International Journal of Pure and Applied Physics
ISSN 0973-1776 Volume 4 Number 1 (2008) pp. 71–76

http://www.ripublication.com/ijpap.htm

Molecular association of amides with 1-propanol in non-polar solvent : Dielectric study

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Abstract

Experimental results of dielectric investigations of X-band microwave bench at 9.86Ghz for amides (Foramide, N-methylforamide and N, N-dimethylformaide) with 1-propanol have been studied in carbon tetrachloride at 303 K. The relaxation time has been determined using the measured dielectric data. The results show that carbonyl group of amide and alkyl chain-length of both the alcohols and amides plays an important role in the determination of the strength of hydrogen bond (O-H:O=C) formed. The most likely association between alcohol and amides is 1:1 complex through the free hydroxyl group of the alcohol and the carbonyl group of amide and the results show a linear dependence of relaxation time on alkyl chain length of alcohols and alkyl amides and also on the nature of the solvent.

Keywords: Dielectric relaxation; Hydrogen bonding; Solvent

Introduction

Amides are the simplest molecules containing a peptide linkage and a study of their hydrogen bonding yields into the nature of protein structure [1]. Amides are used as synthetic reagents. The lower amides like methylamide, ethylamide and dimethylamide are used as starting materials for the preparation of the insecticides and pharmaceuticals. It is a versatile synthetic reagent. Alcohols play an important role in many chemical reactions due to the ability to undergo self-association with manifold internal structures and are in wide use in industry and as reagents, solvents and fuels [2]. Hydrogen bonds constitute a very interesting class of intermolecular interactions, which are of extreme importance in many fields of chemistry and molecular biology. The dielectric investigation of hydrogen-bonded compounds in non-polar solvent provides valuable information regarding molecular complex formation in solution. The study of the H-bonds of the type O=H-----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 amides with 1-propanol in non-polar solvents is expected to provide useful and vital process parameters for efficient design of transesterification processes of industrial interest. Keeping both the industrial and scientific interests in mind, an attempt has been made in the present work to study the hydrogen bonding between free hydroxyl group of 1-propanol and the carbonyl group of amides using dielectric method. This study is expected to provide better understanding of the nature of molecular orientation processes.

The dielectric relaxation behaviors of amides are expected to be similar to that of n-alcohols [3,4].

Experimental details and theory

The measurements of wavelengths in the dielectric and voltage standing wave ratio were made at 9.86 GHz using a slotted line and short circuiting plunger. The calculations of ε' and ε'' were made following the method of Heston adopted for short-circuited termination. The accuracy of measurement of ε' and ε'' is+1% and+5% respectively. The dipolemeter based on the principle of heterodyne beat method was used for the measurement of the static permittivity ε_0 at 300 KHz. Refractive indices were measured by a Abbe's refractometer which, in turn, gives the optical permittivity [5]. The amides used in this investigation were purchased from Aldrich and used without further purification. AnalaR grade carbon tetrachloride and alcohols (>99.5% pure) were purified by standard methods [6-7]. The physical parameters of all the chemicals used here have been checked against their literature values.

The proton donors (alcohols) and the acceptors (amides) under study were separately dissolved at the same molar concentration (0.3 mol .L^{-1}) in the solvents (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 equal molar ratio of the solutes, it is presumed that the deviation is due to the formation of 1:1 complexes alone.

According to Higasi's method [8], the individual relaxation time $\tau_{(1)}$ is described by

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

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

$$\tau_{(2)} = \frac{1}{\omega}\left[\frac{a_o - a'}{a''}\right] \tag{2}$$

Where ω is the angular frequency a_o, a', a'' and a_∞ are defined by equation-3

$$\begin{aligned} \varepsilon_o &= \varepsilon_1 + a_o W_2 \\ \varepsilon' &= \varepsilon_1 + a' W_2 \\ \varepsilon'' &= a'' W_2 \\ \varepsilon_\infty &= \varepsilon_{1\infty} + a_\infty W_2 \end{aligned} \quad (3)$$

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 frequency measurements and w2 is the weight fraction of the solute.

