INVESTIGATION OF TEMPERATURE DEPENDENT DIELECTRIC RELAXATION STUDIES OF BINARY MIXTURES OF NICOTINAMIDE AND 1-BUTANOL

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Abstract: Dielectric relaxation behaviour of the binary mixture of nicotinamide and 1-butanol is studied at four different temperatures viz. 303K, 313K, 323K and 333K in dilute solutions of benzene at a constant frequency 9.385 GHz. The values of different dielectric parameters namely ε_0 (static permittivity), ε' (dielectric constant), ε'' (dielectric loss factor) and ε_∞ (optical permittivity) are determined by using standard methods. The measured values of permittivity and dielectric loss have been used to evaluate the relaxation time (τ) and the dipole moment (μ) by Higasi method at different temperatures. The energy parameters (ΔF_ε, ΔH_ε and ΔS_ε) for dielectric relaxation process of the mixture have been calculated at various temperatures and comparison has been made with the corresponding energy parameters (ΔF_η, ΔH_η and ΔS_η) for viscous flow process. It is found that the dielectric relaxation process can be treated as rate process just like the viscous flow process. Present study suggests the existence of both the intramolecular and overall orientation in the binary mixture. The solute-solute and solute-solvent molecular associations have been predicted.
Keywords: Binary mixtures, Dielectric relaxation, Relaxation time, thermodynamical parameters.

1. Introduction

Dielectric studies of solution containing varying amounts of interacting molecules help in detecting the formation and composition of complexes in them. The dielectric relaxation studies of the binary mixture of polar molecules in non-polar solvents using microwave absorption methods have been attempted by many researchers. The present study is undertaken to do the experimental work concerned with the dielectric relaxation process in the binary mixtures of nicotinamide & 1-butanol so as to understand the molecular association of amides in the binary mixtures. Dielectric relaxation studies in the microwave region provide meaningful information about self association, solute-solute and solute-solvent type of the molecular associations among the polar molecules.

Liquid mixtures containing the amide functional group constitute an important technique in

the structural interpretation of complex materials of biological and pharmaceutical interest. Earlier Sengwa et al. [1-5] have extensively investigated the dielectric properties of amides mixed with various polar solvents at fixed temperatures for understanding hydrogen bonding interactions between the amides and the solvents.

2. Material and Methods

For the present investigations, Nicotinamide and Butanol of AR grade were procured from M/s Sisco Research Laboratories Pvt. Ltd. Mumbai, India and were used without further purification. Benzene was also obtained from M/s SRL, India and was used as a solvent. All the measurements are made at a microwave frequency of 9.385 GHz. By mixing NicotinamideandButanol in the calculated proportion, dilute solutions of the binary mixture of required weight fractions were made in Benzene. Since the molecular weight of Nicotinamide is high as compared to that of 1-Butanol, only a small amount of Nicotinamide is dissolvable in Butanol. Dielectric measurements were made for the dilute solutions of binary mixture of a constant mole fraction of Nicotinamide (0.02) and a constant mole fraction of Butanol (0.98) at different temperatures (303K, 313K, 323K and 333K). In the mixture, the sum of the mole fraction of Nicotinamide and mole fraction of 1-Butanol was kept equal to one mole.

The energy parameters for the binary mixture are calculated from the knowledge of their dielectric parameters (ε_0, ε', ε'' and ε_∞) namely the static permittivity, dielectric constant, dielectric loss factor and optical permittivity. The energy parameters for activated process (ΔF_ε, ΔH_ε and ΔS_ε) are evaluated by using Eyring rate equations and are compared with the corresponding energy parameters (ΔF_η, ΔH_η and ΔS_η) for viscous flow at different temperatures. . In the present study, double minima method for low loss liquids proposed by Heston et al. [6] is used. The static permittivity (ε_0) is determined by using a dipolemeter supplied by M/s Mittal Enterprises, New Delhi. Refractive indices of the solutions are measured by Abbe's Refractometer which in turn give the optical permittivity ($\varepsilon_\infty = n_d^2$) [7]. All the measurements are performed at four temperatures using a constant temperature water bath, fitted with a thermostat having temperature stability of the order of $\pm 0.1°C$.

3. Results and Discussions

In the present study, we are concerned with the interactions of the OH group and C = O group with the surrounding molecules in Benzene. The selected system is nicotinamide with 1-butanol using benzene as solvent. The static permittivity (ε_0), the permittivity at optical

