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PHASE TRANSITION STUDIES IN POLAR AND NONPOLAR
LIQUIDS AT MICROWAVE FREQUENCIES

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A resonant microwave cavity technique was employed to study the dielectric behavior of some polar and non-polar liquids near the phase transition temperatures at microwave frequencies of 7.2, 9.2 and 10.1 GHz. The Slater perturbation equations for a resonant microwave cavity are briefly discussed to show that the above technique can be used to determine both the real and imaginary parts of dielectric response. Abrupt changes in dielectric response were observed near the phase transition temperatures for the polar liquids studied in this investigation.

Dielectric response at room temperature was observed in various polar and non-polar liquids by comparing their slopes with some standard liquids using power-law equations. The room temperature values were normalized to the experimentally observed dielectric relaxation and the real and imaginary parts of dielectric response calculated at different temperatures. Debye equations were used to calculate relaxation times at different temperatures.

The dielectric relaxation phenomenon in liquids has been treated as a chemical rate process and the abrupt

change in the dielectric response of the liquids near phase transition temperatures is shown to be related to the dramatic changes in the free energy of activation of the molecules. Some values of the free energy of activation were deduced for the various compounds from data obtained in this investigation.

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CHAPTER I

INTRODUCTION

The investigation of the dielectric properties of matter has provided an important approach to understand the structure of matter, and, without some understanding of the relation of these properties to matter, our extensive knowledge of dielectric behavior loses much of its significance.

A number of experiments have been performed to investigate the dielectric properties of solids, liquids and gases at various frequencies. Resonant circuit methods have been used up to a frequency of 10^8 Hz, but these methods are not suitable beyond this frequency range because of energy losses into the space. Various techniques have been used to investigate the dielectric behavior of polar and non-polar liquids at low frequencies. The dielectric constant values of water were determined by capacitance measurements made at frequencies varying from 500 cps to 50 kc/sec.¹ Malmberg and Maryott² measured the static dielectric constant of water at frequencies between 3 and 96 KHz.

During the late 1930's some investigations of the dielectric constant of water were done in the MHz region and some idea of the relaxation process was obtained.

The rapid development of microwave valves and guided wave techniques during the second world war made possible the detailed investigation of the GHz, or microwave, region. Definitive measurements were made by Collie et al.³ and independently by Saxton and Lane.^{4,5}

The present investigation involves the use of a microwave resonant cavity to study the dielectric response of various polar and non-polar liquids as they are required to undergo a phase transition.

The microwave resonant cavity displays the same resonant characteristic as a tuned circuit, the basic difference between the two is that the current and voltage of the tuned circuit are replaced by electromagnetic fields. Similar to a waveguide that forms the microwave analogy for the transmission line of ordinary circuit theory, so a hollow cavity forms the analogy for a circuit element.

The quality factor Q which is defined as the ratio of the resonant center frequency to the half-power frequency width of the resonant curve, is determined either in the resonant circuits or the resonant cavity from the shape of the resonant curve. Because of the low resistances in a resonant cavity, a large value for Q can be obtained as compared to a resonant circuit which has a low value of the quality factor Q . As the sample to be studied is placed in the cavity, it perturbs the electric or magnetic field in the cavity depending on what mode the cavity is in, and

from this either electric permittivity or magnetic permeability can be determined. The cavity resonator technique is a standard technique and has been used by several workers. M. Bruma⁶ and S. Chatterjee⁷ used a circular cavity resonating in E_{010} mode with capillary tube specimen and tuning plunger. C. H. Collie et al.⁸ made use of a circular cavity resonating in H_{01} mode with capillary tube specimen. The method can be applied to plasma experiments by placing the plasma in the cavity and determining the electron density from a measurement of resonant frequency shift.⁹ K. H. Hong and J. A. Roberts¹⁰ used a cylindrical cavity resonating near 10 GHz in TM_{010} mode to determine the dielectric properties of liquids and solids.

Perturbation theories were introduced by Bethe et al.¹¹ and by Slater¹² in 1943 and 1946 respectively. These theories are basically the same. The perturbation of the boundaries i.e., the problem of the change of frequency of a resonant cavity, when its boundaries are perturbed, as by pushing a small part of the wall in or out is the same in both the theories. As the sample is introduced into the cavity, it perturbs the electromagnetic fields inside the cavity. Slater's perturbation theory was used to explain the interaction of the material properties and the electromagnetic fields and hence useful expressions were derived to explain the dielectric behavior of the materials under investigation. According to Slater's perturbation theory,

as the sample is introduced into the cavity it causes the resonant frequency shift and the quality factor Q to change in accordance with the characteristic electrical properties of the material loading the cavity. It is a very interesting experiment to find the dielectric response of a material near its freezing or melting point i.e., going from solid to liquid phase or in other words from a ordered to a disordered phase. The dielectric behavior of polar molecules from solid to the liquid phase is of great interest. It has been shown by Smyth¹³ that from measurements of the static dielectric constant of compounds as a function of the temperature, important conclusions concerning the molecular freedom may be drawn. It appears that the degrees of freedom of orientation of the molecular dipoles may disappear when a liquid solidifies. When they do not, then they disappear at lower temperatures, the transitions (lattice changes) being of the second order. The dielectric response of a polar liquid shows a large change at the freezing point. A typical example is that of nitromethane as studied by Smyth and Walls.¹⁴ The measurements in this polar molecule have been carried out at a frequency of about 7×10^4 Hz. The drop in the dielectric constant of nitromethane from 45.5 to 3.93 at the freezing point is caused by the electronic and atomic polarizations. In solid nitromethane the dipole axes are fixed so rigidly in the lattice that the permanent dipoles

cannot orientate in an applied field. This does not exclude all molecular rotations, since a fixed dipole axis still allows rotation of the molecule about this axis. Smyth and Hitchcock¹⁵ made similar measurements on nitrobenzene and found that the dipole relaxation occurred at rather large frequencies. A contribution from permanent dipoles to the polarization in an applied field does not necessarily mean that the molecules have complete freedom of rotation about one or more axes not coinciding with the dipole axis. It is also possible that the dipole axes have a distinct number of positions of relatively minimal potential energy, separated by potential energy barriers. When the rotational energy allows a sufficiently frequent passage over these barriers the contribution of the dipoles to the polarization in an applied field may be the same as in the case of free orientation. In the present investigation the sample under study was placed in a small capillary tube and was driven into the cavity by attaching it to one end of a micrometer drive. The diameter of the sample holder was very small as compared with the wavelength of the cavity field. The cavity was resonating in TE_{011} mode so the perturbation was principally that of the electric field.

The sample under study was cooled below its freezing point and the temperature was kept constant to ensure freezing. Then the system was allowed to warm up and

measurements of the resonant frequency shift and the quality factor Q change were made. The solid-to-liquid phase change was successfully monitored in all the polar and non-polar media by observing the dielectric response at temperatures near the freezing point. In the case of polar molecules a dramatic change in the dielectric response was observed. This change in the dielectric response was further related to the relaxation mechanisms of the molecule.

The relaxation rate is defined as the rate at which a system comes into equilibrium with its surroundings when various physical aspects of its surroundings such as temperature, electric and magnetic fields are changed. According to Kauzmann¹⁶ these relaxation rates may be arranged in two groups, which are determined by how rapidly the relaxation mechanisms change with the temperature. In one group we have those rates which depend on properties like thermal conductivity, the electrical conductivity of metallic conductors, and the velocities of sound and light which do not depend on temperature. On the other hand we have the group in which the relaxation rates do change with the temperature. The rate at which the portion of the dielectric polarization arising from the orientation of permanent molecular dipoles comes into equilibrium with an applied field is temperature dependent. Since the

relaxation rate τ is a measure of the time lag between the applied field and the system's response, it is called the relaxation time.

The nature of the dependence of the relaxation rates on temperature is very significant in understanding the physical nature of the process. In a process in which the relaxation rate depends on the temperature, it is certain that at some stage in the process a molecule, or other unit involved, is forced to wait until it has acquired a considerable amount of energy by thermal fluctuations, in excess of the average thermal energy in the medium. The factors which govern the rate of acquiring large amounts of energy through thermal fluctuations have long been the object of study by chemists in their investigations of the very similar problem of the rates of chemical reactions. Since by now fairly complete ideas about these factors have been developed, it is worthwhile to apply these notions to the phenomenon of dielectric relaxation rates in order to have a thorough understanding of their fundamental mechanisms.

Andrade's¹⁷ theory of viscosity stated that the viscosity of a liquid arises from collisions between two molecules, during which they are momentarily so closely associated that no relative linear motion is possible between them. This is the form of association we recognize as freezing when it involves a large number of molecules

instead of a pair. There is a sharp drop in the electrical permittivity of most polar substances at their freezing points and this drop in the permittivity tends toward the high-frequency value of ϵ for a gas. Thus, in the solid state the permanent dipoles no longer contribute to the polarization. Thus freezing may also prevent relative rotation of the molecules. Nora E. Hill¹⁸ classified such substances as class I. All the substances that we have studied in the present work fall into this class and we have observed a dramatic change in the permittivity of each substance at the freezing point.

