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STUDIES OF DIELECTRIC PROPERTIES OF BINARY MIXTURES OF PARACETAMOL AND PHENACETIN IN DILUTE SOLUTION OF CARBON TETRACHLORIDE AT A FIXED MICROWAVE FREQUENCY 9.27 GHZ

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ABSTRACT

The present research work shows that how the dielectric properties of binary mixtures of Paracetamol and Phenacetin change in the microwave region when they are dissolved in Carbon tetrachloride (a non-polar solvent). The measurements of dielectric parameters are done at different temperatures and weight fractions with the help of an X-Band microwave bench at a fixed frequency of 9.27 GHz using standard methods. The dielectric parameters depend on temperature and this characteristic helps in the determination of relaxation behavior of polar compounds in the microwave region. The aim of the present investigation is to determine different thermodynamical parameters like free activation energy ($\Delta F\varepsilon$), molar enthalpy of activation ($\Delta H\varepsilon$) and molar entropy of activation ($\Delta S\varepsilon$) for dielectric relaxation process and free activation energy ($\Delta F\eta$), molar enthalpy of activation ($\Delta H\eta$) and molar entropy of activation ($\Delta S\eta$) for viscous flow process to know the structural and molecular behavior of the paracetamol and Phenacetin. Dielectric studies at microwave frequencies provide information regarding molecular configuration of the system.

Keywords- *Dielectric relaxation studies, Phenacetin, viscous flow process, Microwave bench, molar enthalpy.*

INTRODUCTION

The dielectric relaxation studies of polar mixtures help in communicating suitable models for liquid relaxation and offer information regarding the relaxation process in polar mixtures. These studies are also good for some industrial and biological uses. Many studies show that the ratios of the binary mixture in the non-polar substance and its concentration play an important role in dielectric relaxation studies. [4]. In the microwave region, such dielectric studies are able to describe the alignment of neighbouring molecules and types of molecular association in the system of mixture. With the help of such studies, we can also analyse the

molecular configuration of the samples at microwave frequencies. [5]. So to know more about the structural and molecular behavior of Phenacetin and its binary mixtures with Paracetamol are prepared in the present study. Different binary mixtures are prepared from these compounds to make dilute solutions in carbon tetrachloride with Paracetamol for different weight fractions to calculate different dielectric parameters using standard methods.

PREPARATION OF SAMPLES

For the present investigation, we have prepared the binary mixtures of Paracetamol with Phenacetin by dissolving it in carbon tetrachloride for the dielectric studies. Both the compounds are of AR grade and purchased from Central Drug House, Delhi, India. For the present study we are using these compounds without any further purification. To make samples, both Paracetamol and Phenacetin are added in equal proportions by mole i. e. 0.02 mole of Paracetamol and 0.02 mole of Phenacetin are mixed together and then this mixture is divided into five parts as 0.3gm, 0.6gm, 0.9gm, 1.2gm and 1.5gm. Now to make dilute solutions, each of the above binary samples is dissolved in 1 mole of Carbon Tetrachloride. The dielectric studies for these binary mixtures were done at a fixed frequency of 9.27 GHz and at four different temperatures viz. 303K, 313K, 323K and 333K. Thus we have prepared the binary mixture of Phenacetin with Paracetamol in a ratio of 1:1 and dilute solution are made by dissolving them in CCl_4 and experiments are done to find their dielectric properties.

Experimental Procedure to Measure Different Parameters

The experiments are performed of all binary mixtures for different weight fractions and temperatures. The values of dielectric constant (ε') and dielectric loss (ε'') are measured with the help of X-band microwave bench at a fixed microwave frequency 9.27 GHz using Heston et al. method. Also the values of static and optical permittivity (ε_o and ε_∞) measured with the help of Dipole meter and Abbe's refractometer respectively for all the binary mixtures. A constant temperature water bath is fitted with a thermostat to vary the temperature which has temperature stability of the order of ± 0.1°C. By using Higasi method [6-7], different values of relaxation times (τ_0, τ_1 and τ_2) are also determined from the equations 6, 7 and 8 for all samples.

