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STUDY OF THE EFFECT OF TEMPERATURE AND MAGNETIC FIELD VARIATION ON DIELECTRIC PROPERTIES OF ORGANIC LIQUIDS USING A MICROWAVE CAVITY SPECTROMETER

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The temperature and magnetic field variation have been studied for the dielectric properties of 2chlorobutane, acetonitrile and nitrobenzene in their pure **state** using microwave cavity spectrometer at *9.0* **GHz.** The analysis of the observed data of width, shift and amplitude of resonance profile has been camed **out** by using Slater perturbation equations for the computation of relaxation time, activation energy and for the relative study of permittivity and dielectric loss. **This** work provides fruitful information about the macroscopic structure of the organic liquids chosen.

Keywords: Dielectric properties; Organic liquids

1. INTRODUCTION

The dielectric properties [I, **21** are important to study the structure of the matter. The Microwave Cavity Spectrometer **[3-61** is one of the accurate techniques and it is advantageous that this technique requires a very small volume of the sample ($\approx 0.001 \text{ cm}^3$). The dielectric

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relaxation of the organic liquid sample loaded in the microwave cavity can be related to the shift in the resonance frequency and to the change in the width of the resonance profile. The shift and width provide relative information about the permittivity and the dielectric loss respectively. **In** this paper we have measured amplitude, width of the resonance profile and shift of the resonance frequency by varying the magnetic field strength and the temperature. The cavity has been operated in TM₀₁₀ mode at frequency 9.0 GHz. The relaxation time as well as activation energy are calculated for 2-chlorobutane, acetonitrile and nitrobenzene in their pure state.

2. EXPERIMENTAL

The experimental setup of the microwave cavity spectrometer has been described elsewhere **[3** - **61. A** cylindrical microwave cavity is shown in Figure 1. The sample has been studied in a thin walled pyrex test tube of diameter **1.5mm** and then inserted in the cavity, operated in the

FIGURE 1 A sketch of the microwave cavity in the TM_{010} mode.

 $TM₀₁₀$ mode. The data of shift in the resonance frequency, width and amplitude of the resonance profile have been measured for each sample of the organic liquids at a **fix** frequency 9.0 GHz. A permanent record of the signal and markers was produced **on** a dual pen chart recorder. The traces of the resonance profile of the cavity are displayed **on** one channel of the dual pen chart recorder while markers for calibration are displayed **on** the another one. A specific record is shown in Figure 2. **In** the present work two temperatures are chosen for each system. The temperatures set for 2-chlorobutane; acetonitrile and nitrobenzene are 19°C and 31°C; 19°C and 27°C and 19°C and 255°C respectively. The magnetic field in the range 0.0 to **1.5** kGauss was applied.

The permittivity (ε') and the dielectric loss (ε'') are related [7,8] to the relative shift in the resonance frequency (Δf) and relative change in width of the resonance profile (Δw) respectively. The loss tangent (tan δ) gives the comparison of the permittivity and the dielectric loss

FIGURE 2 A dual pen chart trace of the second derivative of the absorption power for Nitrobenzene at 19°C. The markers are separated by 4 MHz.

and it is used to calculate the relaxation time by **using** Debye's single relaxation time mechanism **[9].**

The shift in the resonant frequency and width of the resonance profile are measured before and after putting the sample in the cavity. The observed data have been analyzed using Slater **[7,8]** perturbation equations mentioned below:

$$
\Delta f/f_0 = -[(\varepsilon' - 1)/2]F(\mathbf{E}) \tag{1}
$$

and

$$
\Delta(1/Q) = \Delta w/f_0 = \varepsilon'' F(\mathbf{E}) \tag{2}
$$

where Δf is the frequency shift, Δw is the width of the resonance profile and f_0 is the cavity resonance frequency. ε' and ε'' are permittivity and dielectric loss respectively for the material in the cavity. *F(E)* is the functional form of the field interacting with the sample loading the cavity and the energy stored per cycle in the cavity which is expressed as follows:

$$
F(\mathbf{E}) = \frac{\int_{\nu} \mathbf{E}_s \cdot \mathbf{E}_0 d\nu}{\int_{\nu} \mathbf{E} \cdot \mathbf{E}_0 dV}
$$
(3)

In this expression **E** represents the electric field applied to the cavity, \mathbf{E}_0 is the unperturbed component of the electric field in the cavity volume without the sample, ν is the volume of the sample and V is the cavity volume.

Hence, the loss tangent is defined as follows

$$
\tan \delta = (\varepsilon''/\varepsilon') \approx \Delta w/2\Delta f, \quad \text{for } \varepsilon' \gg 1 \tag{4}
$$

and the relaxation time using Debye's single relaxation time mechanism [9] is computed from the following relation

$$
\tau = (1/\omega) \times (\Delta w/2\Delta f) \tag{5}
$$

where $\omega (=2\pi f)$ is the angular frequency.

energy (ΔG) is given here below The relation between the relaxation time (τ) and the activation

$$
\Delta G = 2.303RT \log (\tau kT/h) \tag{6}
$$

where R is the molar gas constant, h is the Plank's constant, k is the Boltzmann constant and T is the absolute temperature.