The solid-to-liquid phase change was successfully monitored in several polar and non-polar liquids by observing the dielectric response near the freezing point and this change in dielectric response of polar molecules as they undergo phase-change was found to be quite dramatic.

Dielectric relaxation is the cause of anomalous dispersion in which the dielectric constant decreases with increasing frequency. From a structural point of view, the most interesting dielectric relaxation is that involving orientation polarization, which depends on the internal structures of the molecules and on the molecular arrangement of the dielectric. In terms of the theory of this phenomenon as developed by Debye¹⁹, dielectric relaxation is the lag in dipole orientation behind an alternating field. The strong dependence of relaxation rate on

temperature indicates that during the relaxation process there comes a stage that a particle needs a certain amount of energy in excess of the average thermal energy to overcome a potential barrier. The molecule must wait until it has acquired the required amount of energy by thermal fluctuations and this accounts for the strong dependence of relaxation rate on temperature. The same is true for the exponential temperature dependence of the macroscopic viscosity coefficient. Thus, the exponential temperature dependence of τ and η is similar to that of chemical reaction rates where we also consider the case that a particle has to acquire a certain activation free energy.

Eyring²⁰ first approached the phenomenon of dielectric relaxation as a chemical rate process. Using his rate equations he derived the relaxation times in ice and water. Since then the rate theory has been successfully applied to the dielectric behavior of several substances including nitrobenzene,²¹ ortho and meta nitrotoluene²² and other organic compounds.²³⁻²⁵ Several workers²⁶⁻²⁹ in the past have studied the dielectric behavior of water, but a comprehensive treatment is that given by Franks.³⁰ Most of these authors have shown that their results in explaining the dielectric behavior of water satisfied single relaxation time equations. A value of 0.014 for the distribution parameter α for water as calculated by Schwan

et al.³¹ suggested that there is not so large a deviation in the relaxation phenomenon from that predicted by the Debye equations.

Hence, we have followed the simple Debye model to explain our results on dielectric behavior. Therefore, we have explained the abrupt change in the dielectric response near the phase transition in terms of the rate theory and correlated these changes with the sharp decrease in activation energy of dipole relaxation process as the substance melts. The approach seems to successfully explain the dielectric behavior of liquids studied near phase change.

In the next chapter a discussion is given of how a microwave spectrometer can be used to monitor the real and imaginary components of the dielectric response of a medium undergoing phase change.

CHAPTER II

MICROWAVE CIRCUIT ELEMENTS AND TECHNIQUES

Resonant Cavity Theory and Design

A cavity resonator has in principle the same resonant characteristic as a tuned inductance and capacitance circuit. The main difference between the two is that the current and voltage of the tuned circuit are replaced by electromagnetic fields. Cavity resonators are used widely in spectroscopy as absorption cells and also as wavemeters. The fact that their Q values can be made of the order of 20,000 means that they can store a large amount of microwave energy, as well as acting as highly selective tuned circuits. This ability to store energy means that a substance placed inside the cavity will be in radiofrequency magnetic and electric field strengths very many times larger than those existing in the waveguide feeding the cavity.

Like any other resonant device a cavity resonator possesses a resonant loss factor Q defined as

$$Q = \frac{2\pi f \times \text{maximun stored energy}}{\text{Power loss}} \quad (2.1)$$

This value is determined by the proportion of energy that is lost as the induced radio-frequency currents flow through the resistance of the cavity walls. Expressions for the Q-values of both rectangular and cylindrical cavities can be derived.³²⁻³³

In this investigation a cylindrical cavity was used with the dimensions as shown in Figure (1). The cavity was resonating in the TE_{011} mode. In Figure (2) it can also be seen how the cylindrical cavity may be tuned by the movement of an internal adjustable disk or piston and thus change the resonant frequency of the cavity.

The equations of interest in this investigation are outlined as follows:

By solving the Maxwell's equations with appropriate boundary conditions the field patterns or the modes of the cavity resonators can be derived.³⁴ In general the modes of an electric field are designated by TE_{mnp} , where m comes from θ equation of E_r . But in a way it is the order of Bessel's function. Physically the designation represents how many times the field pattern repeats itself when we go from $\theta = 0$ to $\theta = 2\pi$. It can be seen that for TE_{011} modes the field patterns are not repeated along θ . The subscript n is the n th zero of a Bessel's function. Physically n represents the number of half wave-lengths of the fields lying along r -direction. Thus $n = 1$ will give only $\lambda/2$ along the r direction for the electric field. The

Fig. (3.4)

- (a) Cylindrical coordinates for the cavity.
 (b) Electric Field patterns for TE_{011} mode.
 (c) Magnetic Field patterns for TE_{011} mode.

Fig. 1. Microwave cavity geometry and fields.

$R = 4.9 \text{ cm.}$

Fig. 2. Tunable cylindrical cavity operated in TE_{011} mode used in this investigation.

subscript p is the number of half wave-lengths of the field along the z-direction. All these conditions are necessary in order to satisfy the boundary conditions for Maxwell's equations.

For a cylindrical resonant cavity, operating in TE_{011} mode the solutions of Maxwell's frequency dependent field equations, yield solutions for $\vec{E}$ and $\vec{H}$ fields which can be expressed as follows

$$E_r = E_z = 0 \quad (2.2)$$

$$E_\theta = -CD\gamma J_1(\gamma r) \sin\left(\frac{\pi}{b} z\right) e^{i\omega t} \quad (2.3)$$

$$H_z = CD \left[\omega\epsilon - \frac{\pi^2}{\mu\omega b^2} \right] J_0(\gamma r) \sin\left(\frac{\pi}{b} z\right) e^{i(\omega t - \pi/2)} \quad (2.4)$$

$$H_r = \frac{-\gamma\pi CD}{\mu\epsilon b} J_1(\gamma r) \cos\left(\frac{\pi}{b} z\right) e^{i(\omega t - \pi/2)} \quad (2.5)$$

$$H_\theta = 0 \quad (2.6)$$

where J_0 and J_1 are the Bessel functions of the first kind. C and D are the constants, and γ is given by the following equation

$$\gamma = \left[\mu\epsilon\omega^2 - \left(\frac{\pi}{b}\right)^2 \right]^{1/2} \quad (2.7)$$

μ and ϵ are the dielectric permeability and dielectric permittivity of the medium respectively and p is an integer. The radius of the cavity is 'a' and the vertical Z-dimension is shown in Figure (1).

The field patterns for the TE_{011} mode in the cylindrical cavity were assumed to be as drawn in Figure (1). We see from this figure that the E field has a circular component in this mode. It does not have a Z or r component and is maximum at $r = a/2$ and $Z = b/2$. Magnetic field has no θ dependence. Just like E-field, it is also symmetric with respect to θ . Note that there is no tangential component of the electric field inside the cavity. It is because of the physics of electromagnetic waves inside a conductor, and not because of the existence of currents in the inside walls, and that is the reason we always have a finite Q of a cavity.

Coupling to the Wave Guide

For wavelengths below 3 cms. iris holes are used to couple cavity resonator to the waveguide. The size of the hole and thickness of intervening wall determines the tightness of the coupling.³⁵ Tight coupling will reduce the effective Q of the resonator, and hence also the absorption produced by the specimen. In a cavity, coupling is accomplished by one or two holes in the cavity wall. Usually coupling is designed to excite preferentially some particular mode by making the electric or magnetic lines of

force at the coupling region coincide with those of the desired mode. For instance the TE_{01p} mode in a cylindrical cavity may be excited by two diametrically opposite holes in the end wall.³⁶ These holes coincide with holes in the narrow face of the waveguide approximately $\lambda_g/2$ apart. The cavity used in this investigation was coupled to the waveguide by two holes drilled in the E-plane of the waveguide.

Cooling and Heating System of the Cavity

In this investigation each sample studied was cooled below its freezing point by a heat exchange mechanism. The samples were placed along the symmetry axis of the cavity. Temperature control of the sample was achieved by flushing cold nitrogen gas around the resonant cavity with the nitrogen gas passed through a heat exchanger consisting of a 5 liter dewar filled with liquid nitrogen in which a coil of copper pipe rested. The rate of flow of the nitrogen gas through the heat exchanger determined the rate of cooling of the cavity. The cavity temperature was monitored using a thermocouple calibrated and referenced in the standard manner. The calibration curve for the copper constantan thermocouple was obtained by using a simple program in the HP-2000 basic computer system. Figure (3) shows the calibration curve for the copper-constantan thermocouple. Sufficient time was allowed to elapse at each reading in order to enable the sample and cavity to

Fig. 3. Calibration curve for a copper-constantan thermocouple with the reference junction at 273 K.

come to equilibrium temperature. For some measurements the sample was heated above room temperature by passing hot gas through the copper coil around the cavity. The hot gas was obtained by passing gas through a hot oil bath. The rate of heating was controlled by varying the gas flow rate.

Microwave Source

The detailed construction of the klystron is out of the scope of this paper and is given in standard microwave electronic books.^{37,38} A V-58 type reflex klystron was used in this investigation. The microwave signal generated by the reflex klystron gives only a narrow frequency interval as shown in Figure 4 (i) and needs to be modulated in order to get a band of frequencies to drive the resonant cavity.