frequencies (ε_∞), dielectricconstant at microwave frequency (ε') and dielectric loss factor (ε''), for binary mixtures of nicotinamide with 1-butanol in dilute solutions with benzene are determined at four different temperatures, their values are displayed in Table 1. It is found from the perusal of this table that both ε' and ε'' vary linearly with the weight fraction of solute in Benzene for the binary mixture. This shows that there is no change in the nature of the rotating molecular entities in the Benzene solution [8]. The calculated values of the various relaxation times (τ_1, τ_2 and τ_0) and dipole moment values are also presented in Table 1.It may be observed from this table that both τ_1 and τ_2 decrease systematically with the increase in temperature from 303K to 333K for the binary mixture. This behaviour may possibly be due to two reasons namely, (i) due to increase in the molar volume and (ii) due to increase in size of the dipole with increase in temperature. In these mixtures, we may expect more than one mechanism at all the temperatures, as the differences between τ_1 and τ_2 are significantly large. This implies that the dielectric absorption by its molecules is not solely contributed by their rotation as a single unit, but also contains contribution from the intramolecular rotations, i.e. it indicates the existence of an intramolecular relaxation process in addition to the overall relaxation process. From these observations, it may be concluded that in these mixtures, the intramolecular rotations are dominant as compared to the molecular rotations. The average relaxation time (τ_0), as shown in the Table decreases with increase in temperature from 303K to 333K for the mixtures investigated in the present study.

Table 1: Values of the dielectric parameters, relaxation time and dipole moment for binary mixture of Nicotinamide and 1-Butanol at different temperatures and different weight fractions of solute in dilute solution of Benzene.

Weight fraction (W_2)	ε'	ε''	ε_0	ε_∞	τ_1(ps)	τ_2 (ps)	τ_0 (ps)	μ_H in Debye
Temperature:303K								
0.00951	2.313	0.061	2.372	2.256	2.88	6.30	3.72	1.43
0.01269	2.335	0.061	2.399	2.270				
0.01587	2.358	0.063	2.411	2.282				
0.01904	2.381	0.064	2.449	2.296				
0.02222	2.402	0.067	2.462	2.312				

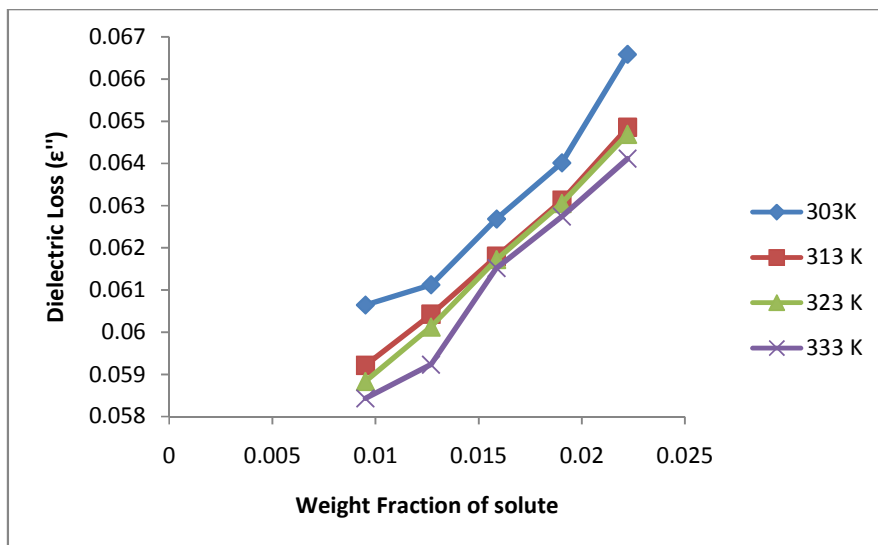| Temperature:313K								
0.00951	2.295	0.059	2.357	2.256	2.59	5.83	3.34	1.49
0.01269	2.320	0.060	2.387	2.269				
0.01587	2.335	0.062	2.406	2.280				
0.01904	2.365	0.063	2.437	2.294				
0.02222	2.387	0.065	2.449	2.311				
Temperature:323K								
0.00951	2.278	0.059	2.322	2.252	2.37	5.33	3.01	1.62
0.01269	2.295	0.060	2.354	2.265				
0.01587	2.317	0.062	2.366	2.280				
0.01904	2.337	0.063	2.392	2.293				
0.02222	2.378	0.065	2.427	2.306				
Temperature:333K								
0.00951	2.259	0.058	2.316	2.238	2.34	4.32	2.75	1.67
0.01269	2.286	0.059	2.342	2.251				
0.01587	2.306	0.062	2.361	2.269				
0.01904	2.322	0.063	2.390	2.280				
0.02222	2.361	0.064	2.413	2.289				

Figure 1: Variation of dielectric loss (ε'') with weight fraction of the binary mixture of 0.02 mole of Nicotinamide in 0.98 mole of 1- Butanol in dilute solutions with benzene at different temperatures
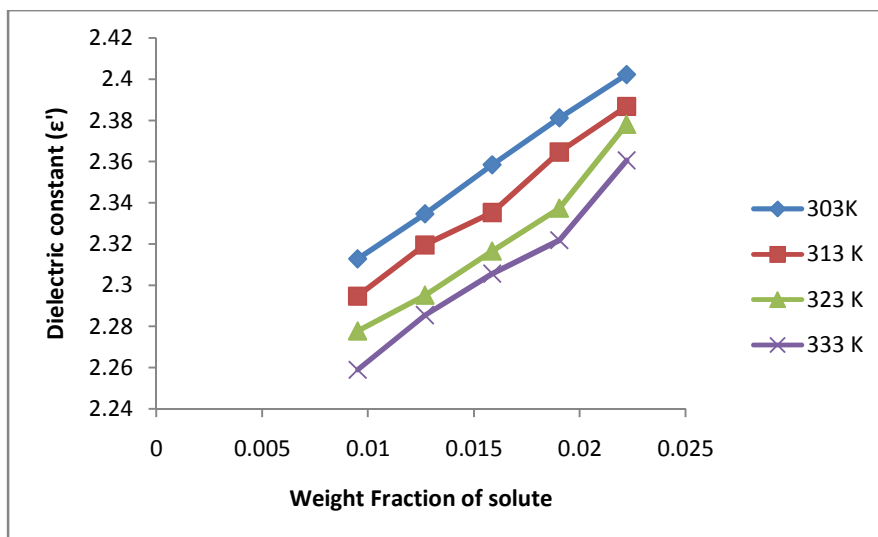