The values of ε' and ε'' are obtained from the following set of equations:

$$\varepsilon' = \frac{\varepsilon_0 - \varepsilon_\infty}{1+\omega^2\tau_0^2} + \frac{\varepsilon_0 - \varepsilon_\infty}{1+\omega^2\tau_1^2} \qquad (1)$$

$$\varepsilon'' = \frac{2\omega\tau_0(\varepsilon_0 - \varepsilon_\infty)}{1+\omega^2\tau_0^2} \frac{d\omega}{d\ln} \qquad (2)$$

where

$$\rho = \frac{\sin \theta}{\left(2 - \cos^2 \theta\right)^{\frac{1}{2}}} \tag{3}$$

and

$$\rho = \frac{\Delta x}{\lambda_g} \tag{4}$$

Here, λ_0 is the free space wavelength, λ_c is the cut-off wavelength, λ_g is the wavelength in the empty waveguide and λ_d is the wavelength in the dielectric medium. 'ρ' denotes the inverse voltage standing wave ratio, Δx represents double minima width and 'n' is the number of minima. The accurateness of the measurements of the given X-Band microwave test bench is ±0.01 cm. corresponding to this accuracy value, the error in the measurements of ε′ and ε″ are estimated. The error in measurements are calculated by using error analysis method [8]. From this method, we can measure the accuracy level upto ± 1% for ε′ and ± 5% for ε″.

For dilute solution in non polar solvents ε′, ε″, ε_0 and ε_∞ can be expressed as linear functions of concentration in the [6, 7 and 9] following manner:

$$\begin{aligned} \varepsilon' &= \varepsilon'_1 + a' W_2 \\ \varepsilon'' &= a'' W_2 \\ \varepsilon_0 &= \varepsilon_{10} + a_0 W_2 \\ \varepsilon_\infty &= \varepsilon_{1\infty} + a_\infty W_2 \end{aligned} \tag{5}$$

Here subscript 1 refers to the pure solvent, 2 refers to the solute, 0 is for the zero frequency measurements in the static field and ∞ is for the values at very high frequency, W_2 represents the weight fraction of the solute. The slopes of these linear equations are denoted as a′, a″, a_o and a_∞ respectively. The values of relaxation times (τ_1, τ_2 and τ_0) are determined by the method given by Higasi et al.

The relaxation time for overall molecular rotation (τ_1) is defined by:

$$\tau_1 = \frac{a''}{\varepsilon_1 \left(a' + a_\infty\right)} \tag{6}$$

While the relaxation time for intramolecular rotations (τ_2) is given by:

$$\tau_2 = \frac{\left(a_0 - a'\right)}{\omega a''} \tag{7}$$

Here 'ω' is the angular frequency.

The most probable relaxation time (τ_0) is then obtained by employing the following relation:

$$\tau_0 = \sqrt{\tau_1 \tau_2} \quad (8)$$

By using the values of a_0 and a_∞, dipole moment of all the three binary mixtures are calculated at different temperature and weight fractions of the given compounds. The dependency of the dielectric parameters on temperature also helps to find several thermodynamical relaxation parameters. The values of dipole moment of all the samples are determined by using Higasi's method. According to this method the value of dipole moment is given by:

$$\mu = \left[\frac{27kTM_2}{4\pi N(\varepsilon_{01}+2)\ d_1}\right]^{\frac{1}{2}} (a_0 - a_\infty)^{\frac{1}{2}} \quad (9)$$

By plotting a graph between ln(τT) and 1/T a straight line is observed which shows that it is a rate process. A plot between ln(η) and 1/T also shows a linear relationship i. e. it can also be considered as a rate process. The values of activation energy for relaxation process (ΔF_ε) and viscous flow process (ΔF_η) are calculated by using the following equations:

$$\Delta F = RT \ln \frac{kT}{h} \quad (10)$$

$$\Delta H = RT \ln \frac{V}{hN} \quad (11)$$

The values of enthalpy for both the processes can be calculated with the help of following equations:

$$\Delta F = \Delta H - T\Delta S \quad (12)$$

$$\Delta H = \Delta F + T\Delta S \quad (13)$$

RESULT AND DISCUSSION

For the present study, the selected binary sample is the mixture of Phenacetin and Paracetamol using carbon tetrachloride as a solvent. We have determined the values of different dielectric parameters (ε_0, ε_∞, ε' and ε'') for five different mole fractions of this binary mixture in the dilute solution of carbon tetrachloride. By the help of these dielectric parameters, we have determined the values of all the three relaxation times (τ_1, τ_2 and τ_0), dipole moment (μ) [25]and distribution parameters (α) which are mentioned in Table 1.

From this table, it is noticed that as we increase the temperature from 303K to 333K, the values of both $\tau_1$and τ_2 decreases systematically. This decrease in relaxation times may be due to increase in molar volume or in size of dipole with temperature. In this binary mixture we may expect more than one relaxation mechanism at all four temperatures because of the significant difference in the values of τ_1 and τ_2. It indicates that the molecules of this mixture contribute to

its dielectric absorption through their rotation as a single unit as well as through their intramolecular rotations also [19]. This implies that an intramolecular relaxation process also exists with the overall relaxation process in the system. Such observations confirm that intramolecular rotations dominant over molecular rotation in the present system. From Table 1 we noticed that for each binary mixture, the value of average relaxation times (τ_0) decreases with the increase in temperature.