Signal Modulation and Detection

Since the unmodulated source gives a single frequency, in order to get a time varying signal the reflex klystron had to be modulated. This was done in the following manner.

1. The klystron was modulated with the horizontal sawtooth sweep voltage from the oscilloscope thus giving a signal which was synchronized with the klystron frequency output. The modulated signal from the klystron appears as shown in Figure 4(ii).

(i) Klystron mode shape (unmodulated width).

(ii) Klystron mode shape modulated.

(iii) Reflected power absorption by cavity.

Fig. 4. MICROWAVE ABSORPTION SIGNALS

2. Considerable improvement in signal-to-noise ratio can be obtained by a small frequency modulation of the klystron oscillator at, say, a frequency of the order of 100kc in addition to the slower sweep frequency.^{39,40} This type of modulation can be easily achieved by adding a 100kc sine or square wave sweep voltage to the repeller of the klystron to chop the signal.

In the present investigation the microwave signal was generated by a reflex klystron, which was voltage controlled by several signals. The principal voltages and mechanical tuning were set to drive a signal frequency near the cavity resonance with two additional signals added for sweep and signal control. A sawtooth ramp voltage, derived from the time base of a Tektronic Model 561A oscilloscope, sweeps the klystron over the range of frequencies desired while simultaneously a chopper signal of 31 kHz is impressed upon the klystron repeller electrode to produce an a.c. signal of that frequency at the detector. This arrangement allows for a synchronized sweep of frequency with the voltage scan of the oscilloscope. The 31 kHz signal enables high-gain tuned amplifiers to be employed to detect the signal arriving at the r.f. detector. The chopper signal also serves as a reference signal for the PSD, in case phase coherent detection is desired.

The nature of the display sought determines what final stages of amplification and processing are desired for the signals.

The next important device in this operation is a crystal detector which is used for the radio-frequency wave. Crystal detectors have wide use in the microwave field because of their sensitivity and simplicity. They are used as "video detectors" to provide either a d-c output when unmodulated microwave energy is applied, or a low frequency a-c output (up to tens of mHz or higher) when the microwave signal is modulated. The essential parts of a crystal detector are a semiconducting wafer and a metal "whisker" which contacts the wafer.⁴¹ In the present experimental technique two crystal detectors were used, one of which was installed in the reflectometer to provide dc output when the klystron modulated signal is reflected from the resonant cavity. Another crystal detector was mounted in a directional coupler to mix the modulated klystron signal with the nth harmonic waves from the standard frequency multiplier. The frequency multiplying technique will be discussed in the later sections of this chapter.

For accurate frequency measurement and to reject unwanted noise which might be near the resonances being observed, a tuned amplifier was used. The signal output

of the tuned amplifier was observed on the oscilloscope along with the frequency marker which gave relative and absolute frequency values.

Directional Coupler

There are two forms of the directional couplers commonly used in microwave work. One employs coupling via two iris holes in the narrow side of the guide, while the other uses just a single hole in the wide side. Since only the longitudinal $\vec{H}$ component is present along the narrow side of the guide, the coupling in the first case will be entirely magnetic, and each hole will radiate equally in both directions into the second guide. If the two coupling holes are $\lambda_g/4$ apart, interference will take place between them, both holes adding to a wave traveling in the same direction as in the first guide, but producing a combined phase change of π for a backward-traveling wave. As an example, for a standard K band (1.25 cm) guide with 0.04 inch wall thickness there will be coupled power ratio of 75 dB for a hole diameter of 0.05 in., and a coupling ratio of 30 dB for a hole diameter of 0.14 in.⁴² A more complete discussion of the directional coupler is given by Townes and Schawlow.⁴³ In the present investigation two directional couplers were used. One leads the microwave power to the frequency measuring section of the waveguide system which consists of a crystal diode detector that mixes and

multiplies the frequency reference signal. The other serves as a reflectometer arm to which the resonant cavity is attached.

Frequency Multiplication

It is often desirable to take an ordinary radio frequency signal, and multiply it to the microwave range, so as to make absolute standardization of microwave frequencies in terms of known standards of lower frequencies. This multiplication can be done by conventional frequency multipliers, using ordinary devices, until we obtain frequencies in the microwave range. The other application would be to produce very high frequencies through harmonic generation from klystrons. Klystrons become more difficult to construct as the frequency becomes higher and higher, on account of the reduced size of the cavities and other parts of the resonant circuit.

Systems which are rich in the generation of harmonics can be used as frequency multipliers. All the single tube amplifiers possess this characteristic due to the non-linearity existing in the plate current curve when the signal e.m.f.s. are applied in the grid. Therefore, one or more intermediate amplifier applied in r.f. channel may act as a frequency multiplier. Frequency multipliers which are used in the early stages of microwave standards are not

essentially different from those used in radio transmitters.⁴⁴ A discussion of frequency multipliers is also given in reference 42, pp. 365-374.

To produce microwave frequencies a higher order of multiplication is needed, especially if one starts from an oscillator in the region of 100 kc. In some microwave-frequency standards conventional tubes are used up to a frequency of some hundreds of megacycles, and then followed by a silicon crystal harmonic generator. The crystal harmonic generators receive fundamental microwave power from klystron, and because of the nonlinear response of the semiconductor to the microwave field, they produce harmonics of the fundamental. Generally good harmonic generators involve efficient matching of the fundamental microwave power into a crystal and appropriate nonlinear characteristics. They also require efficient radiation of the generated and desired harmonics into the waveguide region where frequency comparisons are to be made.

In the present investigation two different kinds of frequency multipliers were used. One kind was Model 900 B Sweep Signal Generator made by Jerrold Electronic Corporation which was calibrated to Model 1112 A and 1112 B General Radio Standards slowed to a 105 B quartz oscillator made by Hewlett-Packard. The frequency multiplication

in both of these units is basically the same. The operation of the frequency standard can be followed from the block diagram shown in Figure (5).

This 1112 A, B frequency standard utilizes a chain of frequency multipliers and r-f amplifiers to produce the higher frequencies from a 5 MHz oscillator stabilized by a quartz crystal. The standard frequencies are 10 MHz, 100 MHz and 1000 MHz. The highest of these frequencies is applied to one electrode of the mixer crystal and the other two lower frequencies and the receiver are connected to the other electrode. To prevent loss of the higher frequency power into the low frequency circuits, a small capacitance and an inductance are provided at the lower frequency end of the crystal. Line stretchers vary the lengths of the coaxial cables; and a tuning stub shorted at the end, adjusts the line impedance at the crystal. A meter monitors the crystal current and a variable resistor adjusts the bias on the crystal to optimize the non-linearities for maximum harmonic production. A plunger in the mixer can be adjusted to give a maximum microwave field at the crystal.

The crystal mixer rectifies the r-f signal and the rectified wave is known to be the resultant of components of a harmonic wave. Through the Fourier analysis of the non-sinusoidal periodic wave form, it can be seen that the rectified wave is made of sinusoidal components whose

Figure 5--Block diagram of the frequency determination arrangement employed in this investigation. (A) Circuit diagram for frequency comparisons between the main standard frequency source and the secondary standard. (B) Marker mixer circuit for generating frequency markers.

frequencies are integral multiples of the fundamental frequency of the non-sinusoidal periodic wave form. Through the multiplication process the initial frequency of 5 MHz in the crystal oscillator is increased to the required frequency. This process of multiplication is continued until finally a high order harmonic output is delivered into the mixer and the mixing process occurs. Since the arbitrary n th harmonic wave from the frequency multiplier can be matched to the modulated klystron frequency, the frequency difference can be received by the radio receiver. The radio receiver used for the interpolation method was a model 1330 A bridge oscillator made by General Radio Company. The radio receiver responds to only the frequency difference between the klystron resonant frequency and an n th harmonic from the frequency multiplier. This difference of frequency can be expressed mathematically by the following equation,

$$f_m = n f_a \pm l f_b \pm m f_c \pm f_r \quad (2.8)$$

where f_m is the microwave frequency, f_a , f_b and f_c are the standard frequencies, f_r is the frequency to which the interpolation receiver is tuned, l , m and n are integers. The plus or minus sign in the above equation shows that the local oscillator signal can mix from either a sum or difference with the center frequency of the klystron. The resulting frequency difference yields two frequency

markers which are displayed on the oscilloscope. The appearance of the markers, displayed on one channel of a dual trace oscilloscope, depends strongly upon the wave form, frequency, and amplitude of the klystron modulation.

Two kinds of modulation are generally employed, square wave and sine wave. In the case of square wave modulation each marker will appear, split in frequency. The following equation holds for square wave modulation.

$$2\delta\nu = 2(\sqrt{3}\Delta\nu)^{-1}(1 + \omega'^2\Delta\nu^2/4 + \nu^2\Delta\nu^2) \quad (2.9)$$

where $2\delta\nu$ is the observed separation between maximum and minimum of the derivative contour, ω' is the change in source frequency with each swing of the modulating voltage, ν is the angular frequency of the modulating voltage and $\Delta\nu$ is the half-width at half power maximum for the resonance. In case of a sine wave modulation signal, the marker appearance is not so simple. In this case, a series of markers will appear with separation, $\nu/2\pi$, given by the modulation frequency. In this investigation modulation signals were minimized and the modulation correction could be reduced to $\Delta\nu = \sqrt{3} \delta\nu$.