3. RESULTS *AND* **DISCUSSION**

The observed data of Δf , Δw , Δh , τ , ΔG and $(\Delta w/2\Delta f)$ for the organic liquids in their pure states are plotted against magnetic field strength at two different temperatures. The description of the observed data for each organic liquid as a function of magnetic field is given in the forthcoming paragraphs.

3.1. 2-Chlorobutane [CH₃-CH(Cl)-CH₂-CH₃]

The variation of $(\Delta f, \Delta w, \Delta h)$; $(\Delta w/2\Delta f)$; τ and ΔG observed at 19°C, with respect to the magnetic field are plotted in the Figures $3(a) - (d)$.

FIGURE 3 Variation of (a) amplitude (Δh) , width (Δw) , shift (Δf) ; (b) loss tangent *(Awl2Af);* (c) relaxation time *(7);* (d) activation energy **(AG)** as a function of magnetic field; (e) relative width (Δw) *versus* relative shift (Δf) for 2-chlorobutane at 19°C.

The variation of Δw versus Δf is given in Figure 3(e). These data at 31° C are given in Figures 4(a)-(e) respectively.

The comparison of the data obtained at both temperatures reveal that the trend of variation of the shift, width, amplitude, loss tangent and activation energy as shown in Figures $3(a) - (d)$ respectively for 19°C temperature are similar to those for 31°C temperature as given in Figures $4(a) - (d)$ respectively. The variation of the width with respect to the shift correspondingly indicate the changes in dielectric loss (ε'') *versus* permittivity (ε') . The traces of width with respect to the shift at 19°C as indicated in Figure 3(e) for the shift in the range from 2.30 to 2.67MHz and at 31°C as indicated in Figure 4(e) for the shift in the range from 2.28 to 2.61 MHz have the

FIGURE 4 Variation of (a) amplitude (Δh) , width (Δw) , shift (Δf) ; (b) loss tangent $(\Delta w/2\Delta f)$; (c) relaxation time (τ) ; (d) activation energy (ΔG) as a function of magnetic field; (e) relative width (Δw) *versus* relative shift (Δf) for 2-chlorobutane at 31°C.

same trend of variation. The overall response of the dielectric properties show that the values significantly change with temperature. From this analysis of the observed data, we infer that the permittivity, dielectric **loss** and relaxation time exhibit temperature and magnetic field effects.

3.2. Acetonitrile $[CH_3-C= N]$

The plots of the data of $(\Delta f, \Delta w, \Delta h)$; $(\Delta w/2\Delta f)$; *7* and ΔG observed at 19° C, with respect to the magnetic field are shown in Figures $5(a)$ – (d). The variation of Δw versus Δf is given in Figure 5(e). These observations at **27°C** are given in Figures 6(a)-(e) respectively.

FIGURE 5 Variation of (a) amplitude (Δh) , width (Δw) , shift (Δf) ; (b) loss tangent $(\Delta w/2\Delta f)$; (c) relaxation time (τ) ; (d) activation energy (ΔG) as a function of magnetic field; (e) relative width (Δw) *versus* relative shift (Δf) for Acetonitrile at 19°C.

FIGURE 6 Variation of (a) amplitude (Δh) , width (Δw) , shift (Δf) ; (b) loss tangent $(\Delta w/2\Delta f)$; (c) relaxation time (τ) ; (d) activation energy (ΔG) as a function of magnetic field; (e) relative width (Δw) *versus* relative shift (Δf) for Acetonitrile at 27°C.

The shift (Δf) , width (Δw) and amplitude (Δh) observed at 19^oC and 27°C as a function of magnetic field are plotted in Figures 5(a) and 6(a) respectively. The shift variation have nearly same trend whereas the width (Δw) at 19^oC and 27^oC show similar trend for the magnetic field in the range from 0.0 to 0.5 kGauss but as the magnetic field increases in the range from 0.5 **to** 1.5 kGauss, the width first decreases then increases for 19°C while at 27"C, the width increases first and then decreases. The plots of the amplitude (Δh) for both the temperatures show a linear trend of change. The loss tangent (Δw) $2\Delta f$) in Figure 5(b), relaxation time (τ) in Figure 5(c) and activation energy (ΔG) in Figure 5(d) for 19^oC exhibit the same trend as those of 27° C in Figures 6(b)-(d) for the magnetic field range from 0.0 to 0.5 kGauss thereafter the plots at 19°C show first decreasing trend then increasing characteristics while the plots for 27°C show the increasing trend and then they decrease. The variation of the width versus shift for 19°C in Figure 5(e) shows the non-linear behaviour having a peak $(\Delta w = 1.78 \text{ MHz})$ at shift $(\Delta f = 3.56 \text{ MHz})$ then the width first decreases thereafter it increases to a maximum value whereas for the temperature 27"C, in Figure 6(e), the width shows the increasing nature and attains a sharp peak ($\Delta w = 1.96 \text{ MHz}$) at shift (Δf = 4.33 MHz) thereafter it acquires the decreasing trend.

