |

**Table 3. Variation of dielectric parameters, relaxation time and activation energies in ternary systems of Acetamide with Cycloalcohols using X-band**

| System | Ratio | $\varepsilon_0$ | $\varepsilon_\infty$ | ε ' | ε '' | Relaxation time (ps) $\tau_{(1)}$ | $\tau_{(2)}$ | $\tau_{(0)}$ | $\Delta F\tau$ KJ/mol | $\Delta F\eta$ KJ/mol |
|---|---|---|---|---|---|---|---|---|---|---|
| Acetamide + Cyclopentanol | 3:1 | 2.4338 | 2.2200 | 2.3384 | 0.0930 | 20.12 | 16.34 | 18.13 | 11.94 | 13.22 |
| | 2:1 | 2.5104 | 2.2220 | 2.3567 | 0.1220 | 21.48 | 20.14 | 20.80 | 12.28 | 12.66 |
| | 1:1 | 2.4255 | 2.2201 | 2.3128 | 0.1580 | 43.78 | 10.52 | 21.45 | 12.36 | 12.49 |
| | 1:2 | 2.4725 | 2.2230 | 2.3482 | 0.1290 | 22.42 | 15.44 | 19.82 | 12.16 | 12.36 |
| | 1:3 | 2.4858 | 2.2250 | 2.3714 | 0.1300 | 16.10 | 17.70 | 16.88 | 11.76 | 12.32 |
| Acetamide + Cyclohexanol | 3:1 | 2.4161 | 2.2245 | 2.3332 | 0.1190 | 29.47 | 11.15 | 18.13 | 11.94 | 13.21 |
| | 2:1 | 2.4191 | 2.2260 | 2.3175 | 0.1230 | 41.58 | 13.18 | 23.41 | 12.58 | 13.21 |
| | 1:1 | 2.4266 | 2.2260 | 2.3129 | 0.1320 | 49.12 | 13.32 | 25.58 | 12.81 | 13.22 |
| | 1:2 | 2.4169 | 2.2280 | 2.3270 | 0.1210 | 35.02 | 11.86 | 20.38 | 12.24 | 13.21 |
| | 1:3 | 2.3771 | 2.2305 | 2.3255 | 0.1100 | 34.617 | 07.49 | 16.12 | 11.64 | 13.12 |
| Acetamide + Cycloheptanol | 3:1 | 2.4279 | 2.2305 | 2.3384 | 0.160 | 40.04 | 08.30 | 18.27 | 11.69 | 12.85 |
| | 2:1 | 2.4217 | 2.2275 | 2.3504 | 0.127 | 37.91 | 13.03 | 22.31 | 12.45 | 12.86 |
| | 1:1 | 2.4003 | 2.2230 | 2.3107 | 0.186 | 85.96 | 08.46 | 26.98 | 12.94 | 12.96 |
| | 1:2 | 2.3815 | 2.2260 | 2.3107 | 0.157 | 62.55 | 07.26 | 21.32 | 12.35 | 12.88 |
| | 1:3 | 2.3505 | 2.2290 | 2.3082 | 0.125 | 56.86 | 05.43 | 17.58 | 11.86 | 12.84 |

**Table 4. Variation of dielectric parameters, relaxation time and activation energies in ternary systems of cycloalcohols with acetamide using J-band**