The absolute frequency measurements were determined by comparison of the secondary standard to a General Radio Model 1112 A and 1112 B set of harmonic generators properly stabilized. To measure the coarse frequencies, a Narda Model 810 wavemeter was employed in this investigation.

This wavemeter was calibrated by using the General Radio Standard Models 1112 A and 1112 B. The calibration curve for the wavemeter is shown in Figure 6.

Attenuators

Attenuators are used to increase the power range of sensitive instruments, to measure gain or loss, and to act as buffers which reduce interaction between instruments. A common use is in providing signal generators with accurate output adjustment for precise measurements. Use of attenuators in the system helps to reduce standing waves since reflected waves must pass an attenuator twice in each back-and-forth trip through the waveguide. Attenuation can be obtained by inserting a strip of lossy material into the guide through a longitudinal slit in the center of the broad face. The simplest way to construct a fixed attenuator is to attach a strip of lossy dielectric to the narrow wall of the waveguide.

Experimental Operation and Procedure

Each sample to be tested was placed along the symmetry axis of the cavity through a micrometer drive. The cavity resonating in TE_{011} mode was placed into a thermal bath. Temperature control of the sample was achieved by flushing cold nitrogen gas through a copper coil which was wrapped around the cavity, with the nitrogen gas passed through a heat exchanger consisting of a 5 liter dewar filled with

Fig. 6. Calibration curve for the wavemeter (Narda Model 810) used in this investigation.

liquid nitrogen in which the copper coil was resting. The rate at which the nitrogen gas was flushed around the cavity determined the rate of cooling. Each sample was cooled down below its freezing point. Then the temperature was allowed to rise in suitable steps and resonant frequency shifts Δf and ΔW were measured for each temperature until sufficient data were obtained to determine the behavior of the dielectric response of the system over the transition region. At each reading sufficient time was allowed to elapse so that the sample and cavity come to temperature equilibrium. The temperature of the cavity was monitored by using a copper-constantan thermo-couple, by attaching it to the cavity wall. The thermocouple was calibrated and referenced in the standard manner.

The block diagram of the spectrometer used in this investigation is shown in Figure 7. The microwave signal is generated from klystron and is transmitted through the waveguide. The directional coupler divides this signal into two parts. A part of the signal goes to the cavity and is reflected. The power absorption reflected by the cavity and is detected by a crystal rectifier in the reflectometer and is amplified by means of a 31 kHz tuned amplifier. The absorbed signal due to the unloaded cavity is modulated and a differential display of the resonance profile is obtained as shown in Figure 8.

Fig. 7. Block diagram of the microwave cavity spectrometer employed in this investigation.

(i) Enlarged drawing for power absorption by the cavity.

(ii) Chopper wave modulated signal.

(a)

(i) First derivative of resonance absorption.

(ii) Resonant frequency shift and width change due to insertion of the sample into cavity.

(b)

Fig. 8. -Power absorption and perturbation signal of the cavity.

Now as the sample is inserted into the cavity, it perturbs the electromagnetic fields in the cavity. As a result the resonant frequency shifts and the cavity Q changes. With the help of the marker produced by harmonic generator (as discussed in the earlier sections) we can find the values of $\Delta f = (P_0' - P_0)$ and $\Delta W = (P_2' - P_1') - (P_2 - P_1)$ as shown in Figure 8. Figure 9 shows an actual picture of the signal taken from the oscilloscope along with the markers.

Fig. 9. Dual trace oscilloscope display for frequency markers and cavity derivative profile for a typical scan.

CHAPTER III

THEORETICAL BACKGROUND

In order to understand how the perturbing sample interacts with the applied electric field a basic understanding of how the dielectric response of a medium arises. A discussion is given below to enable a better understanding of the basic procedures occurring in media subjected to applied fields.

The dielectric constant of a polar liquid arises from the orientation of molecular permanent electric dipoles and the electrical distortion of the molecules. Both of these effects can be expressed in terms of a quantity P , the polarization, or dipole moment per unit volume of a continuous material:

$$P = (N_0/V) \bar{\mu}_0 \quad (3.1)$$

where $\bar{\mu}_0$ is the average dipole moment per molecule, N_0 is Avogadro's number, and V is the molar volume. The polarization process always involves rapidly forming polarization which consists mainly of electronic polarization, and may also involve slowly forming polarization. The electronic polarization is due to the displacement of the electrons in the atoms relative to the positive nuclei with the relaxation

time of about 10^{-15} sec. and corresponds to the frequency of ultraviolet light. A relatively small atomic polarization arises from the displacement of atoms relative to one another in the molecule. The relaxation time for this process is about 10^{-12} to 10^{-14} sec. and this corresponds to the frequency of infrared light. Resonance absorption corresponding to changes in rotational energy levels may occur in the microwave region to give rise to microwave spectra, but the energy loss is normally small. For small molecules in liquids of low viscosity, the time required for relaxation process is about 10^{-11} to 10^{-10} sec., corresponding to the frequency which lies in the microwave region.

Relaxation may be defined as the time lag in the response of a system to a change in the physical forces to which it is subjected. The term relaxation mainly applies to linear systems where a response and a stimulus are proportional to one another in equilibrium. Relaxation, is a delayed response to a changing stimulus in such a system. Dielectric relaxation occurs in dielectrics. The stimulus is almost always an electrical field, the response a polarization. The time lag between field and polarization implies an irreversible degradation of free energy to heat. The relaxation time may be defined as the time in which this polarization is reduced to $1/e$ times its original value, e being the natural logarithmic base.

Debye¹⁹ in his theory explained the relaxation phenomenon and showed that the polarization of a dielectric medium in an electric field might arise from the partial orientation of permanent molecular dipoles by the field as well as from the distortion of electronic orbits in the molecules. The theory starts with an assumption about the time variation of the polarization in response to a step function removal of field. The simplest assumption is of an exponential decay:

$$P(t) = P_0 e^{-t/\tau} \quad (3.2)$$

where τ is the relaxation time. The physical meaning of such a decay is that the rate of change of polarization is proportional to the difference between the instantaneous polarization and its final value. This relaxation assumption is often used in the theory of the return to equilibrium of a perturbed system.

For the application of a harmonically time-dependent field of angular frequency $\omega = 2\pi\nu$ described by

$$E(t) = E_0 e^{j\omega t} \quad (3.3)$$

where E_0 is independent of time t , the frequency-dependent complex dielectric constant which is defined as

$$\epsilon^* = \epsilon' - j \epsilon'' \quad (3.4)$$

was shown to be

$$\epsilon^* = \epsilon_{\infty} + \frac{(\epsilon_s - \epsilon_{\infty})}{(1 + j\omega\tau)} \quad (3.5)$$

where ϵ_s is the static dielectric constant for time-invariant fields and ϵ_{∞} the residual dielectric constant appropriate to frequencies much higher than that of the relaxation process; at sufficiently high frequencies permanent dipoles make no contribution to the dielectric constant and only atomic and electronic polarizations contribute.

Debye obtained the expression given in equation (3.5) using a very specialized model, that of spherical molecules in a viscous fluid; a quantity containing the viscosity of the fluid, ϵ_s , ϵ_{∞} and other factors replace τ .

Rationalizing equation (3.5) yields

$$\epsilon' = \epsilon_{\infty} + \frac{(\epsilon_s - \epsilon_{\infty})}{(1 + \omega^2\tau^2)} \quad (3.6)$$

and

$$\epsilon'' = \frac{(\epsilon_s - \epsilon_{\infty})\omega\tau}{(1 + \omega^2\tau^2)} \quad (3.7)$$

These are known as the Debye equations for relaxation of a medium driven by a time dependent field as given by equation (3.3).

Experimentally one usually measures the quantities ϵ' and the loss tangent

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (3.8)$$

and it is convenient to know the Debye equations in terms of the loss tangent. Equations (3.6) and (3.7) can be used to get

$$\tan \delta = \frac{(\epsilon_s - \epsilon_\infty) \omega \tau}{\epsilon_s + \epsilon_\infty + \omega^2 \tau^2} \quad (3.9)$$

Further, using his simple model, Debye explained the process of molecular relaxation by assuming the dipolar molecule to be a sphere of radius a moving in a continuous viscous fluid possessing a coefficient of internal friction η and obtained an expression for the relaxation time

$$\tau = \frac{4\pi a^3}{kT} \eta \quad (3.10)$$

The above equation is valid for the systems in which there is no interaction between dipoles which require dilute solutions of dipolar molecules in a non-polar liquid.