Figure 2: Variation of dielectric constant (ε') with the weight fraction of the binary mixture of 0.02 mole of Nicotinamide in 0.98 mole of 1- Butanol in dilute solutions with benzene at different temperatures

It may also be observed from the table that the values of dipole moment of molecules for the binary mixtures increase as the temperature increases. The increase in the dipole moment values may be attributed to the increase of the size of the dipole with increase in temperature. For the binary mixtures of nicotinamide and 1-butanol, it is found that variation between ln (τT) and (10^3/T) is a straight line as we can observe from Figure 3.
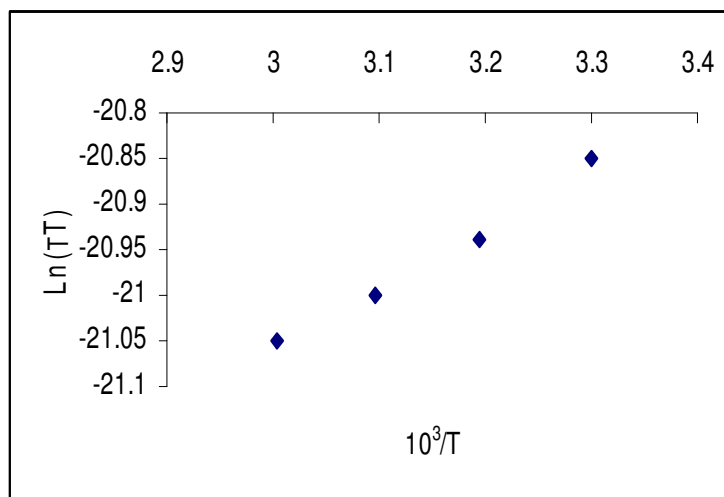
Figure 3: Plot of Ln (τT) versus 10^3 / T for the binary mixture of 0.02 mole of Nicotinamide in 0.98 mole of 1-Butanol in dilute solutions with benzene.

This indicates that the dielectric relaxation process can be considered as a rate process. The energy parameters for the dielectric relaxation process have been calculated using Eyring's rate equation. The energy parameters (ΔF_η, ΔH_η, ΔS_η) for viscous flow have also been calculated by treating the viscous flow as the rate process. It is found that the dielectric relaxation process may be treated as the rate process just like the viscous flow process. The values of the different energy parameters (ΔF_ε, ΔH_ε and ΔS_ε) and (ΔF_η, ΔH_η and ΔS_η) for binary mixtures at four different temperatures, viz. 303K, 313K, 323K and 333K are given in Table 2.

Table 2: Values of the energy parameters (in calorie) for the binary mixture at different temperatures

Temperature	$\Delta F\varepsilon$	$\Delta H\varepsilon$	$\Delta S\varepsilon$	$\Delta F\eta$	$\Delta H\eta$	$\Delta S\eta$
303K	1891.83		-1.67	4272.57		-6.42
313K	1907.92	1385.20	-1.67	4335.29	2327.65	-6.41
323K	1922.91		-1.66	4397.84		-6.41
333K	1942.65		-1.67	4465.78		-6.42

It is evident from the present study that the molar free energy of activation for viscous flow (ΔF_η) is greater than (ΔF_ε) the free energy of activation for the dielectric relaxation process [9]. This is in agreement with the fact that the process of viscous flow involves greater

interference by neighbours than does the dielectric relaxation as the latter takes place by rotation only whereas the viscous flow involves both the rotational and translational forms of motion. It can also be seen from Table 2 that ΔH_η is larger than ΔH_ε. The enthalpy of activation depends on the local environment of the molecules. Difference in the values for enthalpy of activation indicates that the dielectric relaxation process and viscous flow process involve the breaking of bonds with the neighbouring molecules in a different way and to a different extent. Entropy of a system is a measure of the orderly nature of the system. If the environment of the system is co-operative for the activated process, then the change in entropy (ΔS_ε) for the activated process indicates the non-cooperative environment of the system and the activated state is unstable. In the present case, it is observed that the change in entropy of the dielectric relaxation process is negative, indicating that the environment of the system is cooperative like that of the activated viscous flow state.

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