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# Microwave dielectric measurements of binary mixtures of nicotinamide and 1-propanol in benzene solutions at a constant temperature

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The properties of the binary mixtures of nicotinamide and 1-propanol have been studied at constant temperature 303 K in dilute solutions of benzene at microwave frequency 9.385 GHz. The values of different dielectric parameters namely; static permittivity ($\varepsilon_0$), dielectric constant ($\varepsilon'$), dielectric loss factor ($\varepsilon''$) and optical permittivity ($\varepsilon_\infty$) have been determined for five different mole fractions of nicotinamide in 1-propanol. The values of permittivity and dielectric loss are used to evaluate relaxation time for overall molecular rotation ($\tau_1$), relaxation time for intramolecular rotations ($\tau_2$), most probable relaxation time ($\tau_0$) and dipole moment ($\mu$) at a constant temperature. Different values of relaxation times are found to increase with the mole fraction of nicotinamide in all binary mixtures while the values of dipole moment decrease with the increase in the mole fraction of nicotinamide. The energy parameter ($\Delta F_\varepsilon$) for dielectric relaxation process of the mixtures is also calculated which increases with the mole fraction of nicotinamide. It is found that the dielectric relaxation process can be treated as a rate process. Present investigations suggest the existence of both the intramolecular and overall orientation in the binary mixtures.

**Keywords**: Binary mixtures, 1-propanol, Dipole moment, Nicotinamide, Relaxation time

## 1 Introduction

Nicotinamide is a water soluble vitamin and is a part of vitamin-B group. It is very useful for the maintenance of cellular energy balance. It decreases the tumor necrosis factor because of the anti-inflammatory properties. It is beneficial for the treatment of pellagra and also for inflammatory skin conditions. Nicotinamide is dissolvable in alcohols, but only in small proportions. Nicotinamide is rapidly and almost completely absorbed from all portions of the gastro-intestinal tract. When nicotinamide doses of less than 500 mg are orally administered, only small amount of the unchanged vitamin are excreted in the urine. When doses above this level are administered, unchanged nicotinamide represents the major urinary component.

Nicotinamide is thought to lessen the risk of developing diabetes by protecting the beta cells from attack by the immune system. Nicotinamide is also used for treating acne. Amides are also regarded as the templates for protein backbones. The understanding of mutual interaction between amides and hydroxyl groups is important in relation to the conformational stability of proteins. Many poor aqueous soluble drugs have been solubalized in nicotinamide. The enhancement of solubility mechanism has been reported[1] to be due to stacking complexation between drug and nicotinamide and not by covalency or miceller mechanisms.

Alcohols are industrially and scientifically important organic compounds and the hydroxyl group of alcohols largely determines their physical and chemical properties. 1-Propanol is used as a safest antiseptic compound and is also used in the manufacture of insecticides. It is very effective against a broad spectrum of microorganisms including bacteria, fungi and viruses such as HIV, hepatitis-B etc. Because of the wide uses of nicotinamide and 1-propanol, experimental work concerned with the dielectric relaxation process in the binary mixture of the above two compounds is carried out and molecular association in the different concentration ranges of nicotinamide in the binary mixtures is tried to understand during present course of work.

During last several years, investigations of dielectric relaxation phenomena have provided an important approach to explore the structural behaviour of complex organic polar molecules in non-polar solvents. To study the structural behaviour of molecules, it is necessary to determine various dielectric parameters which are related with inter and intramolecular association and internal rotation with

temperature variation. Recently, dielectric behaviour of mixture of different industrial and biological useful polar solvent molecules under varying conditions of compositions has evoked considerable interest[2-4] because it helps in formulating adequate models of liquid relaxation and obtaining information about the relaxation process in a polar mixture. The relaxation studies of polar liquids and their binary mixtures in dilute solutions of non-polar solvents provide valuable information about solute-solute and solute-solvent interaction[5-7]. Several researchers have studied dielectric relaxation behaviour of binary mixtures in dilute solutions of non-polar solvents and observed interesting abrupt behaviour due to formation of complexes in the mixture of polar molecules[8-10]. Shankar *et al*[11]. have studied H-bonded complexes of benzamide and nicotinamide with alcohols. Kannappan *et al.*[12] investigated the molecular interactions of benzamide in 1,4-dioxan with alcohols. In the present paper, the dielectric properties of binary mixtures of nicotinamide and 1-propanol at different concentrations and constant temperature (303 K) in dilute solutions of benzene have been studied.

