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Dielectric Relaxation Phenomena of nicotinamide with1-propanol from Conductivity Measurement under 9.385 GHz Electric Field

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ABSTRACT

Dielectric relaxation studies of nicotinamide (j) and 1-propanol(k) dissolved in nonpolar solvent(i)benzene (C_6H_6) at 25^0C are attempted by measuring the conductivity of the solutions under 9.385 GHz electric field using Debye theory. The estimated relaxation time (τ_{jk}'s) and dipole moment (μ_{jk}'s) agree well with the reported values signifying the validity of the proposed method. Solute-solvent and solute-solute molecular associations are ascertained in different molecular environments. The associational aspects are taken into consideration from theoretical μ_{theo} from the standpoint of inductive, mesomeric and electromeric effects within the polar groups of the molecules. The thermodynamic energy parameters are calculated from Eyring rate theory to predict the molecular dynamics of the system.

Keywords

Binary mixture, dipole moment, relaxation time, solute-solvent association.

1.INTRODUCTION

Dielectric investigations in polar liquids dissolved in non polar solvents provide meaningful information on structural and associational aspect as well as formation of molecular complexes in GHz electric field under varying conditions of complexation, temperature and environmental factors because of the capacity of microwaves to detect weak molecular association [1-2]. Nicotinamide being a constituent of polar mixtures has wide biological importance. It forms a part of water soluble vitamin B group which is useful in maintenance of cellular energy balance. Two human genes encoding nicotinamideriboside kinases that are highly specific for activation of a class of anticancer, antiviral and immunosuppressive prodrug. It protects beta cell reducing the risk of developing diabetes. 1-propanol, on the other hand, is used as a solvent in the pharmaceutical industry mainly for resin and cellular estar. Dielectric behaviors of mixtures of different industrial and biological important polar solvents like amides and alcohols under different concentration have gained considerable interest[3,4]because it helps in formulating adequate models of liquid relaxation and information on solute-solute and solute-solvent molecular association from the relaxation process in polar mixtures. The understanding of the mutual interaction between amides and hydroxyl group of alcohols is important in relation to the conformation stability of proteins. Hetero molecular hydrogen bond dynamics may play a significant role in conformational changes of the binary polar mixtures under investigation using conductivity measurement of relaxation parameters. We, therefore, thought to make an extensive study on nicotinamide and 1-propanol polar mixture dissolved in non-polar solvent C_6H_6 in terms of measured real σ_{ijk}' and imaginary σ_{ijk}'' parts of high for different mole fractions M_j's of polar solute nicotinamide under 9.385 GHz electric field at 25^0C. The conductivity measurement technique is concerned with bound molecular charge of the polar molecules unlike permittivity $\in_{ij}$'s and susceptibility χ_{ij}'s which are related to all types of polarization and orientational polarization respectively. In recent past, conductivity measurement technique [5] in the microwave electric fields has been successfully applied on binary polar mixture [6] dissolved in nonpolar solvents. However, no such rigorous study has been made so far on nicotinamide + 1-propanol mixture dissolved in C_6H_6 at 25^0C temperature under 9.385 GHz electric field using conductivity measurement technique. The purpose of the conductivity measurement technique concerning bound molecular

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charge of the polar molecule allows one to link the results of dielectric studies to throw light on structure and dynamics of polar liquid mixture in solution inferred from other techniques [7]. The aim of the present paper is also to see the applicability of conductivity measurement technique within the frame work of Debye model in liquid polar-non polar mixture under high frequency (9.385 GHz) electric field like earlier [8].