The fact that the relaxation rate depends so strongly on the temperature indicates that at some stage in the relaxation process a particle needs a certain amount of energy in excess of the average thermal energy to overcome a potential barrier. The molecule must wait until it has acquired--by thermal fluctuations--the required amount of energy and this accounts for the strong temperature dependence of the relaxation rate. The same is true for the exponential temperature dependence of the macroscopic

viscosity coefficient. Thus the exponential temperature dependence of τ and η is similar to that of chemical reaction rates where we also deal with the case that a particle has to acquire a certain activation free energy.

This possibility of approaching the dielectric relaxation from the standpoint of chemical rate theory was first pointed out by Eyring,^{20,46,47} and developed by Kauzmann.¹⁶

The theory of rate processes operates with rate constants rather than relaxation times. For reaction $A \rightarrow B$ a rate constant K may be defined by the equation

$$\frac{dN_A}{dt} = -kN_A \quad (3.11)$$

where N_A is the number of molecules of species A and K is the number of molecules A disintegrating/time. This equation is a relaxation equation. The definition chosen implies that the end product B is removed so that the speed of the reaction depends entirely on the rate at which species A decomposes, as in radioactive decay. Equation (3.11) implies a relaxation time which can be described as

$$\tau = \frac{1}{K} \quad (3.12)$$

The theory of rate process operates with the concept of a potential hill in the sense that for the reaction $A \rightarrow B$ to proceed, species A has to obtain energy in order to be able to change into species B. It has to attain an

"activated" state which may be pictured as somehow located at the top of potential hill. Activation involves a change of potential energy and may also involve a change in entropy. A free energy of activation may be defined as

$$\Delta G_{\epsilon}^{\ddagger} = \Delta H_{\epsilon}^{\ddagger} - T \Delta S_{\epsilon}^{\ddagger} \quad (3.13)$$

where $\Delta H_{\epsilon}^{\ddagger}$ is the heat of activation and $\Delta S_{\epsilon}^{\ddagger}$ is the entropy of activation for dipole relaxation.

It must be emphasized that $\Delta G_{\epsilon}^{\ddagger}$ for dipole relaxation does not have the same value in the cases of dipole relaxation and viscous flow, since in the latter case both translational and rotational motions of the molecules arise whereas in the case of dipole relaxation only rotational motions are considered. This is one of the reasons why the use of the macroscopic viscosity η in the Debye formula (3.10) should be considered to be only a rough approximation.

An important quantity in Eyring's rate theory is the dipole relaxation rate or jump rate K . The jump rate is related to the probability P what a dipole molecule will move from an orientation θ, ϕ into a new position θ', ϕ' within a solid angle $d\Omega'$ in an interval of time dt . This relationship is given by

$$P(\theta, \phi \rightarrow \theta', \phi') = \frac{1}{4\pi} K(\theta, \phi \rightarrow \theta', \phi') dt d\Omega' \quad (3.14)$$

In the absence of an external field, K is assumed to be independent of θ and ϕ and of the nature of the jump.

According to Eyring's rate theory the jump rate K is related to the free energy of activation $\Delta G_{\epsilon}^{\ddagger}$ by the following expression:

$$K = \frac{kT}{h} e^{-\Delta G_{\epsilon}^{\ddagger}/RT} \quad (3.15)$$

where k is Boltzmann's constant, h is Planck's constant and R is the gas constant.

Thus we obtain for the relaxation time ($\tau = \frac{1}{K}$)

$$\tau = \frac{h}{kT} e^{\Delta G_{\epsilon}^{\ddagger}/RT} \quad (3.16)$$

Using equation (3.13), the above equation can be written as

$$\tau = \frac{h}{kT} e^{\Delta H_{\epsilon}^{\ddagger}/RT} \cdot e^{-\Delta S_{\epsilon}^{\ddagger}/R} \quad (3.17)$$

In equations (3.6) and (3.7), ϵ' represents the phase shift related to the relaxation time τ and ϵ'' is the damping term which is related to the momentum transfer within the molecular system and leads to changes in quality factor of the cavity in which the sample is placed.

Rearranging equations (3.6) and (3.7) yields

$$\omega\tau = \frac{\epsilon_S - \epsilon'}{\epsilon''} \quad (3.18)$$

According to Slater's perturbation theory the phase shift and the cavity Q changes are functions of the dielectric properties and its perturbation change. The derivation of the perturbation equations along with some necessary steps is given in Appendix (A). In this chapter only the final form of the perturbation equations is given below.

$$\frac{\Delta\omega}{\omega} = - \frac{\epsilon' - 1}{2} \frac{\int \vec{E}_s \cdot \vec{E} dv}{\int \vec{E} \cdot \vec{E}_a dv} \quad (3.19)$$

$$\Delta\left(\frac{1}{Q}\right) = \epsilon'' \frac{\int \vec{E}_s \cdot \vec{E} dv}{\int \vec{E} \cdot \vec{E}_a dv} \quad (3.20)$$

where $\vec{E}$ represents the electric field of the perturbed cavity, $\vec{E}_a$ is the electric field of the unperturbed cavity, $\vec{E}_s$ is the local field of the sample, and v and V are the volumes of the sample and the cavity respectively.

The shift in ω and change in Q are dependent upon the location as well as the dielectric nature of the perturbing sample. In this investigation the perturbing sample was placed along the symmetry axis of a cylindrical cavity operating in TE_{011} mode. The resultant change in ω and change in Q were monitored as the cavity temperature was varied. The two parameters, ω and Q are related to the real and imaginary parts of the permittivity of the perturbing sample and measurements on these two parameters enable the values for ϵ' and ϵ'' to be obtained via equations (3.19) and (3.20).

In the next chapter a discussion of various experimental parameters obtained in this investigation can be found.

CHAPTER IV

EXPERIMENTAL RESULTS AND ANALYSIS

The experimental results are divided into five categories and are presented under the following headings.

- A. Dielectric relaxation in polar and non-polar compounds near the phase transition temperature at microwave frequencies.
- B. Mass dependence of dielectric response of polar and non-polar compounds at room temperature.
- C. Temperature dependence of the dielectric response of polar and non-polar compounds at microwave frequencies.
- D. Temperature dependence of the relaxation mechanisms of polar and non-polar compounds at microwave frequencies.
- E. Temperature dependence of the free energy of activation of the compounds at microwave frequencies.

Dielectric - Relaxation

In this investigation a study was made to determine how the values of ΔW and Δf for a resonant microwave cavity change when the cavity is loaded with different compounds subjected to different temperatures. ΔW is the change in

width of the resonance at half power points and Δf is the shift in the resonance frequency under loaded conditions. The compounds were varied over temperature ranges which would cycle them through a phase change of solid-liquid.

All the polar and non-polar liquids studied in this investigation are listed in Table I, along with their transition temperatures and dipole moments as cited in the literature.^{48,49} The selection of the liquid samples was based mainly on the dipole moments, since the main aim of the investigation was to study the dielectric relaxation phenomenon over phase change in various polar and non-polar compounds using a microwave resonant cavity as a probe. All the samples have transition temperatures reasonably near zero degrees C so that phase changes could be obtained with minimum temperature change in the cavity thus reducing the correction required for geometrical changes of the cavity. All the compounds studied were commercially available and were of American Chemical Society Standard Reagent Grade.

Each sample tested was placed along the symmetry axis of the cavity and the resonant frequency and quality factor of the cavity profile determined for that specific temperature. The temperature was altered in suitable steps over the temperature range of interest and Δf and ΔW measured until sufficient data were obtained to determine the behavior of the dielectric response of the system over the transition region. First the dielectric behavior of water at phase change near freezing point was monitored successfully. Then

TABLE I

LIST OF THE COMPOUNDS STUDIED IN THIS INVESTIGATION
WITH THEIR MELTING POINTS AND DIPOLE MOMENTS

FORMULA	COMPOUND NAME	*MELTING POINT (DEGREES C)	**DIPOLE MOMENT (D)	STATE OF SOLVENT	TEMPERATURE (DEGREES C)
$C_7H_7NO_2$	O-NITROTOLUENE	-9.55	3.61-3.94 3.84+0.01	LIQUID LIQUID	9-25 30-110
H_2O	WATER	0.0	3.11	LIQUID	20
C_6H_6	BENZENE	5.5	0.03	LIQUID	25
$C_6H_5NO_2$	NITROBENZENE	5.7	4.16-3.684 4.18+0.02	LIQUID LIQUID	20-170 30-100
$CHBr_3$	BROMOFORM	8.3	1.02+0.03	BENZENE	25
$C_6H_5ClO_2S$	BENZENE-SULFONYL CHLORIDE	15-17	4.59	DIOXANE	25
$C_7H_7NO_2$	M-NITROTOLUENE	16	3.21-3.50 3.88+0.02	LIQUID LIQUID	9-25 30-110

* SEE REFERENCE 48

** SEE REFERENCE 49

the experiment was extended to study the phase transition in several other polar and non-polar molecules. The other polar molecules studied in this investigation were nitrobenzene, benzenesulfonyl chloride, ortho, and meta nitrotoluene. Experiments were also conducted on the weakly polar molecule bromoform and the non-polar molecule benzene.