## 2 Experimental Details

Nicotinamide and 1-propanol used in these investigations were purchased AR grade from M/s Sisco Research Laboratories Pvt Ltd. Mumbai, India. Benzene was also procured from M/s SRL, India and used as a solvent without further purification. All the measurements at microwave frequencies are carried out at frequency 9.385 GHz by using X-band microwave bench. The binary mixtures of the required mole fractions are prepared by mixing nicotinamide with 1-propanol in the calculated proportions. Dilute solutions of the binary mixtures of nicotinamide and 1-propanol in the benzene are then prepared. Dielectric measurements are done for the dilute solutions of binary mixtures of different mole fractions of nicotinamide (0.01, 0.015, 0.02, 0.025 and 0.03) and 1-propanol at a constant temperature 303 K. In all mixtures, the sum of the mole fractions of nicotinamide and mole fractions of 1-propanol is kept equal to one mole.

The energy parameters for the binary mixtures have been calculated from the knowledge of their dielectric parameters viz. $\varepsilon_0$ (static permittivity), $\varepsilon'$ (dielectric constant), $\varepsilon''$ (dielectric loss factor) and $\varepsilon_\infty$ (optical permittivity). From the experimental studies, it is found that the dielectric relaxation process depends on the solute-solute association. The energy parameter for activated process $\Delta F_\varepsilon$ is evaluated by using Eyring rate equations at a constant temperature 303 K. For the present investigations, double minima method for low loss liquids due to Heston *et al.*[13] is used. The values of $\varepsilon'$·and $\varepsilon''$ according to this method, are given by:

$$\in' = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2 \qquad \ldots(1)$$

$$\in'' = \frac{2}{\pi}\left(\frac{\lambda_g}{\lambda_d}\right)\left(\frac{\lambda_0}{\lambda_d}\right)^2\left(\frac{d\rho}{dn}\right) \qquad \ldots(2)$$

where

$$\rho = \frac{\sin\theta}{(2-\cos^2\theta)^{1/2}} \qquad \ldots(3)$$

$$\text{and } \theta = \frac{\pi\Delta x}{\lambda_g} \qquad \ldots(4)$$

where $\lambda_c$ is the cut-off wavelength, $\lambda_0$ the free space wavelength, $\lambda_d$ the wavelength in the dielectric medium and $\lambda_g$ is the wavelength in the empty wave-guide. Parameter $\rho$ is the inverse voltage standing wave ratio, $n$ the number of minima and $\Delta x$ is the double minima width in the standing wave patterns. The precision of measurement for the wavelength with the available X band microwave test bench is ±0.001 cm. Corresponding to this accuracy value, the error in the measurement of $\varepsilon'$ is estimated. For simplification, involved errors due to non-zero impedance of the short circuit plunger are ignored. The errors of measurement are calculated by using the conventional method of error analysis[14]. Overall estimated accuracy of measurements for $\varepsilon'$ and ε" by this method is about ±1% and ±5%, respectively. The static permittivity ($\varepsilon_0$) is measured by using a dipole meter supplied by M/s Mittal Enterprises, New Delhi. Refractive indices of the solutions are obtained by Abbe's Refractometer which in turn give the optical permittivity [15] ($\varepsilon_\infty = n_d^2$) and the results are obtained at a constant temperature 303 K.

For dilute solutions in non-polar solvents, $\varepsilon'$, $\varepsilon''$, $\varepsilon_0$ and $\varepsilon_\infty$ can be expressed as linear functions of concentrations[16, 17] in the following manner:

$$\varepsilon' = \varepsilon_1' + a' W_2 \qquad \ldots(5)$$

$$\varepsilon'' = a'' W_2 \qquad \ldots(6)$$

$$\varepsilon_0 = \varepsilon_{10} + a_0 W_2 \qquad \ldots(7)$$

$$\varepsilon_\infty = \varepsilon_{1\infty} + a_\infty W_2 \quad \ldots(8)$$

Here subscript 1 refers to the pure solvent, 2 to the solute, 0 refers to the static or low frequency case and $\infty$ refers to the infinite or optical frequency case, $W_2$ is taken as the weight fraction of the solute. $a'$, $a''$, $a_0$ and $a_\infty$ are the slopes of above mentioned linear equations. The dielectric relaxation time ($\tau$) is evaluated by using Higasi *et al.*[18] method. The relaxation time for overall molecular rotation ($\tau_1$) is defined by:

$$\tau_1 = \frac{a''}{\omega(a' - a_\infty)} \quad \ldots(9)$$

The relaxation time for intramolecular rotations ($\tau_2$) is given by:

$$\tau_2 = \frac{(a_0 - a')}{\omega a''} \quad \ldots(10)$$

where $\omega$ is the angular frequency. The most probable relaxation time[19] ($\tau_0$) is then obtained by employing the following relation:

$$\tau_0 = (1/\omega)\,[(A^2+B^2)/C^2]^{1/2(1-\alpha)} \quad \ldots(11)$$

where

$$A = a''\,(a_0 - a_\infty)$$
$$B = (a_0 - a')\,(a' - a_\infty) - (a'')^2$$
and $$C = (a' - a_\infty)^2 + (a'')^2$$