| System | Ratio | $\varepsilon_0$ | $\varepsilon_\infty$ | $\varepsilon'$ | $\varepsilon''$ | Relaxation time (ps) | | | $\Delta F\tau$ KJ/mol | $\Delta F\eta$ KJ/mol |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $\tau_1$ | $\tau_2$ | $\tau_0$ | | |
| **Acetamide + Cyclopentanol** | 3:1 | 2.4338 | 2.2200 | 2.4191 | 0.0710 | 09.96 | 04.53 | 06.72 | 09.44 | 12.81 |
| | 2:1 | 2.5104 | 2.2220 | 2.4527 | 0.0836 | 09.72 | 15.11 | 12.12 | 10.92 | 12.66 |
| | 1:1 | 2.4255 | 2.2201 | 2.3175 | 0.0981 | 19.80 | 12.03 | 15.43 | 11.53 | 12.49 |
| | 1:2 | 2.4725 | 2.2230 | 2.4279 | 0.0931 | 12.34 | 10.67 | 11.48 | 10.79 | 12.36 |
| | 1:3 | 2.4858 | 2.2250 | 2.4712 | 0.7730 | 08.31 | 04.13 | 05.86 | 09.09 | 12.31 |
| **Acetamide + Cyclohexanol** | 3:1 | 2.4161 | 2.2245 | 2.3665 | 0.0600 | 13.27 | 17.36 | 14.56 | 10.94 | 13.20 |
| | 2:1 | 2.4191 | 2.2260 | 2.3585 | 0.0637 | 15.29 | 20.78 | 15.87 | 11.60 | 13.21 |
| | 1:1 | 2.4266 | 2.2260 | 2.3527 | 0.0814 | 21.30 | 19.85 | 20.56 | 12.25 | 13.22 |
| | 1:2 | 2.4169 | 2.2280 | 2.3582 | 0.0683 | 17.04 | 18.77 | 17.89 | 11.90 | 13.20 |
| | 1:3 | 2.3771 | 2.2305 | 2.3459 | 0.0566 | 17.14 | 12.04 | 14.37 | 11.35 | 13.18 |
| **Acetamide + Cycloheptanol** | 3:1 | 2.4217 | 2.2305 | 2.3663 | 0.0965 | 16.41 | 17.41 | 16.91 | 11.76 | 12.85 |
| | 2:1 | 2.4279 | 2.2275 | 2.3504 | 0.0777 | 21.24 | 21.82 | 21.55 | 12.37 | 12.86 |
| | 1:1 | 2.4003 | 2.2230 | 2.3293 | 0.0948 | 32.82 | 16.38 | 23.19 | 12.56 | 12.96 |
| | 1:2 | 2.3815 | 2.2260 | 2.3329 | 0.0716 | 24.54 | 14.82 | 19.07 | 12.07 | 12.88 |
| | 1:3 | 2.3505 | 2.2290 | 2.3247 | 0.0652 | 27.11 | 08.66 | 15.33 | 11.52 | 12.84 |