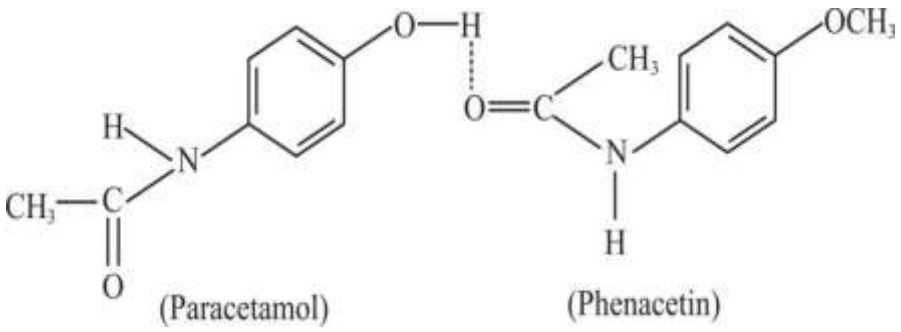

Figure: 1 Hydrogen bonding between –OH group of Paracetamol and CH_3CO– group of Phenacetin

In this binary mixture of Phenacetin and Paracetamol the values of relaxation times are higher than the relaxation time values of individual components. It shows the presence of strong hydrogen bonding in this binary mixture. For this binary mixture hydrogen bonding takes place between hydrogen atom of –OH group of Paracetamol & CH_3CO– group of Phenacetin (Figure:1); hydrogen atom of –NH group of Paracetamol & CH_3CO– group of Phenacetin (Figure:2) and hydrogen atom of –NH group of Phenacetin & CH_3CO– group of Paracetamol (Figure: 3).

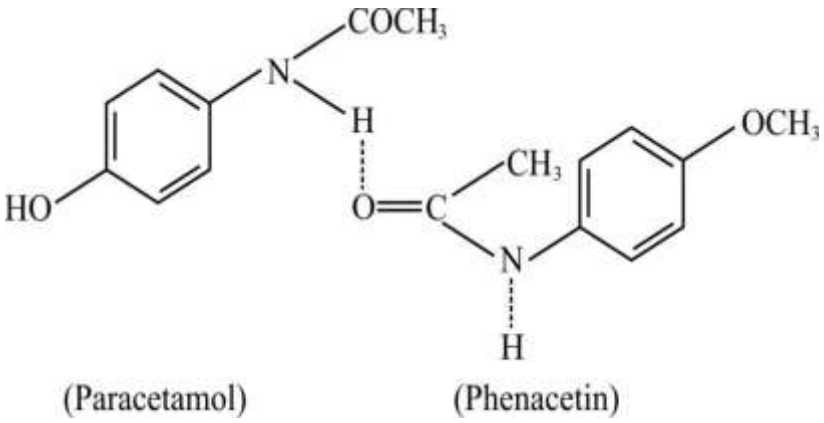

Figure: 2 Hydrogen bonding between –NH group of Paracetamol and CH_3CO– group of Phenacetin

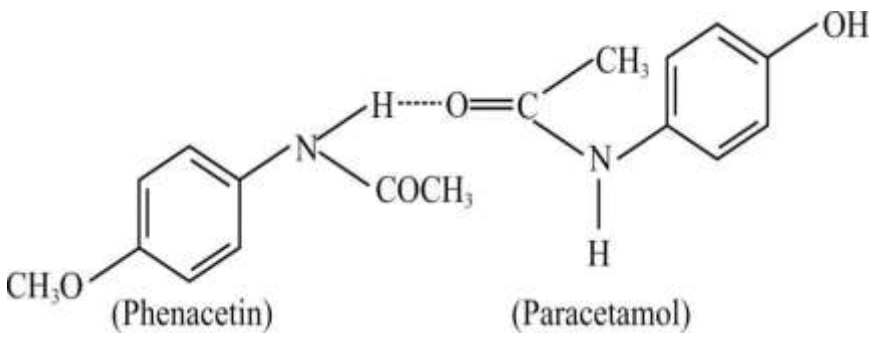

Figure: 3 Hydrogen bonding between –NH group of Phenacetin and CH_3CO– group of Paracetamol