The values of the dipole moments ($\mu$) of the solute molecules for all the binary mixtures are calculated by using the method proposed by Higasi[20]:

$$\mu = \left( \frac{27kTM_2}{4\pi N(\varepsilon_{01}+2)^2 d_1} \right)^{1/2} (a_0 - a_\infty)^{1/2} \quad \ldots(12)$$

where $a_0$ and $a_\infty$ are the slopes of linear plots drawn between $\varepsilon_0$ versus $W_2$ and $\varepsilon_\infty$ versus $W_2$ and $M_2$ is the molecular weight of solute, $d_1$ the density of solvent, $k$ the Boltzman constant, $N$ the Avogadro's number and $T$ is the temperature at which the experiment is performed. After knowing the values of $a_0$ and $a_\infty$, $\mu$ is obtained from Eq. (12) at a constant temperature $T$.

The temperature dependence of relaxation time has been utilized to obtain the values of molar free energy of activation ($\Delta F_\varepsilon$). From the theory of relaxation time as a rate process, developed by Eyring[21], the relaxation time ($\tau$) is given by:

$$\tau = (A/T)\exp(\Delta F_\varepsilon/RT) \quad \ldots(13)$$

where $A = h/k$ and the other symbols have their usual meaning. From Eq. (13), we obtain:

$$\Delta F_\varepsilon = RT \ln(kT\tau/h) \quad \ldots(14)$$

Thus knowing the value of $\tau$ and $T$, the value of $\Delta F_\varepsilon$ can be calculated.

## 3 Results and Discussion

The system selected for the present study is the binary mixtures of nicotinamide and 1-propanol using benzene as a solvent. The dielectric parameters ($\varepsilon_0$, $\varepsilon_\infty$, $\varepsilon'$ and $\varepsilon''$) for different mole fractions, relaxation times ($\tau$) and dipole moment values ($\mu$) for binary mixtures of nicotinamide with 1-propanol in dilute solutions with benzene for different weight fractions are determined at a constant temperature 303K and presented in Table 1.

Both values of $\varepsilon'$ and $\varepsilon''$ vary linearly with the weight fraction of solute in benzene for all the binary mixtures (Table 1). This suggests that there is no change in the nature of the rotating molecular entities in the benzene solution. It is observed from Table 1 that both values of $\tau_1$ and $\tau_2$ increase systematically with the increase in the mole fractions of nicotinamide in all the binary mixtures. This may possibly be due to increase in the molar volume. The increase in the values of various relaxation times ($\tau_1$, $\tau_2$ and $\tau_0$) with the concentration of nicotinamide may provide useful indicators for absorption of drugs dissolved in nicotinamide. Since the differences between $\tau_1$ and $\tau_2$ are significant, at all mole fractions, we may expect more than one mechanism in these mixtures. 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 ($\tau_0$) is found increased because the mole fraction of nicotinamide in the binary mixture is increased. The increase in relaxation time may be attributed to the increase in effective radius of the rotating unit. In the binary mixture of nicotinamide and 1-propanol, the $CH_3$ group is attached to the same carbon atom to which the -OH group is attached. This increases the overall size of

Table 1 — Values of the dielectric parameters ( $\varepsilon'$, $\varepsilon''$, $\varepsilon_0$ and $\varepsilon_\infty$), relaxation time ($\tau_1$, $\tau_2$, $\tau_0$), dipole moment ($\mu$) and molar free energy of activation ($\Delta F_\varepsilon$) for different mole fractions of nicotinamide and 1-propanol at different weight fractions of solute at 303 K

