

Studies of Hydrogen Bonding Between N, N-Dimethylacetamide and Primary Alcohols

M.S. Manjunath*, P. Sivagurunathan^a and J. Sannappa

*Department of Physics, Yuvaraja's College, University of Mysore,
Mysore, Karnataka, India*

**Corresponding author. E-mail: manjumsphy@yahoo.com*

*^aDepartment of physics, Annamalai University, Annamalai Nagar,
Tamilnadu-608002, India*

Abstract

Hydrogen bonding between N, N-Dimethylacetamide (DMA) and alcohols has been studied in carbon tetrachloride solution by an X-band Microwave bench at 936GHz. The dielectric relaxation time τ of the binary system are obtained by both Higasi's method and Gopalakrishna method. The most likely association complex between alcohol and DMA is 1:1 stoichiometric complex through the hydroxyl group of the alcohol and the carbonyl group of amide. The results show that the interaction between alcohols and amides is 1:1 complex through the free hydroxyl group of the alcohol and the carbonyl group of amide and the alkyl chain-length of both the alcohols and amide plays an important role in the determination of the strength of hydrogen bond (O-H: C=O) formed and suggests that the proton donating ability of alcohols is in the order: 1-propanol < 1-butanol < 1-pentanol and the accepting ability of DMA.

Introduction

Alcohols are industrially and scientifically important organic compounds and the hydroxyl group of alcohol are largely determines their physical and chemical properties. Amides are the simplest molecules containing peptide linkage and a study of their hydrogen bonding ability yields insight into the nature of protein structure. The role of non-covalent interactions in stabilizing polypeptide structure was studied by Lcao-Mo-SCF method¹. X-ray diffraction² and NMR method³ Amides are associated through inter-molecular hydrogen bonding and also show strong dependence on solvent environment, temperature and concentration^{4,5}. To understand the molecular behavior of associating molecules it is necessary to determine the

various dielectric parameters, which are related to inter- and intra-molecular association and internal rotation with temperature variation⁶. The Kirkwood theory of dipolar liquids⁷ defines the short-range dipolar interactions through a dimensionless parameter (g).

In the present work, the hydrogen bonding between hydroxyl group of alcohol and carbonyl group of DMA in carbon tetrachloride has been studied.

Material and Method

The N, N-dimethylacetamide (>99% pure) used in this investigation were purchased from Aldrich and used without further purification. AnalaR grade alcohols and carbon tetrachloride (>99.5% pure) were purified by standard methods⁸. The physical parameters of all the chemicals used here have been checked against their literature values.

The measurement of dielectric constant (ϵ') and dielectric loss (ϵ'') were carried out in the X-band microwave frequency of 9.84 GHz. The experimental set-up and the procedure employed were the same as reported by Aggarwal et al⁹. The values of ϵ' and ϵ'' so obtained are accurate within $\pm 1\%$ and $\pm 5\%$, respectively. The static dielectric constants (ϵ_0) were measured by heterodyne beat method at 303 K using a commercial instrument, Dipole meter DM 01 supplied by wissenschaftliche Technische Werkstatter, Germany operated at 220 volts. Error in the measurement of ϵ_0 is less than $\pm 0.5\%$. The refractive indices were measured by an Abbe's refractometer with an accuracy of ± 0.0005 . The percentage of deviation in the measurement of refractive index is about $\pm 0.02\%$. The temperature of all the measurements were maintained at $30 \pm 0.1^\circ\text{C}$ using water circulating thermostat.

The proton donors (alcohols) and the acceptors (N, N-dimethylacetamide) under study were separately dissolved at the same molar concentration in the solvent carbon tetrachloride. Their dielectric constants were measured separately. Then the two solutions were mixed in different proportions but with the total concentration kept at a fixed value and were subjected to the dielectric constant measurements. As the maximum deviation of dielectric constant for all the systems studied occurs at equimolar ratio of the solutes, it is presumed that the deviation is due to the formation of 1:1 complexes alone.

The dielectric relaxation time τ have been calculated by Higasi's method¹⁰, the overall dielectric relaxation time $\tau_{(1)}$ is best described by

$$\tau_{(1)} = \frac{a''}{\omega(a' - a_\infty)} \quad \text{-----}[1]$$

While the average dielectric relaxation time $\tau_{(2)}$ is given by,

$$\tau_{(2)} = \frac{(a_0 - a')}{\omega a''} \quad \text{-----}[2]$$

The most probable mean relaxation time $\tau_{(0)}$ is obtained by,

$$\tau_{(0)} = \sqrt{\tau_{(1)} \tau_{(2)}} \quad \text{-----}[3]$$

Where ω is the angular frequency selected for the measurements and assuming ϵ' , ϵ_0 , ϵ_∞ and ϵ'' vary linear with weight fraction w_2 of the solute.