2. EXPERIMENTAL PROCEDURE

Polar as well as non-polar materials taken for investigation are AR grade and used without further purification. Different mole fractions of nicotinamide dissolved in non-polar solvent will be prepared using micro pipet and a magnetic stirrer to make dilute solutions. Five different weight fractions of each polar-non polar mixture will be studied with help of a Network Analyzer assembly using high temperature dielectric probe technique for dielectric property (Permittivity, ε) measurement of polar-non polar mixture. The High Temperature Probe measurement procedure consists of Rohde & Schwarz made ZNB-20 Vector Network Analyzer, Dielectric Assessment Kit (DAK) and DAK Evaluation software as shown in Fig. 1. The probe will be immersed into the polar-non polar mixture sample. The fields at the probe end "fringe" into the material and changes as they come into contact with the material. The resulting measured reflections (reflection coefficient, S_{11}) are then converted into dielectric properties values (permittivity, ε) via DAK Evaluation software. The system is capable of determining permittivity up to 20 GHz. Prior to usage, the high temperature dielectric probe kit needs to be calibrated using three elements and the software. The elements are air, a metallic shorting block and water. The temperature of the dielectric cell was maintained through circulating water and a thermostat. The measured $\in_{ij}'$ and $\in_{ij}''$ are accurate within ±0.5% and ±1.67% respectively.

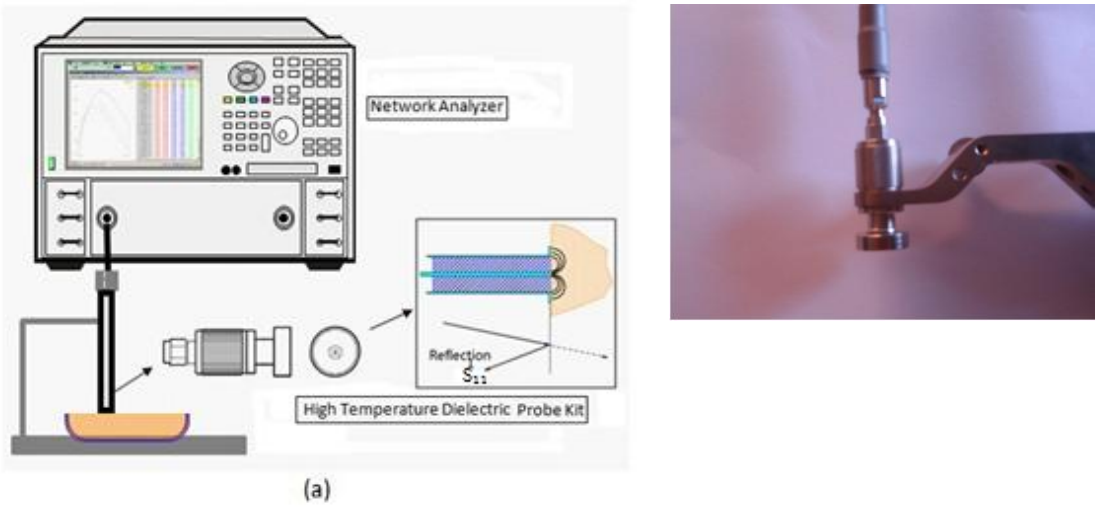

Fig. 1.(a) Network Analyzer Setup; (b) Coaxial Probe with flange

3. THEORETICAL FORMULATIONS

The high frequency conductivity of binary solution can be written by simple normalization of permittivity data as [6]

$$\sigma^*_{ijk} = \sigma_{ijk}' + j\sigma_{ijk} \qquad (1)$$

where $\sigma_{ijk}' = \omega\in_0\in_{ijk}''$ and $\sigma_{ijk}'' = \omega\in_0\in_{ijk}'$ are the real and imaginary parts of complex conductivity σ^*_{ijk} at different weight fractions w_{jk}'s of polar mixture and placed in Table 1.

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The imaginary parts of conductivity σ_{ijk}'' is related to σ_{ijk}' by the following relation [6]

$\sigma_{ijk}'' = \sigma_{\infty ijk} + (1/\omega\tau_{jk})\,\sigma_{ijk}'$ or, $\tau_{jk}=1/\omega\beta'$ (2)

where, β' is the slope of σ_{ijk}''- σ_{ijk}' linear relation of Fig. 2 as shown in Table 2. Both σ_{ijk}'' and σ_{ijk}' are the functions of w_{jk}'s at different mole fractions of nicotinamide.