The results for width change ΔW and frequency shift plotted as a function of temperature for several of these molecules are shown in Figures 10 and 11 respectively at a resonant frequency of 7.2 GHz. Experiments were also conducted on these molecules at resonant frequencies of 9.2, and 10.1 GHz. Results for both Δf and ΔW as a function of temperature showed the same general trend i.e., dramatic behavior in dielectric response at phase transition temperature as shown in Figures 12 - 17.

By definition the quality factor Q of a resonant cavity is related to the width W of its absorption signal (see Figure 8) by

$$Q = \frac{f_o}{P_2 - P_1} = \frac{f_o}{W} \quad (4.1)$$

where f_o is the resonant frequency of the system and W is the width of the resonance at half power maximum.

Therefore we have the following relation [with modulation correction, Equation (2.8)]

$$\Delta\left(\frac{1}{Q}\right) = \frac{\sqrt{3}\Delta W}{f_o} \quad (4.2)$$

Fig. 10--Width change of a resonant microwave cavity as a function of temperature for some polar and non-polar compounds at a resonant frequency of 7.2 GHz.

Fig. 11--Frequency shift of a resonant microwave cavity as a function of temperature for some polar and non-polar compounds at a resonant frequency of 7.2 GHz.

Fig. 12--Width change of a resonant microwave cavity as a function of temperature for some polar and non-polar compounds at a resonant frequency of 9.2 GHz.

Fig. 13--Frequency shift of a resonant microwave cavity as a function of temperature for some polar and non-polar compounds at a resonant frequency of 9.2 GHz.

Fig. 14--Width change of a resonant microwave cavity as a function of temperature for some polar and non-polar compounds at a resonant frequency of 10.1 GHz.

Fig. 15--Frequency shift of a resonant microwave cavity as a function of temperature for some polar and non-polar compounds at a resonant frequency of 10.1 GHz.

Fig. 16--Width change of a resonant microwave cavity as a function of temperature for water at three different frequencies.

Fig. 17--Frequency shift of a resonant microwave cavity as a function of temperature for water at three different frequencies.

Abrupt changes in ΔW and Δf were observed for the compounds under investigation near their phase transition temperatures. Since $\Delta(\frac{1}{Q})$ or ΔW and Δf correlate with ϵ'' and ϵ' via the Slater equations (3.19) and (3.20), this behavior in ΔW and Δf demonstrates the dielectric response ϵ'' and ϵ' near phase change.

In order to determine if the dielectric response was asymmetric about the phase transition temperature, each sample was tested for both liquid to solid and solid to liquid transition. There appears to be no measurable asymmetry behavior about the transition temperature for the sample studied as each sample is cycled through phase change for both decreasing and increasing temperature. The quantity ΔW is defined as $\Delta W = W_L - W_S$ where W_S is the width of the signal when the sample is in solid state and W_L is the corresponding width when the sample has melted. The values of ΔW for all the polar compounds, as given in Table XIII are different at different frequencies. This behavior is explained in Appendix B.

Mass Dependence - Dielectric Response

In order to determine how the mass of each sample affected the resonant frequency and Q of the cavity a test was conducted.

Each sample was advanced into the cavity in small amounts along the symmetry axis with the corresponding values

of the frequency shifts and Q-changes recorded. The frequency shifts and Q-changes are related to the real and imaginary parts ϵ' and ϵ'' of the complex dielectric constant ϵ^* through the perturbation equations (3.19) and (3.20). Since the precise nature of the field in the cavity could not be ascertained relative values of ϵ' and ϵ'' were calculated for all the molecules in this investigation with respect to water as standard. Constant parameters to be used in the Slater perturbation equations were obtained for water in the following way. Standard size capillary tubes made in the shape of small test tubes were used as carriers for each sample in order to reduce the geometric effect to minimal value. These small "test tubes" were filled with the appropriate sample to be tested. Water was chosen initially and the resulting constants needed to get values of ϵ' and ϵ'' which agreed with accepted values, were then used to balance the perturbation equations for the other sample studied. The changes in Δf and $\Delta(\frac{1}{Q})$ as a function of mass of the sample residing in the cavity could be expressed by a simple power-law equation.⁵⁰ The data fitted to equations of the form

$$\Delta f = A + B (\Delta m)^N \quad (4.3)$$

and

$$\Delta(\frac{1}{Q}) = C + D (\Delta m)^N \quad (4.4)$$

where A and C are the intercepts, B and D are the slopes, Δm is the fraction of sample mass advanced into the cavity and N is a constant which depends upon the geometry of the electromagnetic fields inside the sample holder and the cavity. A computer analysis was made of the experimental data in order to determine what power of N led to a "best fit" for the data. The best value of N appeared to be 1.6. A plot of some of the data using $N = 1.6$ is shown in Figure 18.

Using equations (4.3) and (4.4) along with Slater's perturbation equations one can write

$$\frac{\Delta f}{(\Delta m)^N} = B = f_0 \frac{\epsilon' - 1}{2} F(E) \quad (4.5)$$

and

$$\frac{\Delta(\frac{1}{Q})}{(\Delta m)^N} = D = f_0 \epsilon'' F(E) \quad (4.6)$$

where $F(E)$ is given by

$$F(E) = \frac{\int_V \vec{E}_s \cdot \vec{E} dv}{\int_V \vec{E} \cdot \vec{E}_a dv} \quad (4.7)$$

and is a functional form of how the field interacts with the sample. The other parameters in equation (4.7) have been defined earlier.

Figure 18--Frequency shift (MHz) as a function of mass (mg) and $(\text{mass})^{1.6}$ for water at a resonant frequency of 10.1 GHz.

All the samples were placed into small capillary tubes of constant diameter of 2mm to eliminate any geometrical effects. Now if $F(E)$ is of the same form for all the samples, there arises a characteristic B_x and D_x for each sample of x . If B_w and D_w are the corresponding values for water one can express relative values for dielectric material as follows:

$$\frac{B_w}{B_x} = \frac{\epsilon_w' - 1}{\epsilon_x' - 1} \quad (4.8)$$

and

$$\frac{D_w}{D_x} = \frac{\epsilon_w''}{\epsilon_x''} \quad (4.9)$$

Equations (4.8) and (4.9) were used to calculate ϵ' and ϵ'' for all the compounds under investigation at room temperature of 25°C. This was done by comparing the slopes of nitrobenzene, ortho and meta nitrotoluene and benzenesulfonyl chloride with that of water by assuming that the dielectric response of these compounds is not very different from that of water. The literature values of $\epsilon' = 61.3$ and $\epsilon'' = 29.7$ were used for water at 25°C and at a resonant frequency of 10.1 GHz. Similarly the slopes of weakly polar compounds bromoform and benzene were compared with that of teflon, taking the literature values of $\epsilon' = 2.08$ and $\epsilon'' = 4.16 \times 10^{-4}$ at 25°C for teflon near 10 GHz, and ϵ' and ϵ'' were calculated for bromoform and benzene. The calculated values

of ϵ' and ϵ'' at 25°C for all the compounds in this investigation are listed in Table II. Average values of the slopes for water and teflon are 3.03×10^{-2} and 4.44×10^{-3} (for frequency shift), 2.52×10^{-2} and 1.17×10^{-3} (for width change) respectively, in MHz/(mg)^N units, where N = 1.6.

Temperature Dependence - Dielectric Response

By keeping a constant amount of the sample in the cavity, the cavity was cooled below the phase transition temperature of the sample. A sufficient time was allowed to ensure the sample was frozen. The system was allowed to warm up and ΔW and Δf noted at different temperatures. The experiment was repeated a number of times for each compound of interest.

The average values of Δf and ΔW were recorded for all the compounds under investigation at various temperatures going from solid to the liquid phase. These values of Δf and ΔW at various temperatures and frequencies are listed in Tables XV through XX. The frequency shifts and the Q-changes are related to the real and imaginary parts of the dielectric constant through the perturbation equations (3.19) and (3.20) as follows:

$$\frac{\Delta f}{f_0} = \frac{\epsilon' - 1}{2} F(E) \quad (4.10)$$

and

$$\Delta\left(\frac{1}{Q}\right) = \epsilon'' F(E) \quad (4.11)$$

using equation (4.2), equation (4.11) can be written as follows:

TABLE II

EXPERIMENTAL VALUES OF MICROWAVE PARAMETERS AT 25°C FOR
DIFFERENT COMPOUNDS AT A RESONANT FREQUENCY
OF 10.1 GHz

Compound	ϵ'	ϵ''
Nitrobenzene	7.21	11.3
Benzene Sulfonyl Chloride	5.42	7.12
Ortho-Nitrotoluene	7.6	10.67
Meta-Nitrotoluene	6.72	9.43
Bromoform	4.33	0.928
Benzene	2.2736	1.72×10^{-3}

$$\sqrt{3} \frac{\Delta W}{f_o} = \epsilon'' F(E) \quad (4.12)$$

where $F(E)$ was defined in equation (4.7).