| | Weight fraction ($W_2$) | $\varepsilon'$ | $\varepsilon''$ | $\varepsilon_0$ | $\varepsilon_\infty$ | $\tau_1$ (ps) | $\tau_2$ (ps) | $\tau_0$ (ps) | $\mu$ (in Debye) | $\Delta F\varepsilon$ (in calorie) |
|---|---|---|---|---|---|---|---|---|---|---|
| | 0.00933 | 2.2875 | 0.0572 | 2.3198 | 2.2473 | 2.52 | 3.92 | 2.57 | 1.72 | 1671.75 |
| 0.01 mole of nicotinamide in 0.99 mole of 1-propanol | 0.01244 | 2.3038 | 0.0599 | 2.3423 | 2.2565 | | | | | |
| | 0.01556 | 2.3261 | 0.0621 | 2.3656 | 2.2579 | | | | | |
| | 0.01867 | 2.3494 | 0.0646 | 2.3811 | 2.2614 | | | | | |
| | 0.02179 | 2.365 | 0.066 | 2.404 | 2.267 | | | | | |
| | 0.00942 | 2.294 | 0.059 | 2.331 | 2.248 | 2.79 | 4.22 | 3.11 | 1.45 | 1785.18 |
| 0.015 mole of nicotinamide in 0.985 mole of 1-propanol | 0.01259 | 2.3142 | 0.0608 | 2.3549 | 2.2573 | | | | | |
| | 0.01573 | 2.3351 | 0.0617 | 2.3781 | 2.2665 | | | | | |
| | 0.01889 | 2.3618 | 0.0653 | 2.3973 | 2.2781 | | | | | |
| | 0.0220 | 2.38 | 0.07 | 2.42 | 2.29 | | | | | |
| | 0.00952 | 2.307 | 0.060 | 2.337 | 2.252 | 2.84 | 5.37 | 3.43 | 1.38 | 1844.64 |
| | 0.0127 | 2.3258 | 0.0609 | 2.3639 | 2.2618 | | | | | |
| 0.02 mole of nicotinamide in 0.98 mole of 1-propanol | 0.01587 | 2.3439 | 0.0621 | 2.3854 | 2.2733 | | | | | |
| | 0.01905 | 2.3723 | 0.0642 | 2.4017 | 2.2827 | | | | | |
| | 0.0222 | 2.39 | 0.07 | 2.43 | 2.30 | | | | | |
| | 0.00962 | 2.312 | 0.062 | 2.344 | 2.261 | 3.76 | 5.32 | 4.17 | 1.32 | 1961.31 |
| 0.025 mole of nicotinamide in 0.975 mole of 1-propanol | 0.01283 | 2.3341 | 0.0636 | 2.3716 | 2.2786 | | | | | |
| | 0.01603 | 2.3558 | 0.0659 | 2.3947 | 2.2895 | | | | | |
| | 0.01924 | 2.3795 | 0.0681 | 2.4155 | 2.3047 | | | | | |
| | 0.0224 | 2.40 | 0.07 | 2.44 | 2.32 | | | | | |
| | 0.00972 | 2.320 | 0.066 | 2.358 | 2.280 | 4.24 | 5.56 | 4.61 | 1.28 | 2020.79 |
| 0.03 mole of nicotinamide in 0.97 mole of 1-propanol | 0.01296 | 2.3389 | 0.0677 | 2.3851 | 2.2881 | | | | | |
| | 0.01619 | 2.3606 | 0.0699 | 2.4068 | 2.3019 | | | | | |
| | 0.01944 | 2.3841 | 0.0722 | 2.4279 | 2.3136 | | | | | |
| | 0.0227 | 2.41 | 0.07 | 2.45 | 2.33 | | | | | |

the molecule and may cause hindrance to the group rotation, which may give rise to increased relaxation time.

The dipole moment of mixture under test decreases as the mole fraction of nicotinamide in binary mixtures increases (Table 1). This may possibly be due to the shifting of charge centers in the dilute solutions. It may also be realized that increased solute-solute interaction leads to the decrease in contribution to the total absorption from –OH group rotation because number of relaxing hydroxyl groups decrease due to association. Probably this effect is partly responsible for the corresponding decrease shown by the apparent dipole moments.

For the binary mixtures of nicotinamide and 1-propanol, it is found that the variation of ln ($\tau$T) with (1/*T*) is linear. This indicates that the dielectric relaxation process can be considered as a rate process[22]. The energy parameters for the dielectric relaxation process have been calculated using Eyring's rate equation. From Table 1, the values of energy parameter ($\Delta F_\varepsilon$) for different compositions of binary mixtures at a temperature 303 K are found to increase with increase in mole fraction of nicotinamide, which indicates that force of hindrance experienced by the molecules for dipolar rotation is a factor dependent on the nature of molecules. This also indicates that the nicotinamide may cause improvements in energy production in body cells due to its role as a precursor of NAD (nicotinamide adenosine dinucleotide) which is an important molecule involved in energy metabolism. On increasing nicotinamide concentrations, the available NAD molecules increase which may take part in energy metabolism, thus increasing the amount of energy available in the cell.

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