The above inferences explain the temperature and magnetic field have influence **on** the values of the shift, width, amplitude, relaxation time, activation energy and correspondingly the dielectric properties are affected.

3.3. Nitrobenzene $\left(\bigotimes \limits_{n} N\right)$

The observations at 19°C for $(\Delta f, \Delta w, \Delta h)$; $(\Delta w/2\Delta f)$; τ and ΔG *versus* magnetic field are exhibited in Figures $7(a) - (d)$. The changes in the Δw with Δf are illustrated in Figure 7(e) whereas the observed data at 25.5 \degree C are plotted in Figures 8(a)-(e) respectively.

The amplitude at 19°C in Figure 7(a) shows nearly linear trend and remains approximately unaffected at 255°C. This indicates that the amplitude of the resonance profile is not disturbed by increasing temperature. The shift (Δf) for 19°C in Figure 7(a) shows a peak $(\Delta f = 2.43 \text{ MHz})$ at 0.6 kGauss of the magnetic field while for 25.5°C in Figure 8(a), the shift has a peak (Δf = 2.18 MHz) at 0.2 kGauss of the magnetic field. As the temperature is increased, the peak occurs earlier at lower value of the magnetic field than that at relatively lower temperature. The width (Δw) in Figure 7(a) for the system at 19°C has a peak ($\Delta w = 2.75 \text{ MHz}$) at the magnetic field 0.075 kGauss while in Figure 8(a) for 25.5°C temperature, the peak($\Delta w = 2.18 \text{ MHz}$) occurs at 0.2 kGauss. **This** reveals that by increasing temperature from 19°C to 25.5"C, the peak occurs at larger value of the magnetic field than that found at lower temperature. The loss tangent $(\Delta w/2\Delta f)$, relaxation time (τ) and activation energy (ΔG) at 19^oC are shown in Figures $7(b)$ -(d) while for 25.5°C those observed parameters are given in Figures $8(b) - (d)$ respectively show non-linear trend of change with respect to magnetic field applied. More fluctuations are found at 255°C. There occurs a peak in the plot of loss tangent at 0.075 kGauss for 19 \textdegree C, while for 25.5 \textdegree C, there appears a dip in the plot. A similar characteristic is also found in the plots of the relaxation time and

FIGURE 7 Variation of (a) amplitude (Δh) , width (Δw) , shift (Δf) ; (b) loss tangent $(\Delta w/2\Delta f)$; (c) relaxation time (τ) ; (d) activation energy (ΔG) as a function of magnetic field; (e) relative width (Δw) *versus* relative shift (Δf) for Nitrobenzene at 19°C.

activation energy. **This** indicate that change in the temperature affects the loss, relaxation time and activation energy significantly. The plot of the width (Δw) *versus* the shift (Δf) in Figure 7(e) for 19^oC and for **25.5"C** in Figure 8(e) are entirely different. For **19°C** temperature, the width shows increasing trend and attains a peak $(\Delta w = 2.75 \text{ MHz})$ at the shift $(\Delta f = 2.50 \text{ MHz})$ then it decreases while for 25.5°C temperature, the width shows the decreasing nature and there comes a dip $(\Delta w = 0.64 \text{ MHz})$ at shift $(\Delta f = 2.10 \text{ MHz})$ then it acquires an increasing trend and attains a maxima in the curve. **This** significantly indicates that the dielectric loss (ε'') is changed entirely at higher temperature with respect to the permittivity(ε').

FIGURE 8 Variation of (a) amplitude (Δh) , width (Δw) , shift (Δf) ; (b) loss tangent $(\Delta w/2\Delta f)$; (c) relaxation time (τ) ; (d) activation energy (ΔG) as a function of magnetic field; (e) relative width (Δw) *versus* relative shift (Δf) for NitroBenzene at 25.5°C.

The comparison of the data for nitrobenzene at temperatures 19°C and 25.5"C indicates that the shift, width, loss tangent, relaxation time and activation energy exhibit the increased values **on** the increment of the temperature.

It is also observed that the application of the magnetic field of 1.3 kGauss changes relaxation times are in the order 1.45, **7.07** and $3.36~\text{ps}$ from those 2.26 , 3.69 and $13.78~\text{ps}$ in the absence of the magnetic field for 2-chlorobutane, acetonitrile and nitrobenzene respectively. These polar organic liquids have molecular weights 92.5, 41 and 123 respectively showing that relaxation time is more sensitive to magnetic field in comparison to molecular weights of the systems considered. Further, nitrobenzene is relatively less affected in comparison to the other two organic liquids which may be due to more

degree of association of molecules and its highest molecular weight among the systems chosen.

4. CONCLUSION

The work reported in this paper indicates that the temperature and magnetic field significantly influence the dielectric properties of the organic liquids considered. The relative variation of permittivity(ε) and dielectric loss (ε'') and molecular collisions can fruitfully be studied using microwave cavity spectrometer. The form factor *F(E)* is required for the calculation of absolute values of ε' and ε'' which may be done using the method [3] of fitting the data of dielectric response for the organic liquids chosen.

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