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MOLECULAR INTERACTION STUDIES OF SOME PHENYL ACETONOTRILE IN BINARY SOLUTIONS

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ABSTRACT

Nitriles ascertain its uses in different therapeutic and industrial application. The dielectric studies of phenylacetonitrile and p-Nitro phenylacetonitrile in the dilute solutions of benzene,1, 4-Dioxane and Carbon Tetra Chloride at 303K were calculated. The dielectric relaxation of binary mixtures of polar liquids along with non polar solvents at microwave frequencies has been attempted. These types of research afford momentous information about intermolecular and intramolecular involvement between the solutes and solvent molecules. The static dielectric constants of phenylacetonitrile and p-Nitroacetonitrile binary solutions in benzene , 1,4-Dioxane and in Carbon Tetra chloride was calculated at 303K by LCR Bridge. Different dielectric parameters at optical frequency have been determined with the help of X-band microwave bench of frequency 9.37 GHz.

Keywords* : *Dielectric relaxation, , phenylacetonitrile, p-Nitrophenyl acetonitrile, Dielectric Constant Molecular Interaction

I. INTRODUCTION

The studies of dielectric constant, dielectric loss, relaxation time of certain pharmacologically important substance play very important role in medical fields. This type of studies gives excellent exploration regarding the structure of the molecules of the system. In liquids, the molecule has greater rotational freedom and its dispersion occurs at microwave frequency in an improved manner . Hence studying the dielectric properties at microwave frequency will reveal the dielectric relaxation of polar molecules and its variation with respect to the interaction with the neighboring polar as well as non polar molecules. The nature and structure of the liquid mixtures can be better understood by the dipole moment determination. Molecular interaction studies and theoretical estimation of ultrasonic speeds using scaled particle theory in binary mixtures of toluene with homologous nitriles at different temperatures were studied by K.Rajagopala et al.[1]. Physicochemical studies of molecular interactions in binary mixtures of toluene with some aliphatic nitriles at different temperatures was also studied by K.Rajagopala et al.[2], Venkatachalam et al[3] investigated hydrogen bonding of nitrile isomers with H2O, HF, NH3 and H2S. Satyen Saha

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et al [4] studied the Effect of Water on the Molecular Structure and Arrangement of Nitrile-Functionalized Ionic Liquids. The molecular electric dipolar relaxation characteristics and structural features in liquids [5]. Shere et al[6]studied the dielectric relaxation of acetonitrile with chlorobenzene at various temperatures and frequencies and showed the changes in the dielectric constants with respect to temperature and concentration. Kalaivani et al [7] studied aniline with acetonitrile with various concentrations at different frequencies. Relaxation studies on phenyl acetonitrile and its para substituted has been carried out by sateesh et a1[8] studied the allyl alcohol with (i) Pyridine, (ii)1,4-Dioxane and (iii)Phenol hydrogen bonded complexes. From the above literature survey it is proved that the molecular interaction studies of nitriles are gaining significance nowadays. In the present studies, in order to provide the binary mixtures of the two nitriles namely Phenyl acetonitrile, p-nitrophenyl acetonitrile in benzne and 1, 4-dioxane at various concentrations, the micro wave region is selected. The investigation anticipated to afford enhanced understanding of the nature of molecular orientation procedure.

II. EXPERIMENTAL DETAILS

In the present investigation, the dielectric relaxation absorption studies of phenyl acetonitrile with p-Nitrophenylacetonitrile is carried out in dilute solutions, Very few organized investigations have been carried out, such as the dielectric behavior and the relaxation behavior of the phenyl acetonitrile, p-Nitrophenylacetonitrile in non-polar solvents, at a temperature of 303K, The measurement of dielectric constant at angular frequency (ε') and dielectric loss (ε'') were carried out in the X-band Microwave bench at 9.37 GHz. In addition the relaxation times τ_1 and τ_2 of solute in the solvent environment were also calculated . The dielectric constant of the liquid at frequency is assumed to be equal to the square of the refractive index ($\varepsilon_\infty = n^2D$) at wavelength λ=5893Å of the visible frequency region. Abbe's Refractometer is used to determine the refractive index of the liquid mixtures. The solutes phenyl acetonitrile and p-Nitrophenylacetonitrile and the solvents benzene, 1-4-Dioxane were purchased from Sigma Aldrich with 99% purification, and used without any further purification.

III. EVALUATION OF DIELECTRIC PARAMETERS

We can see different responses when a material interacts with electric field . Unlike conductors in insulators, electrons do not flow freely, but electronic reorientation or distortions of induced or permanent dipoles can give rise to heating. The material properties of greatest importance in microwave processing of a dielectric are the permittivity (often called the dielectric constant), , and the loss tangent, tanδ. The complex permittivity is a measure of the ability of a dielectric to absorb and to store electrical potential energy, with the real permittivity, characterizing the penetration of microwaves into the material and the loss factor, , indicating the material's ability to store the energy. The most important property in microwave processing is tanδ, indicative of the ability of the material to convert absorbed energy into heat. For optimum coupling, a balanced combination of moderate, to permit adequate penetration, and high loss (maximum and tanδ) is required.