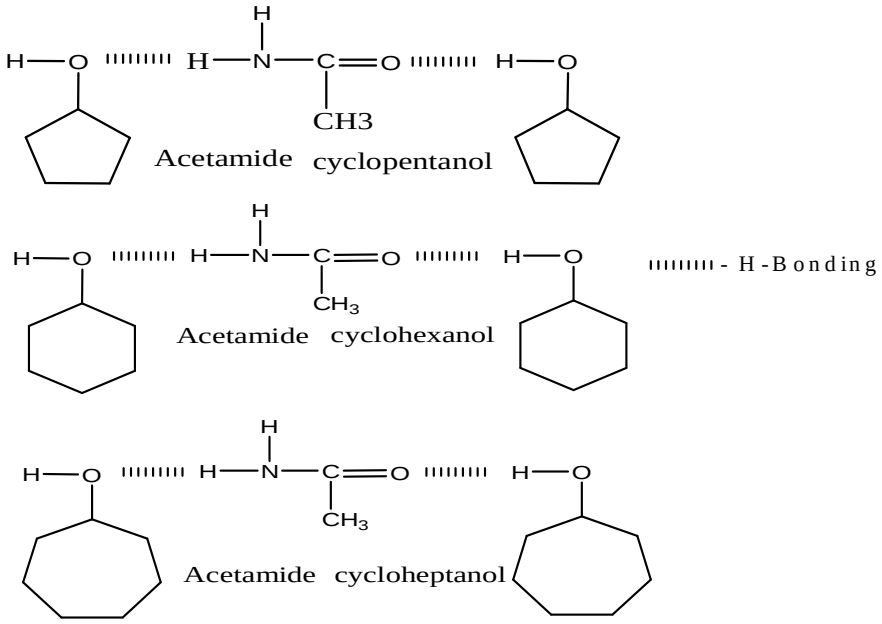


**Fig 3. H-bonding between Acetamide with Cycloalcohol molecules**

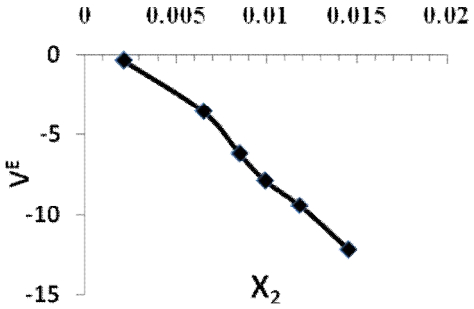


**Fig. 4. Variation of $V^E$ with mole fraction of Acetamide**

Table II shows the variation of dielectric permittivity (ε′), dielectric loss (ε″), relaxation times (τ) by Higasi method, and the activation energy parameters ($\Delta F_\tau$) for relaxation time and ($\Delta F_\eta$) for viscous flow for acetamide + 1,4-dioxane system at X-band (9.43 GHz) and J-band (7.22 GHz) microwave regions with mole fraction of the solute. From Table II it is understood that dielectric permittivity (ε′) values increases as the concentration of acetamide increases in both the X and J-bands. Similar pattern were observed for the dielectric loss (ε″) values also. Further the dielectric permittivity (ε′) value for a particular concentration is observed high for J-band and low for X-band. (i.e) ε′ is inversely proportional to the frequency, $\varepsilon' \alpha \frac{1}{\gamma}$. Similarly the dielectric loss (ε″) is low at X-band and little bit high for J-band for the particular concentration. The value of distribution parameter (α) for both binary and ternary systems are appreciable, which implies more than one relaxation mechanism. In binary system the relaxation ($\tau_0$) time was calculated by Higasi method. $\tau_1$ may due to relaxation time of the complex as a whole and $\tau_2$ may be due to the individual or the base molecule (acetamide). In our case also $\tau_{(1)}$ is found to be higher than that of $\tau_{(2)}$. As the concentration of the solute molecule increases in a non-polar solvent then the mean relaxation time ($\tau_0$) values are also increases for both X and J-bands.

Acetamide is a good proton donor and acceptor. So the molecule takes relaxation for this system is high and intermolecular interaction is high. Table III shows the variation of dielectric quantities such as $\varepsilon_0, \varepsilon_\infty, \varepsilon'$, and ε″, relaxation times $\tau_{(1)}, \tau_{(2)}$ and $\tau_{(0)}$ and activation energies ($\Delta F\tau$) and ($\Delta F\eta$) for three ternary systems of acetamides+cycloalcohols at different ratios for the X-band. In ternary systems we are using three different cycloalcohols namely cyclopentanol, cyclohexanol and cyclopentanol as donor molecules. Acetamide was used as acceptor molecule. The chain lengths of these alcohols were increased step by step by increasing number of carbon and hydrogen atoms. From the cycloalcohols with acetamide in the dielectric medium, the relaxation mechanism is attributed in the OH direction of alcohol with co-direction of amide. In all the three systems studied, the relaxation time is found to be maximum at 1:1 complexation.

Similar observations are also made from the table IV for J-band. From table III and IV it is inferred that the chain length of alcohol increases the relaxation time values are also increases (i.e., at 1:1 complexation). Hence the relaxation time is in the order of cycloheptanol > cyclohexanol > cyclopentanol. Further it is evident from our data that the molar free energy of activation for viscous flow ($\Delta F\eta$) is greater than that of the free energy of activation ($\Delta F\tau$) for dielectric relaxation for both binary and ternary systems. The various H-bonding between Cycloalcohols and Acetamide were shown in fig (3).

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