To eliminate the effect of polar-polar interactions in the estimation of τ_{jk}, one can safely use (2) in following form

$$^{2}_{jk} = \frac{1}{\mu}\frac{^{2}}{_{1}} \qquad (3)$$

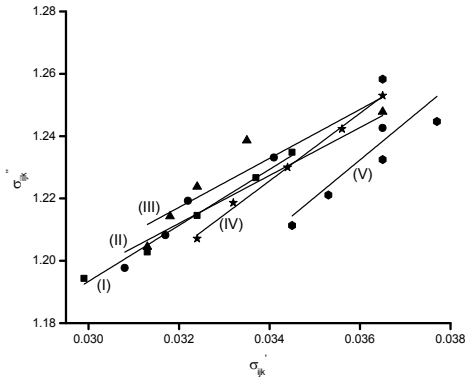

Fig 2: Imaginary part of σ_{ijk}'' against σ_{ijk}' of nicotinamide + 1-propanol dissolved inC_6H_6 at 25^{0}C under 9.385 GHz electric field. (I) —■— at 0.01 (II) —●— at 0.015 (III)— ▲—at 0.020 (IV) —★—at 0.025 (V)—⬢— at 0.03 mole fraction of nicotinamide respectively.

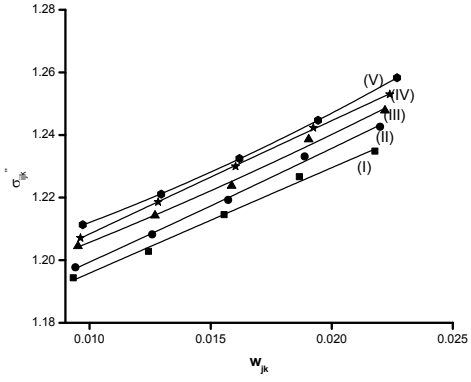

Fig 3: Variation of imaginary part of conductivity (σ_{ijk}'') against weight fraction w_{jk}'s ofNicotinamide + 1-propanol dissolved inC_6H_6 at 25^{0}C under 9.385GHz electric field. : (I) —■— at 0.01 (II) —●—at .015(III)— ▲— at 0.020(IV) —★—at 0.025(V)—⬢— at 0.03 mole fraction of nicotinamide respectively.

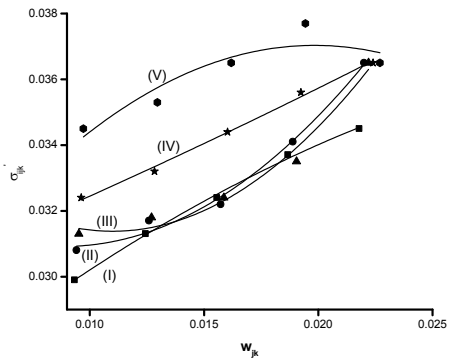

Fig 4: Variation of real part of conductivity (σ_{ijk}') against weight fraction w_{jk}'s of Nicotinamide+ 1-propanol dissolved inC_6H_6 at 25^{0}C under 9.385GHz electric field. (I) —■— at 0.01 (II) —●—at .015(III) — ▲— at 0.020(IV) —★—at 0.025(V) —⬢— at 0.03 mole fraction of nicotinamide respectively.

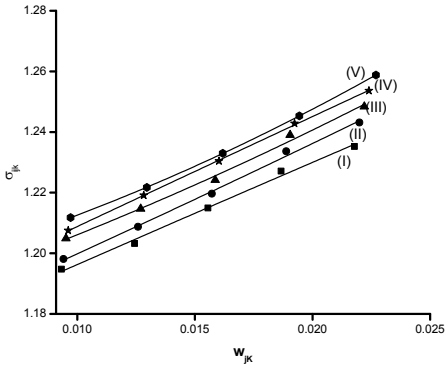

Fig.5:Variation of total conductivity (σ_{ijk}) against weight fraction w_{jk}'s of Nicotinamide+ 1-propanol dissolved in C_6H_6 at 25^{0}C under 9.385GHz electric field.:I) —■— at 0.01 (II)—●— at .015(III) — ▲— at 0.020(IV) —★—at 0.025(V)— ⬢—at 0.03 mole fraction of nicotinamiderepectively.