Using the values of ϵ' and ϵ'' for each compound at room temperature as given in Table II, and the experimental values of Δf and ΔW at room temperature in equations (4.10) and (4.12), the average value of $F(E)$ was calculated. These values of $F(E)$ for each compound are listed in Table XIV in the Appendix. Using the same value of $F(E)$ for one compound and the experimental values of Δf and ΔW at various temperatures, the corresponding values of ϵ' and ϵ'' were calculated for each compound under investigation. These values of ϵ' and ϵ'' for different compounds at microwave frequencies are listed in Table III, through VIII along with some available literature values. It can be seen through these tables that the calculated values of ϵ' and ϵ'' are very close to the literature values. The values of ϵ'' as the samples were frozen were negligible because the change in the width was negligible after taking into account the width change of the frozen empty cavity. Non-polar benzene showed no change in Δf and ΔW through its phase transition temperature.

TABLE III
EXPERIMENTAL AND LITERATURE VALUES OF MICROWAVE
PARAMETERS FOR WATER AT A RESONANT FREQUENCY
OF 7.2 GHz

T (°K)	ϵ' (Expt.)	ϵ'' (Lit.)	ϵ'' (Expt.)	ϵ'' (Lit.)
250	3.175		0	
262	3.2		0	
272.9	3.18	3.2 ^a	9.76×10^{-5}	
275.8	26.0		10.3	
276.5	39.3		27.0	
278	58.8	58.6 ^b	42.25	37.8 ^b
283	62.1	56.0 ^c	41.42	37.0 ^c
288	64.0		38.78	
293	67.3	63.0 ^c	30.87	31.5 ^c
298		69.5 ^d		23.0 ^d
303	71.74	68.4 ^e	15.85	20.26 ^e

a. R.P. Auty and R. H. Cole, J. Chem. Phys., 20 1309 (1952).

Values b-e are taken from reference 30.

Frequencies are given as follows:

b. 7.762 GHz

c. 9.141 GHz

d. 7.2 GHz

e. 7.738 GHz at 308°K

TABLE IV

EXPERIMENTAL AND LITERATURE VALUES OF MICROWAVE PARAMETERS
FOR WATER AT A RESONANT FREQUENCY OF 9.2 GHz

T (K)	ϵ_s (Lit.)	ϵ' (Expt.)	ϵ' (Lit.)	ϵ'' (Expt.)	ϵ'' (Lit.)
252.5	97.4 ^a	3.1	3.2 ^a	6.12×10^{-5}	
262.2	95.0 ^a	3.08			
272.9	91.5 ^a	3.1			
275.5	-	20.41	58.6 ^d 56.0 ^e	19.6	37.8 ^d 38.06 ^f
276.5	-	30.5		28.3	
278	86 ^c	50.5		41.53	
283	84.1 ^c	54.65	63.0 ^e 64.4 ^g 65.8 ^e , 65.34 ^f	40.757	31.5 ^e , 31.83 ^f 28.0 ^g 26.0 ^e , 25.47 ^f
288	82.07 ^b	57.43		35.521	
293	80.4 ^c	62.3		31.65	
298	78.21 ^b	-		-	
303	76.4 ^b	65.76		25.92	

a. See reference (a) Table III

b. Digest of Literature on Dielectrics, National Academy of Sciences, Washington, D.C. 1978.

Values c-f were obtained from reference 30. Frequencies are as follows:

d. 7.762 GHz

e. 9.141 GHz

f. 9.346 GHz

g. 9.2 GHz

TABLE V
EXPERIMENTAL AND LITERATURE VALUES OF MICROWAVE
PARAMETERS FOR WATER AT A RESONANT FREQUENCY
OF 10.1 GHz

T(K)	ϵ' (Expt.)	ϵ' (Lit.)	ϵ'' (Expt.)	ϵ'' (Lit.)
252.5	2.8		0	
262.2	2.83		0	
272.9	2.76	3.2 ^a	6.13×10^{-5}	
275.5	18.7		17.96	
276.5	25.4		24.28	
278	46.38	58.6 ^b , 38.85 ^c	38.85	37.8 ^b , 39.2 ^c
283	52.7	54.89 ^d	36.94	38.06 ^d
288	54.53		34.8	
293	58.15	61.4 ^d	32.67	31.83 ^d
298	-	61.3 ^e	-	29.7 ^e
303	63.65	65.34 ^d	27.83	25.47 ^d

a. See reference (a) Table III

Values (b-e) were obtained from reference 30.
Frequencies are given below:

b. 7.76 GHz

c. 12.82 GHz

d. 9.346 GHz

e. 10.1 GHz

TABLE VI

EXPERIMENTAL AND LITERATURE VALUES OF MICROWAVE PARAMETERS
FOR NITROBENZENE AT A RESONANT FREQUENCY OF 10.1 GHz

T(K)	ϵ_s (Lit.)	ϵ' (Expt.)	ϵ' (Lit.)	ϵ'' (Expt.)	ϵ'' (Lit.)
268		2.29		0	
271	39.3 ^a	2.30	3.0 ^c	9.93×10^{-6}	
273		2.30	-	10^{-5}	
277.8		3.90	-	4.50	
278	38.7 ^a	6.33	6.70 ^a	9.43	9.12 ^a
279.5		6.68		10.0	-
283	37.8 ^a	6.74	6.82 ^a	11.7	9.70 ^a
288		6.98		11.67	-
293	35.9 ^a	7.05	7.12 ^a	11.47	10.9 ^a
298	34.82 ^b	7.21		11.3	

a. S. Mallikarjun and Nora E. Hill, Trans Faraday Soc. 61, 1389 (1965)

b. See reference 48.

c. See reference 21.

TABLE VII

EXPERIMENTAL VALUES OF MICROWAVE PARAMETERS FOR ORTHO, META NITROTOLUENE AND
 BENZENESULFONYL CHLORIDE AT A RESONANT FREQUENCY
 OF 10.1 GHz

O-NITROTOLUENE			M-NITROTOLUENE			BENZENESULFONYL CHLORIDE		
T (K)	ϵ'	ϵ''	T (K)	ϵ'	ϵ''	T (K)	ϵ'	ϵ''
255	1.40	~ 0	280	1.29	0	283	1.40	~ 0
258	1.39	~ 0	283	1.30	0	285	1.37	$\sim 10^{-3}$
260	1.38	0	285	1.28	0	288.9	1.95	2.52
265.5	4.30	6.53	288.8	2.12	2.85	289.7	2.51	3.93
266	6.15	11.35	289.3	4.03	5.31	290.5	4.68	8.07
273	6.67	11.30	290	5.92	10.07	292	4.87	7.89
283	6.76	11.16	291	6.25	9.83	295	5.11	7.71
288	7.03	10.85	292	6.43	9.76	296.5	5.23	7.39
293	7.53	10.74	293	6.58	9.65	298	5.42	7.12
295.75	7.57	10.69	298	6.72	9.43	300	5.64	7.05
298	7.60	10.67	303	6.93	9.12	303	5.87	6.79

TABLE VIII

EXPERIMENTAL AND LITERATURE VALUES OF THE MICROWAVE
PARAMETERS FOR BROMOFORM AND BENZENE AT A
RESONANT FREQUENCY OF 10.1 GHz

BROMOFORM					BENZENE			
T(°K)	ϵ' (Expt.)	ϵ' (Lit.)	ϵ'' (Expt.)	ϵ'' (Lit.)	ϵ' (Expt.)	ϵ' (Lit.)	ϵ'' (Expt.)	ϵ'' (Lit.)
273	1.065		0.088					
278	1.08		0.092					
282.5	1.83		1.318					
283	3.56		2.738					
285	3.69		2.57					
287	3.78		2.37					
290	3.95		1.96					
293	4.08	4.39 ^a	1.61					
295	4.19		1.31					
296.5	4.28		1.09					
298	4.33		0.928		2.2736	2.2738 ^b	1.72x10 ⁻³	1.62 ^{c*}

a. See reference 48.

b. Digest of Literature on Dielectrics, National Academy of Science, New York, 1976.

c. See reference 10. *(This value is to be multiplied by 10⁻³).

Temperature Dependence - Relaxation Times

Equation (3.18) gives an expression for the relaxation time as follows:

$$\omega\tau = \frac{\epsilon_s - \epsilon'}{\epsilon''}$$

The above equation was utilized to find the values of relaxation times for different compounds. In this equation ω is the angular frequency which is related to the resonant frequency by

$$\omega_o = 2\pi f_o \quad (4.13)$$

and ϵ_s is the static dielectric constant. Therefore, by using the calculated values of ϵ' and ϵ'' for different compounds at the resonant frequency ω_o and at different temperatures at which the literature values of ϵ_s were available, the corresponding values of relaxation times were calculated. In case of water and nitrobenzene the values of ϵ_s were available at different temperatures and hence τ could be calculated at those temperatures. For other compounds under investigation (except benzenesulfonyl chloride for which no value of ϵ_s could be found) the values of ϵ_s could be found only at room temperature and therefore τ could be calculated only at that temperature.

These calculated values of the relaxation times τ for different compounds at different temperatures are given in

Tables IX and X along with some of the literature values. It can be seen through these tables that the calculated values of τ are in good agreement with the literature values.

Temperature Dependence - Energy of Activation

The relaxation time τ is related to the energies of activation for dipole relaxation through equation (3.17).