The average relaxation time is given by $\tau_{(0)} = \sqrt{\tau_{(1)}\tau_{(2)}}$ (4)

Results and discussion

The systems selected were amides (Foramide, N-methylforamide, N, N-dimethylformamide) with proton donors (1-propanol) using carbon tetrachloride.

The dielectric parameter [9] ε_o, ε', ε'', ε_∞ for different molar ratio and the individual relaxation time $\tau_{(1)}$, overall dielectric relaxation $\tau_{(2)}$ and average relaxation time $\tau_{(0)}$ of amides with proton donors in carbon tetrachloride at 303 K temperatures have been provided in tables 1 – 3. A perusal of tables 1 – 3 shows that, the value of relaxation time for 1:1 molar ratio is higher than other molar ratio. Form this we can interfere the maximum molecular association between amides with alcohols are at 1:1 ratio. . Several workers [10,11] have reported that the relaxation and thermodynamic parameters increased in ternary solutions (two polar solute in non-polar solvent) if association occurs. The increasing relaxation time is due to increasing chain length of alcohols and amides 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.

The observed higher value of NMF can be attributed to the larger size of NMF molecule in comparison to those of Formamide and DMF molecules. In these systems, the complex formation is likely to occur between Hδ+ of alcohols and $O^{\delta-}$ of C=O group of amides (figure 1). Oxygen atom is sp^3 hybridized and in the amides structure there is a lot of voids available for O—H to penetrate and enter into complexation and also provides information regarding the hydrogen bond between interacting components. The association between amides with 1-propanol are shown in figure-1.

It is also noticed that, though the τ value of mixtures lie between the individual component values, they are in general, different from the averaged value because of the change in the molecular environment and in the size of the relaxing unit. Such behaviors are due to simple overlap of two individual Debye regions. The relation between chemical structure and the relaxation dielectric properties of liquids presents a fascinating puzzle to physical chemists.

From the tables 1 – 3, the value relaxation time is greatest for NMF and least for Formamide. This indicates that solute—solute interaction is in the order of Formamide > DMF > NMF. A large difference in relaxation time values in this molecule is due to the large difference in the two mechanisms viz., the end-over-end rotation and O=H group rotation. The figure-2 shows the variation of static dielectric constant with respect to the relaxation time. The increase in relaxation time may be due to the increase in effective radius of the rotating unit. This may be due to the fact that the CH_3 group attached to the same carbon atom to which the O=H group is attached. This increases the size of the molecule and may cause hindrance to the group rotation, which may give rise to increased relaxation time.

Conclusions

The results of dielectric investigations for amides and alcohols have been studied in dilute solution of carbon tetrachloride. The dielectric properties of the above systems studied are depending on the alkyl chain length of alcohols and amidesThe most likely association between alcohol and amides is 1:1 complex through the free hydroxyl group of the alcohol and the carbonyl group of amide. From the above result it may be conclude that, the proton accepting ability is increasing order Formamide >N, N-dimethylformamide > N-methylformamide.

Acknowledgment

The authors are acknowledges our thanks to Mr. P. Sivagurunathan, Mr. K. Darmalingam and Mr. K. Ramachandran, Annamalai University, for their support of this work.

Table 1 : Values of Dielectric constant, relaxation time (τ) for different mole Ratio (f_2) of formamide and 1-propanol at 303 K.

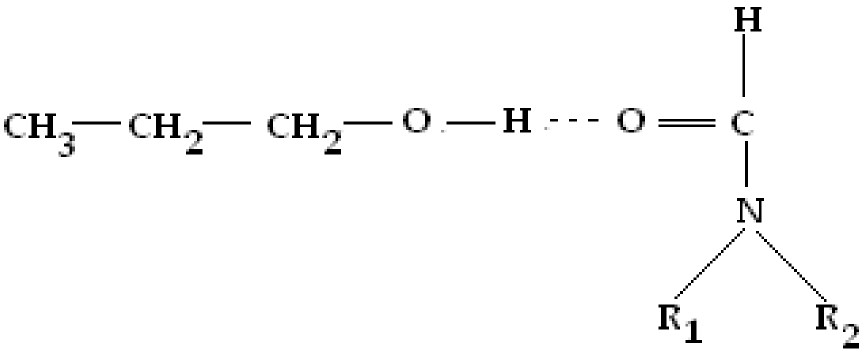
f_2	ε'	ε''	ε_0	ε_∞	τ_1 (Ps)	τ_2 (Ps)	$\tau_{(0)}$ (Ps)
Systems: Foramide+ 1-Propanol with CCl_4							
3:1	2.6109	0.3014	2.9021	2.0078	13.24	14.50	13.85
2:1	2.6385	0.3206	2.9231	2.0091	13.97	15.20	14.57
1:1	2.6582	0.3394	2.9357	2.0093	14.70	15.90	15.29
1:2	2.6281	0.2983	2.8842	2.0076	12.64	14.59	13.58
1:3	2.6014	0.2726	2.8363	2.0064	11.50	12.77	12.12