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Table 1.Reports measured dielectric relaxation parameters like real ±$_{ijk}^{à}$ and imaginary ±$_{ijk}^{ð}$parts of high frequency complex conductivity ±$_{ijk}^{*}$ for different weight fractions w_{jk} of binary polar mixture (Nicotinamide+1-propanol) in benzene for 0.01, 0.015, 0.20, 0.025 & 0.030 mole fractions x_j of Nicotinamide at 25îC temperature respectively under 9.385 GHz electric field.

System	Mole fraction	Weight fraction	±$_{ijk}^{à}$ (t $^{-1}$m^{-1})	±$_{ijk}^{ð}$(t $^{-1}$m^{-1})	±$_{ijk}$(t $^{-1}$m^{-1})
Nicotinamide + 1-propanol	0.01	0.00933	0.0299	1.1943	1.1947
		0.01244	0.0313	1.2028	1.2032
		0.01556	0.0324	1.2145	1.2149
		0.01867	0.0337	1.2266	1.2271
		0.02179	0.0345	1.2348	1.2352
Nicotinamide + 1-propanol	0.015	0.00942	0.0308	1.1977	1.1981
		0.01259	0.0317	1.2082	1.2087
		0.01573	0.0322	1.2192	1.2196
		0.01889	0.0341	1.2331	1.2336
		0.022	0.0365	1.2426	1.2431
Nicotinamide + 1-propanol	0.020	0.00952	0.0313	1.2045	1.2049
		0.0127	0.0318	1.2143	1.2147
		0.01587	0.0324	1.2238	1.2242
		0.01905	0.0335	1.2386	1.239
		0.0222	0.0365	1.2478	1.2484
Nicotinamide + 1-propanol	0.025	0.00962	0.0324	1.2071	1.2075
		0.01283	0.0332	1.2186	1.2191
		0.01603	0.0344	1.23	1.2304
		0.01924	0.0356	1.2423	1.2428
		0.0224	0.0365	1.253	1.2536
Nicotinamide + 1-propanol	0.030	0.00972	0.0345	1.2113	1.2118
		0.01296	0.0353	1.2211	1.2217
		0.01619	0.0365	1.2325	1.233
		0.01944	0.0377	1.2447	1.2453
		0.0227	0.0365	1.2583	1.2588

whereβ_1 and β_2 are the slopes of σ_{ijk}''- w_{jk} and σ_{ijk}'- w_{jk} curves (Fig. 3 & Fig. 4) at $w_{jk}\rightarrow 0$ as shown in Table 2. τ's are estimated from both the methods of (2) and (3) and they are placed in Table 2 along with reportedτ's due to Higasi[7].

In the high frequency region, $\sigma_{ijk}''\approx\sigma_{ijk}$, equation(2) can now be written as

$$\beta = \frac{1}{\omega\tau_j}\left(\frac{d\sigma_{ij}'}{d\omega_j}\right)_{w_j\rightarrow 0} \quad (4)$$

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TABLE 2. Measure relaxation time τ's using ratio of slopes of (σ_{ijk}''-w_{jk}) and (σ_{ijk}'-w_{jk}) curves when $w_{jk} \rightarrow 0$ of equation (3) as well as the σ_{ijk}''- σ_{ijk}' linear curve equation (2), reported τ's due to Higasi method of Nicotinamide + 1-propanol dissolved in C_6H_6 for 0.01, 0.015, 0.20, 0.025 & 0.030 mole fractions x_j of Nicotinamideat 25^{0}C respectively under 9.385 GHz electric field.