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According to Higasi's method [9], the average relaxation time τ_1 is described by

$$\tau_1 = \frac{a''}{(a'-a_\infty)}$$

While the overall dielectric relaxation $\tau_2$and the mean relaxation time τ_0 is given by,

$$\tau_2 = \frac{(a_0 - a')}{(\omega a'')}$$

$$\tau_0 = \sqrt{\tau_1 \times \tau_2}$$

Where ω is the angular frequency, a_0, a', a'' and a_∞ are defined by the following equations

$$\epsilon_0 = \epsilon_{01}\ a_0 w_2$$

$$\epsilon' = \epsilon_1' + a' w_2$$

$$\epsilon_\infty = \epsilon_{1\infty} + a_\infty w_2$$

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 w2 is the weight fraction of the solute.

TABLE.1. Dielectric parameters for P-nitro Phenyl Acetonitrile+ Phenyl Acetonitrile

W	ε_0	ε'	ε''	ε_∞	Tan (ε''/ ε') $\times 10^{-4}$
Phenylacetonitrile + p-nitro Phenylacetonitrile (Ratio 1:3) with benzene (Ratio 1:3)					
0.004	2.3832	2.3424	0.0211	2.2276	1.5721
0.008	2.3942	2.3577	0.0321	2.2290	2.3762
0.012	2.4054	2.3728	0.0531	2.2305	3.9058
0.016	2.4176	2.3874	0.0633	2.2320	4.6276
0.020	2.4285	2.4021	0.0733	2.2335	5.3258
Phenylacetonitrile + p-nitro Phenylacetonitrile (Ratio 1:3) with 1-4 Dioxane					
0.004	2.3069	2.2591	0.1041	1.9952	8.0441
0.008	2.3181	2.2733	0.1343	1.9946	10.3117
0.012	2.3293	2.2875	0.1647	1.9980	12.5664
0.016	2.3405	2.3017	0.1949	1.9994	14.7885
0.020	2.3517	2.3159	0.2252	2.0008	16.9717

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Phenylacetonitrile + p-nitro Phenylacetonitrile (Ratio 1:3)with Carbon Tetra Chloride					
0.004	2.4831	2.4421	0.0461	2.4568	3.296
0.008	2.4943	2.4573	0.0583	2.4582	4.1408
0.012	2.5055	2.4725	0.0704	2.4597	4.9695
0.016	2.5151	2.4877	0.0837	2.4612	5.8722
0.020	2.5282	2.5029	0.0959	2.4627	6.6873

IV. DISCUSSIONS

Solvents play a imperative function in the areas of chemical synthesis. Solvents are of two types namely (i) polar solvents and (ii) non-polar classified depending on the dielectric constant. Polar solvents have a strong dielectric constant and they have one or more electronegative atoms. In the present study, there are three non-polar solvents (benzene, CCl4, 1,4-dioxane) with low dielectric constants have choosen. . Bonds between atoms with similar electro negativities will lack partial charges. These lone pairs are being highly electronegative, polarizable with the neighbor protic substance, which leads to increasing relaxation time. Therefore in our binary system, there is a possibility of dipolar interaction with non-polar solvents (benzene, CCl4 &1,4-dioxane). It is seen from the tabular column Table.1, the Double solute systems of Phenylacetonitrile, p-nitro phenylacetonitrile in Benzene, 1,4–Dioxane and Carbon tetra Chloride forms dilute solutions, there is a linear variation of dielectric parameters (ε_0, ε', ε'' and ε_∞) with the increasing concentration. While observing the values of ε_0, ε', and ε_∞ of the binary mixture in dilute solutions, they are found to be morein carbon tetra chloride solution compare ti benzene and 1,4-Dioxane. It is in very good agreement with the literature values[9] , that for aliphatic compounds the dielectric constants are more than the substituted benzene compounds.

The molecular and overall relaxation times along with the distribution parameter α for the system is presented in the table Table.2. The order of variation of the relaxation times and the distribution parameter is found to be good agreement with the literature values. From the Table 2, it is found that the two relaxation times are well separated by representing the rotation of complex as a whole, while the other representing the rotation of one of the interacting polar solute molecule . The significant increase in τ values provides the information regarding the orientation of diploes between the interacting components. Regarding the distribution parameter as suggested by many researchers[10,11,12,13], as the complex is rigid, its distribution parameter is larger. So it noticed that the value of the distribution parameter is more in Nitriles with benzene than in 1, 4-Dioxane. The activation energy increases with the increases of molecular size as reported by Helembe et

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al[14]. The dipole moment of Nitriles is more in 1,4-Dioxane compare to Benzene due to its high dielectric constant and high polarity compare to benzene.

TABLE.2. Higasi Parameters for P-nitro Phenyl Acetonitrile+ Phenyl Acetonitrile

System		τ (1)	τ (2)	τ	A	ΔF_τ $KJMol^{-1}$	μ		
							HD	H&KD	GD
P-nitro Phenyl Acetonitrile+ Phenyl Acetonitrile	Benzene	8.54	34.52	17.17	0.4119	10.044	4.38	4.38	4.39
	1, 4-Dioxane	15.58	52.85	28.70	0.35	11.558	4.49	4.49	4.53
	Carbon Tetra chloride	15.52	52.79	28.69	0334	11.511	4.39	4.39	4.41

V.CONCLUSION

The Weak interactions between the molecules or the intramolecular interactions are the long range forces which are having energies 4-40 kJ/mole [13, 14], while the strong and short range forces will be in the range of 400 kJ/ mole. In the present study, the free energy of activation from dipolar rate process is observed to be around 10-11 kJ/mole. consequently it may be concluded that the systems studied involve themselves only in weak interaction in conformity with Abramaczyk et al[15] that the dipolar interaction is insignificant in Nitrile complexes with OH bonded systems.

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