Table 2 : Values of Dielectric constant, relaxation time (τ) for different mole Ratio (f_2) of N-methylformamide and 1-propanol at 303 K.

f_2	ε'	ε''	ε_0	ε_∞	τ_1 (Ps)	τ_2 (Ps)	$\tau_{(0)}$ (Ps)
Systems: N-methylforamide+ 1-Propanol with CCl_4							
3:1	2.6383	0.2823	3.0768	2.2231	19.79	20.42	20.10
2:1	2.6651	0.2847	3.1053	2.2246	19.87	22.77	21.27
1:1	2.6837	0.2905	3.1106	2.2260	22.62	26.98	24.70
1:2	2.6792	0.22852	3.0821	2.2231	20.01	25.82	22.73
1:3	2.6426	0.2813	3.0672	2.2215	19.57	21.43	20.48

Table 3 : Values of Dielectric constant, relaxation time (τ) for different mole Ratio (f_2) of N, N-dimethylformamide and 1-propanol at 303 K.

f_2	ε'	ε''	ε_0	ε_∞	τ_1 (Ps)	τ_2 (Ps)	$\tau_{(0)}$ (Ps)
Systems: N, N-dimethylformamide+ 1-Propanol with CCl_4							
3:1	2.5928	0.2446	3.0072	2.2127	17.97	18.59	18.28
2:1	2.6241	0.2514	3.0224	2.2141	18.03	19.82	18.91
1:1	2.6543	0.2793	3.0380	2.2156	20.69	24.35	22.45
1:2	2.6392	0.2631	3.0213	2.2112	19.18	21.45	20.28
1:3	2.6028	0.2462	2.9976	2.2112	17.68	19.03	18.34



R_1 = H, R_2 = H; R_1=H, R_2 = CH_3 ; R_1=CH_3, R_2=CH_3

Figure-1 : Hydrogen bond between 1-propanol and Amides

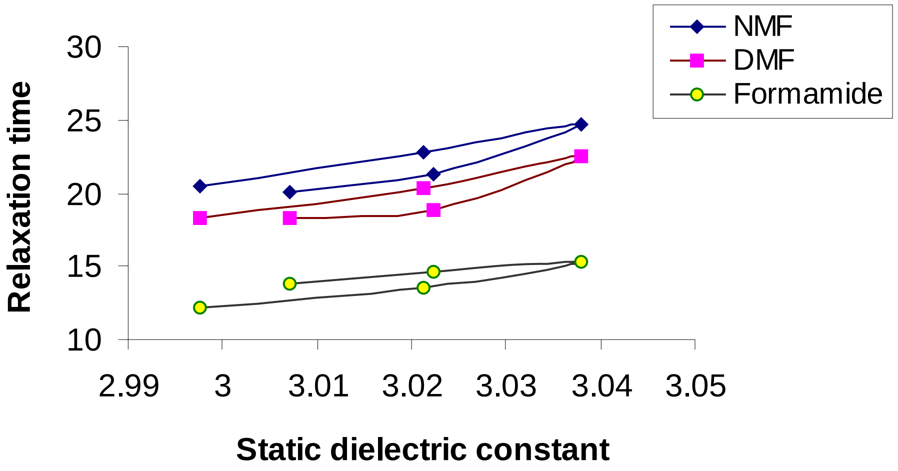


Figure 2 : Variation of dielectric relaxation ($\tau_{(0)}$)with Static dielectric constant (ε_0) of 1-propanol with amides in CCl_4.

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