System		Mole fraction	Ratio of slopes of (σ_{ij}''-w_j) / (σ_{ij}'-w_j) curves at $w_j \rightarrow 0$ from equation(3)	Slope of σ_{ij}''- σ_{ij}' curve from equation (2)	$\tau_{jk}$from equation (3) (psec)	$\tau_j$from equation (2) (psec)	Reported τ_j (psec) (Higasi method)
Nicotinamide + 1-propanol	I	0.010	0.60237	3.41997	2.99	1.89	2.57
	II	0.015	0.5691	3.34983	2.01	2.21	3.11
	III	0.020	0.8620	2.5273	2.13	2.16	3.43
	IV	0.025	0.27908	3.69451	1.28	1.56	4.17
	V	0.030	1.08068	1.82672	10.03	1.41	4.61

TABLE 3. Estimated slopes β's of (σ_{ijk}-w_{jk}) curve at $w_{jk} \rightarrow 0$,measured dipole moment « from ratio of slopes and linear slope method , reported « by Higasi's method in Coulomb-metre(C.m) for nicotinamide+ 1-propanol dissolved in C_6H_6 for 0.01, 0.015, 0.20, 0.025 & 0.030 mole fractions x_j of Nicotinamide at 25^{0}C respectively under 9.385 GHz electric field.

System		Mole fraction	Slopes of (σ_{ijk}-w_{jk}) curves	Dipole moment $\mu_{jk}\times10^{-30}$ in C.m from equation (3) & equation (5)	Dipole moment $\mu_{jk}\times10^{-30}$ in C.m from equation (2) & equation (5)	Reported Dipole moment in C.m(Higasi method)	ΔF_τ KJ/mole	ΔF_η KJ/mole
Nicotinamide + 1-propanol	I	0.010	3.44615	6.59	6.53	5.73	9.17	12.02
	II	0.015	3.35617	6.46	6.47	4.83	9.14	
	III	0.020	2.44971	5.54	5.54	4.60	8.76	
	IV	0.025	3.66209	6.76	6.77	4.40	9.26	
	V	0.030	1.87075	5.61	4.84	4.27	8.43	

where β is the slope of σ_{ijk}- w_{jk} curves of Fig. 5 at $w_j \rightarrow 0$ and placed in Table 3.

On simplification of (4) one gets

$$« _{jk} = \left[\frac{27M_{jk}K_BT}{N°_i(£_i+2)^2\mu}\right]^{\frac{1}{2}} \qquad (5)$$

The symbols used in equation(5) carry usual meanings [8] in SI unit.

The free energy of activation of dielectric relaxation ΔF_τ and viscous flow ΔF_η has been calculated using Eyring's equation[6] and placed in Table 3.

$$\tau = \left(\frac{h}{kT}\right)\exp\left(\frac{\Delta F_\tau}{kT}\right) \qquad (6)$$

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$$\gamma = \left(\frac{Nh}{V}\right) exp\left(\frac{\Delta F_\eta}{kT}\right) \qquad (7)$$

4.RESULTS & DISCUSSION

The normalized conductivity data σ_{ijk}'s at different w_{jk}'s of nicotinamide+1-propanol dissolved in non polar solvent C_6H_6 extracted from the measured permittivity data are utilized to estimate τ's and μ's for experimental temperature 25^0C at 9.385 GHz electric field by adopting Origin programming and using least squares fitting technique. τ's are estimated from the linear relation σ_{ijk}'' against σ_{ijk}' of Fig. 2 at different w_{jk}'s of nicotinamide+1-propanol at 25^0C temperature. Fig. 2 reveals that the curves are perfectly linear as evident from the values of correlation coefficient r; $-1 \leq r \leq +1$. Using the ratio of slopes of σ_{ijk}''- $w_{jk}$and σ_{ijk}' - w_{jk} curves at $w_{jk} \rightarrow 0$ to estimate τ's as shown in Fig. 3 and Fig. 4 where polar – polar interactions are almost eliminated. It is also observed that τ's from both the methods of equations(2) and (3) are found to agree well with the reported τ's due to Higasi method[7] signifying the applicability of both the methods. The straight lines in Fig. 2 are parallel indicating their same polarity[8] for all systems except system I & IV as evident from τ's of Table 2. τ's from ratio of slopes of equation(3) are, however, smaller in magnitude than equation(2) of Murthy et al [6] except systems I & V. This type of behaviour may be due to solute-solute (dimer) molecular association of the mixture resulting in larger size of molecular entity to yield higher τ's according to Debye relaxation mechanism. It is also interesting to see that all the values of σ_{ijk}'' in Fig. 3 are found to increase with w_{jk}'s under high frequency electric field. This type of nature indicates the absorption of electric energy with increase of solute concentration. All the curves of Fig. 4 are parabolic in nature indicating the solute-solute (dimer) molecular association in the higher concentration region. The dipole moments μ_j's in Coulomb-meter (C.m) are estimated in terms of slopes β's of σ_{ijk} - w_{jk} curves from equation (5). The total high frequency conductivity σ_{ijk}'s are plotted against w_{jk}'s at 25^0C temperature to get parabolic curves as shown in Fig. 5. The curves are similar like σ_{ijk}''- w_{jk} curves of Fig. 3 validating the approximation $\sigma_{ijk}'' \cong \sigma_{ijk}$. The theoretical dipole moment μ_{theo}'s of