The Debye equation in terms of a_0, a', a'' and a_∞ yields two independent equations¹¹ [1] and [2].

$$\epsilon_0 = \epsilon_1 + a_0 w_2 \quad \text{-----[4]}$$

$$\epsilon^1 = \epsilon_1 + a^1 w_2 \quad \text{-----[5]}$$

$$\epsilon'' = a'' w_2 \quad \text{-----[6]}$$

$$\epsilon_\infty = \epsilon_{1\infty} + a_\infty w_{2\infty} \quad \text{-----[7]}$$

in which subscript 1 refers to the pure solvent and 2 refers to the solute, 0 refers to the static frequency and ∞ refers to the infinite or optical frequency measurements and w_2 is the weight fraction of the solute.

The values of relaxation time are given in Table 1.

Results and Discussion

In Present study we are concerned with interaction of the OH group and C=O groups with surrounding molecules in Carbon tetrachloride solution. The possibility of solute–solute hydrogen bonding in particular will be investigated.

The systems selected were N, N-dimethylacetamide with proton donors (1-propanol, 1-butanol, 1-pentanol) using carbon tetrachloride as solvent. The static dielectric constant (ϵ_0), dielectric constant at infinite dilution (ϵ_∞), dielectric constant at an angular frequency (ϵ^1), dielectric loss factor (ϵ'') and dielectric relaxation time (τ_0) for N, N-dimethylacetamide with proton donors (1-propanol, 1-butanol, 1-pentanol) in carbon tetrachloride at 303 K are provided in Table 1. A perusal of Table 1 shows that, the value of relaxation time increases with increasing chain length of alcohols and N, N-dimethylacetamide and offers hindrance to the rotation of the molecule. The increase in relaxation time may be due to the increase in effective radius of the rotating unit.

This result indicates the hydrogen bond, that is formation of molecular structure between the hydrogen atom in O-H group of alcohol and the oxygen atom in C=O group of amide and is shown in figure.1 below

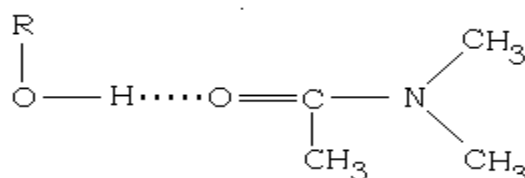


Figure 1: Hydrogen bond between alcohols and DMA.

Where, R = C₃H₇ (1-propanol), C₄H₉ (1-butanol), C₅H₁₁ (1-pentanol)

From figure 2 it is observed that the values of dielectric relaxation time are highest for the system 1:1 molar ratio when compared to 3:1, 1:2, 2:1 and 3:1 molar ratio. This result conforms that molecular association are maximum in 1:1 molar ratio of DMA with Primary alcohol.

Table 1: Values of dielectric constants and relaxation time at 303 K.