Higher values of relaxation time indicate that the hydrogen bonding between the self molecules of individual components is weaker as compared to the intramolecular hydrogen bonding of the binary mixture of Phenacetin and Paracetamol with carbon tetrachloride as we know that higher relaxation time values suggest the presence of stronger hydrogen bonding in the system. Higher values of relaxation times may be due to the increased chain length of Phenacetin and Paracetamol and acidity of proton donor in the mixture. It indicates that the chain length and bulk of clusters increase with the increased degree of co operatively for the reorientation of molecules. Such effects may arise due to increased molecular size and increased viscosity with increased chain length [10, 11 and 12]

The observed values of dipole moments are listed in Table 1. From this table we found that the values of dipole moment increase with the temperature. This increased value of dipole moment may be due to the increased size of dipole with increase in temperature. This slight change in dipole moment with temperature could be explained through solvent effects [13]. It may also occur due to the change in bond angle and due to the stretching of bond length. The change in the dipole moment values vary linearly with temperature in the dilute solution of carbon tetrachloride. [14, 15]

This result confirms the presence of solute-solvent type of molecular association for the binary mixture of Phenacetin and Paracetamol in the carbon tetrachloride solution. Here we may also predict the solute-solute association as this association of molecule is arising due to hydrogen bonding between Phenacetin and Paracetamol. This hydrogen bonding among the solute molecules may be explained on the basis of the fact that the process of dielectric relaxation has the rotation of molecular entities [1-3].

From Figure 3, we can observe that the variation between $\ln(\tau T)$ and $(1/T)$ is found to be a straight line for this binary mixture. It shows that the process of dielectric relaxation can be treated as a rate process. Various energy parameters for dielectric relaxation process (ΔF_ε, ΔH_ε and ΔS_ε) are calculated with the help of [16]. We have also calculated the energy parameters for viscous flow process (ΔF_η, ΔH_η and ΔS_η) by considering viscous flow process also as a rate process. From this analysis we found that the dielectric relaxation process may be treated as a rate process just as the viscous flow process. The values of all these energy parameters at four

different temperatures viz. 303K, 313K, 323K and 333K are listed in Table 2 for the binary mixture of Phenacetin and Paracetamol in the dilute solution of carbon tetrachloride.

From this table we found that the molar free energy of activation for viscous flow process (ΔF_η) is greater than the free energy of activation for dielectric relaxation process (ΔF_ε) [17]. This result shows an agreement with the fact that viscous flow process has more interference of neighboring molecules as compared to dielectric relaxation process because the latter takes place due to rotation only but viscous flow process has both rotational and translational motion of molecules [18]. We also observe higher value of ΔH_η than ΔH_ε from Table 2. The activation enthalpy of the system depends on the local environment of the system. [20] It is also a measure of orderly nature of the system. We found different values of activation energy for viscous flow process and dielectric relaxation process. This difference in the values of enthalpies of activation indicates that the breaking of bonds with the neighboring molecules in both the processes take place in a unique way and to a different extent. If the environment of the system is co operative for the activated state the change in entropy becomes negative which makes activated state stable [21-22]. In our case we observed negative values of change in entropy (ΔS_ε) for dielectric relaxation process which suggests that environment of the system [23-24] is cooperative just like the viscous flow process.

Table: 1 Values of different Relaxation times (τ_1, τ_2 and τ_0), Dipole Moment (μ) and Distribution Parameters (α) for binary mixture of Paracetamol and Phenacetin in dilute solution of carbon tetrachloride at four different temperatures

Temperature	τ_0 (ps)	τ_1(ps)	τ_2(ps)	μ(Debye)	α
303K	2.76	1.68	4.54	2.49	0.101
313K	2.61	1.63	4.17	2.52	0.090
323K	2.41	1.56	3.75	2.55	0.078
333K	2.27	1.51	3.42	2.59	0.068

Table: 2 Experimental values of Energy Parameters for binary mixture of Paracetamol and Phenacetin in dilute solution of carbon tetrachloride at four different temperatures

Temperature	ΔFε (cal/Mol)	ΔHε (cal/Mol)	ΔSε (cal/Mol)	ΔFη (cal/Mol)	ΔHη (cal/Mol)	ΔSη (cal/Mol)
303K	1715.48	694.81	-3.37	3196.64	2618.46	-1.908
313K	1756.08		-3.39	3218.43		-1.916