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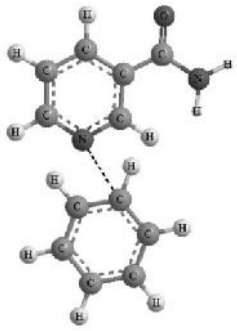

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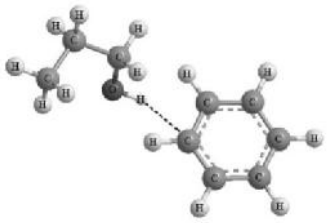

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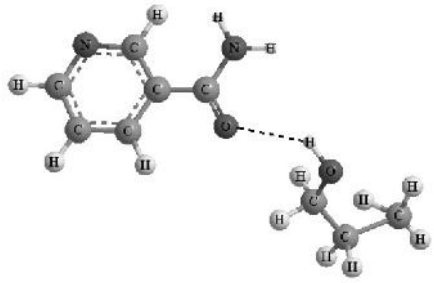

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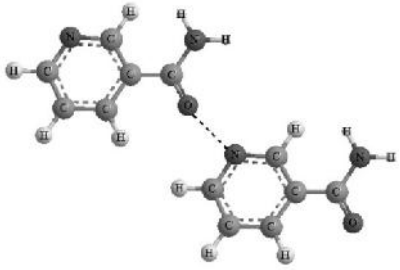

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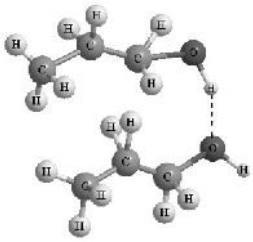

Fig 4: Solute-solvent , solute-solute and self molecularassociations.a) Nicotinamide+C_6H_6 b) 1-propanol+ C_6H_6 c)Nicotinamide+1-propanold) Nicotinamide+Nicotinamide e) 1-propanol+1-propanol.

DMF is ascertained from available bond angle and bond moment of $2.13x10^{-30}$, $1.5x10^{-30}$, $10.33x10^{-30}$, $1x10^{-30}$ for N←CH_3, C←N, C⇐O, and H←C substituent polar groups respectively. The solute-solvent (monomer) molecular association may occur due to interaction of the fractional positive charge (δ+) at the site of N atom of nicotinamideor H atom of 1-propanol andπ delocalized electron cloud in benzene ring as shown in Fig. 6(a) & 6 (b) respectively. The solute-solute(dimer) interaction of nicotinamide and 1-propanol as shown in Fig. 6 (c) may arise due to interaction of the fractional positive charge (δ+) at the site of H atom of 1-propanol and fractional negative charge(δ-) at the site of O atom of nicotinamide. Nicotinamide and 1-propanol molecules undergo self-association through hydrogen bonding as shown in Fig. 6(d) & 6(e). The thermodynamic energy parameters like ΔF_τ's and ΔF_η 's were calculated from equation(7) & (8). ΔF_τ of the polar mixture involves rotation of the participating molecules and at $0.25x_j$'s of nicotinamide with 1-propanol polar mixture faces grater interference from neighbourhood. The estimated $\Delta F_\eta > \Delta F_\tau$ for all polar-non polar mixtures signifying the fact that viscous flow involves both rotational and translational motion whereas dielectric relaxation involves with rotation only.

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