| Mole fraction | System | ϵ_0 | ϵ_∞ | ϵ^l | ϵ^{l1} | Relaxation time (ps) | | |
|---------------|-------------------------------------------------|--------------|-------------------|--------------|-----------------|----------------------|--------------|--------------|
| | | | | | | $\tau_{(1)}$ | $\tau_{(2)}$ | $\tau_{(0)}$ |
| 3:1 | | 2.8096 | 2.2156 | 2.6499 | 0.2681 | 11.3 | 10.1 | 10.68 |
| 2:1 | DMA+ 1-Propanol with carbon tetrachloride | 2.8603 | 2.2164 | 2.5784 | 0.2692 | 13.9 | 17.8 | 15.72 |
| 1:1 | | 2.9546 | 2.2258 | 2.5898 | 0.2765 | 14.2 | 22.4 | 17.83 |
| 1:2 | | 2.8546 | 2.2158 | 2.5765 | 0.2665 | 13.8 | 17.7 | 15.62 |
| 1:3 | | 2.8226 | 2.2153 | 2.574 | 0.2465 | 12.8 | 17.1 | 14.79 |
| 3:1 | | 2.7096 | 2.1156 | 2.4876 | 0.2481 | 12.4 | 15.2 | 13.72 |
| 2:1 | DMA+ 1-Butanol with carbon tetrachloride | 2.8603 | 2.1946 | 2.497 | 0.2662 | 16.7 | 23.2 | 19.68 |
| 1:1 | | 2.9546 | 2.2258 | 2.4998 | 0.2765 | 19.4 | 28.01 | 23.31 |
| 1:2 | | 2.8546 | 2.1798 | 2.4938 | 0.2695 | 16.2 | 22.8 | 19.21 |
| 1:3 | | 2.8226 | 2.1153 | 2.4874 | 0.2465 | 12.3 | 23.1 | 16.85 |
| 3:1 | | 2.6996 | 2.0156 | 2.376 | 0.2181 | 10.9 | 25.2 | 16.57 |
| 2:1 | DMA+ 1-Pentanol with carbon tetrachloride | 2.7803 | 2.0946 | 2.3954 | 0.2462 | 15.6 | 26.6 | 20.37 |
| 1:1 | | 2.8546 | 2.0989 | 2.399 | 0.2545 | 16.1 | 30.4 | 22.12 |
| 1:2 | | 2.7546 | 2.0798 | 2.3938 | 0.2395 | 14.4 | 25.6 | 19.2 |
| 1:3 | | 2.6226 | 2.0153 | 2.3874 | 0.2265 | 12.3 | 17.7 | 14.75 |
| 3:1 | | 2.6996 | 2.0156 | 2.376 | 0.2181 | 10.9 | 25.2 | 16.57 |

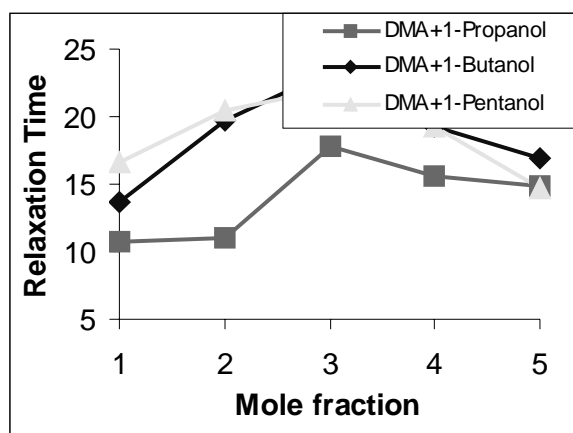


Figure 2: variation of dielectric relaxation time with molefraction.

Conclusion

Hydrogen bonded complexes of DMA with primary alcohols (1-propanol, 1-butanol and 1-pentanol) in carbon tetrachloride were determined. From this study, one may conclude that the proton donating ability of alcohols and the proton accepting ability of amide linearly vary with the alkyl chain length of both alcohols and amides and plays a significant role in the determination of dielectric properties of the above systems studied. It may concluded that from present study the proton donating power of the primary alcohol are in the order of 1-propanol < 1-butanol < 1-pentanol. The relaxation time of proton acceptor increases, as donating ability of solute environment increases. The increasing in relaxation time provides information regarding the orientation of dipoles between the interacting compounds.

References

- [1] J A Jeffrey and W Saeriger, Hydrogen bonding in biological structures (Springer, Berlin,1991)
- [2] M Dreyfus and A Pullman, Theor. Chim. Acta **19**, 20 (1970)
- [3] O F Nielson and P A Lard, Chem. Phys. Lett, **78**, 1981 (1981)
- [4] O F Nielson and P A Sabesan and S Krishna, Mater. Sci. Eng. **B100**, 318 (2003)
- [5] M Malathi , R Sabeen and S Krishna, J. Mol. Liquids. **109**, 11 (2004)
- [6] M Malathi , R Sabeen and S Krishna, Mater. Sci. Eng. **B104**, 1 (2003)
- [7] H Frohlich , Theory of dielectrics (Clarendon Press , Oxford , 1958)
- [8] Vogel, A. I.; *Text Book of Practical Organic Chemistry*. 3rd edn., Longman, London, 1957
- [9] Aggarval, C.; Arya, R.; Gandhi J. M; Sisodia, M. L. *J. Mol. Liq.*, **44** 161 (1990)
- [10] Higasi, K.; Koga Y.; Nagamura, M. *Bull. Chem. Soc. Japan*, , **44** , 988 (1971)