323K	1783.51		-3.37	3247.82		-1.948
333K	1818.63		-3.38	3251.33		-1.900

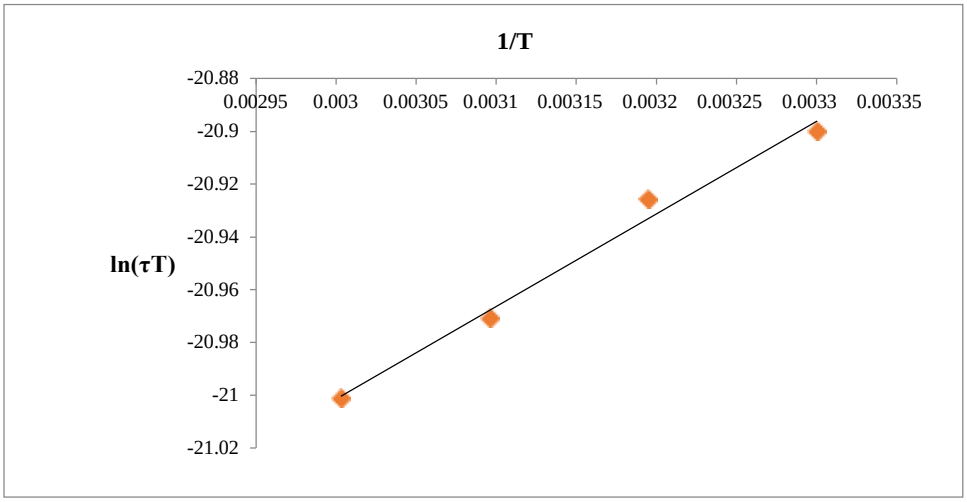

Figure: 3 Plot of ln(τT) versus 1/T for binary mixture of Paracetamol and Phenacetin in dilute solution of CCl_4

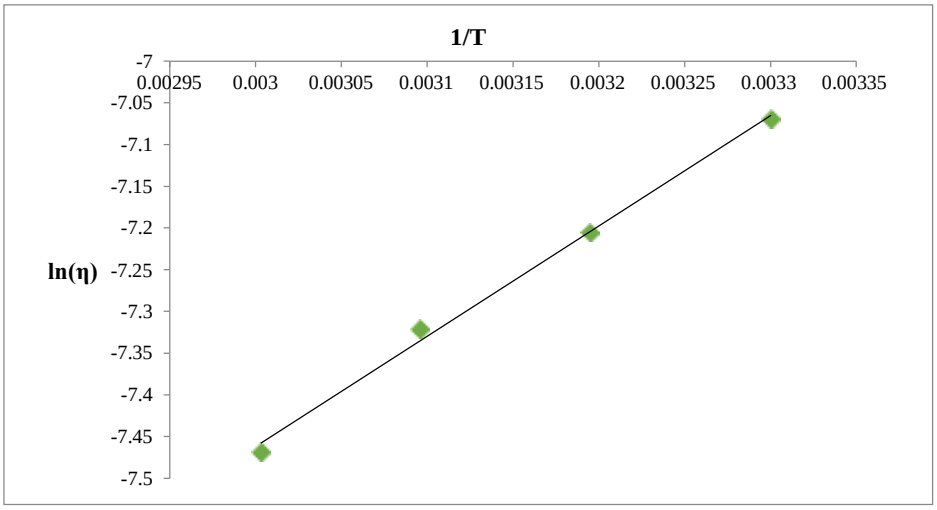

Figure: 4 Plot of ln (η) versus 1/T for binary mixture of Paracetamol and Phenacetin in dilute solution of CCl_4

CONCLUSION

The measured values of different relaxation times τ_1, τ_2 and τ_o for the binary mixtures are decreasing systematically with temperature. It is also observed that the values of τ_2 are higher than that of τ_1 for all binary mixtures and the rate of fall of relaxation time τ_2 with temperature is higher than that for τ_1. Such behavior of relaxation times confirms the presence of hydrogen bonding in the system of molecules. The present investigation shows that in the binary

mixtures, dipole moment values are increasing with the rise in temperature which may be due to the lengthening of effective length of the dipole. The dipole moment of hydrogen bonded complexes provides important information to understand the structure and properties of molecules. The values of ΔF_ε are found to be lesser as compared to the values of ΔF_η in the dilute solution of carbon tetrachloride which indicates that viscous flow process involves both rotational and translational form of motion whereas dielectric relaxation process has only rotational form of motion. The values of enthalpies for all the three samples are found to be small which indicate the presence of intramolecular association in the binary system. The values of ΔS_ε are negative for all mixtures and it suggests that binary mixtures have more aligned activated state. The linear variation of ln (τT) with (1/T) and ln (η) with (1/T) indicates that both dielectric relaxation process and viscous flow process can be considered as a rate processes. The observed values of relaxation time and energy activation parameters are higher for binary mixtures than pure solutions of given compounds in the dilute solution of carbon tetrachloride which suggest that the hydrogen bonding among the molecules of binary mixtures are stronger than the molecules of the dilute solutions of individual components.

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