Equation (3.17) after the inclusion of temperature (T) can be manipulated as

$$\ln \left(\frac{\tau T k}{h} \right) = \left(\frac{\Delta H_{\epsilon}^{\ddagger}}{R} \right) \frac{1}{T} - \left(\frac{\Delta S_{\epsilon}^{\ddagger}}{R} \right) \quad (4.14)$$

It is well established⁵¹ and also indicated by Equation (4.14) that $\ln(\frac{\tau T k}{h})$ when plotted against $1/T$ gives a straight line with the slope equal to $\Delta H_{\epsilon}^{\ddagger}/R$ and intercept equal to $-(\Delta S_{\epsilon}^{\ddagger}/R)$ where $\Delta H_{\epsilon}^{\ddagger}$ and $\Delta S_{\epsilon}^{\ddagger}$ are the enthalpy of activation and entropy of activation for the dipole orientation respectively. The values of $\ln(\frac{\tau T k}{h})$ and $1/T$ for different values of the relaxation times τ at different temperatures (T) for water and nitrobenzene are given in Table XXI. For water average values of the relaxation times τ were taken from the values at different frequencies by considering that the relaxation times are independent of frequency and because the values of τ at different frequencies were fairly close to one another.

TABLE IX

EXPERIMENTAL AND LITERATURE VALUES OF THE RELAXATION TIMES FOR WATER IN SECONDS
AT RESONANT FREQUENCIES OF 7.2, 9.2 AND 10.1 GHz

$T(^{\circ}\text{K})$	$f_{\text{O}} = 7.2 \text{ GHz}$	$f_{\text{O}} = 9.2 \text{ GHz}$	$f_{\text{O}} = 10.1 \text{ GHz}$	$\tau \times 10^{12}$ (Literature)
	$\tau \times 10^{12}$ (Expt.)	$\tau \times 10^{12}$ (Expt.)	$\tau \times 10^{12}$ (Expt.)	
272.9	2.0×10^7	2.5×10^7	2.53×10^7	$2.2^{\text{a}} \times 10^7$
278	14.23	14.78	16.07	$14.6^{\text{b}}, 15.0^{\text{c}}$
283	11.74	12.50	13.39	$12.8^{\text{b}}, 12.6^{\text{d}}$
288	10.30	12.0	12.47	11.0^{b}
293	9.38	9.89	10.73	9.6^{b}
298	8.37	8.53	8.97	8.4^{b}
303	6.50	7.11	7.22	-

- a. See reference (a) Table III. b. See reference 26.
c. P. S. Yastremskii et al., Russ. J. Phys. Chem. 49 (6), 1975.
d. See reference 30.

TABLE X

EXPERIMENTAL AND LITERATURE VALUES OF THE RELAXATION TIMES
FOR VARIOUS POLAR AND NON-POLAR COMPOUNDS AT A
RESONANT FREQUENCY OF 10.1 GHz

T(K)	NITROBENZENE ($\tau \times 10^{12}$) Sec		O-NITROTOLUENE ($\tau \times 10^{12}$) Sec		M-NITROTOLUENE ($\tau \times 10^{12}$) Sec		BROMOFORM ($\tau \times 10^{12}$) Sec		BENZENE ($\tau \times 10^{12}$) Sec	
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
271	5.83×10^7	-								
278	54.09	49.4 ^a								
283	41.83	-								
293	39.6	40.4 ^b	29.15	-	28.1	26.06 ^c	3.03	-		
298	38.5	40.9 ^a							1.83	1.9 ^d

a. G. L. Clark, J. Chem. Phys. 25, 125 (1956)

b. J. Prakash, Indian J. Pure App. Phys. 15, 417 (1977)

c. See reference 25

d. Digest of Literature on Dielectrics, National Academy of Sciences, Washington, D.C. 1976.

The values of $\ln \left(\frac{\tau T k}{h} \right)$ for different values of $1/T$ were fitted into a straight line by simple linear regression analysis. The values of the slopes, intercepts and hence $\Delta H_{\epsilon}^{\ddagger}$ and $\Delta S_{\epsilon}^{\ddagger}$ for water and nitrobenzene along with the correlation coefficients are given in Table XI. The literature values are also cited in the Table.

Using these values of $\Delta H_{\epsilon}^{\ddagger}$ and $\Delta S_{\epsilon}^{\ddagger}$ for water and nitrobenzene in equation (3.13), the values of $\Delta G_{\epsilon}^{\ddagger}$, the free energy of activation for dipole orientation were calculated at different temperatures. In case of other compounds for which relaxation time τ was calculated at a single temperature, the corresponding value of $\Delta G_{\epsilon}^{\ddagger}$ was calculated using equation (3.16). These values of $\Delta G_{\epsilon}^{\ddagger}$ for different compounds are given in Table XII along with the literature values. The calculated values of $\Delta G_{\epsilon}^{\ddagger}$ are in good agreement with the literature values. The error in our measurements is $\pm 10\%$ and reflects one standard deviation in the scattering of the experimental data.

TABLE XI

EXPERIMENTAL RESULTS OBTAINED FROM THE LINEAR REGRESSION ANALYSIS
OF THE DATA IN TABLE XXI USING EQUATION 4.14

Compound	Slope (°K)	Intercept	Correlation Coefficient	$\Delta H_{\epsilon}^{\ddagger}$ (Expt.) K cal/ mole	$\Delta H_{\epsilon}^{\ddagger}$ (Lit.) K cal/ mole	$\Delta S_{\epsilon}^{\ddagger}$ (Expt.) K cal/ mole-K	$\Delta S_{\epsilon}^{\ddagger}$ (Lit.) K cal/ mole-K
WATER	2178.87	-3.3597	0.98786	4.33	2-5 ^a	0.00668	0.0066 ^a
NITROBENZENE	943.382	2.2765	0.805	1.875	-	-0.00452	-0.0047 ^b

$$\text{Slope} = \frac{\Delta H_{\epsilon}^{\ddagger}}{R}, \quad R = 8.314 \text{ J/mole-K}$$

$$\text{Intercept} = - \frac{\Delta S_{\epsilon}^{\ddagger}}{R}, \quad 1 \text{K cal} = 4184 \text{ J}$$

a. B. E. Conway, Can J. Chem. 37, 613 (1959).

b. P. Madan, Can. J. Phys., 51 (1973).

TABLE XII

EXPERIMENTAL AND LITERATURE VALUES OF THE FREE ENERGY OF ACTIVATION FOR WATER AND NITROBENZENE USING EQUATION (3.13) IN TABLE XI AND OTHER POLAR AND NON-POLAR COMPOUNDS USING THE VALUE OF RELAXATION TIME IN EYRING'S RATE EQUATION (3.16)

T(OK)	Ice and Water		Nitrobenzene (Solid and Liquid)		O-Nitrotoluene		M-Nitrotoluene		Bromoform		Benzene	
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
271.0			10.56	9.2 ^c								
272.9	10.12	9.34 ^a										
278	2.47		3.13									
283	2.44	2.42 ^b	3.15									
288	2.41		3.17	3.9 ^c								
293	2.37		3.20		3.02	-	2.99	2.70 ^d	1.7	-	1.44	1.8 ^e
298	2.34		3.22									
303	2.31		3.24									

a. See reference 46.

b. See reference 46.

c. See reference 21.

d. See reference 25.

e. M.I. Shakhparonov et al., Russ. J. Phys. Chem. 46 (2), 287 (1972).

CHAPTER V

SUMMARY

A microwave resonant cavity technique was employed in this investigation to successfully monitor the dielectric relaxation phenomenon in polar and non-polar liquids. The cylindrical cavity used was constructed and tuned to resonate in the TE_{011} mode. The cavity was subjected to a thermal bath so the temperature could be controlled and dielectric relaxation in various compounds could be monitored over their phase transition temperatures. Each polar compound was found to show a dramatic behavior in the dielectric properties near the phase transition temperature.

No change in the dielectric behavior could be detected for the non-polar molecule benzene as it changed phase and the weakly polar molecule bromoform showed only a slight change in the dielectric response. There appeared to be a correlation between the dipole moment strength of each sample and the degree of change in dielectric response over phase change.

The real and imaginary parts of the complex permittivity were calculated for each polar compound at room temperature by studying the dielectric behavior with changing mass. Water was taken as a standard and relative

behavior of the dielectric response was obtained from the slopes frequency shift and width change versus relative mass change.^{1.6} All the polar compounds were compared with water using a suitable set of curves for each sample. Similarly weakly polar bromoform and non-polar benzene were compared with teflon. Teflon was chosen standard as its dielectric response was near that of the non-polar samples. The relative behavior of microwave parameters ϵ' and ϵ'' over temperature for each compound of interest was calculated at various temperatures by normalizing the experimental data with a value calculated at room temperature.

A method used in this investigation could successfully evaluate the relaxation time of a rigid spherical polar molecule at different temperatures. This was done by using the calculated values of the microwave parameters in the Debye equations and thus calculating the relaxation time at a temperature at which the static dielectric constant value was available from the literature. This method is very convenient and useful in devising an experiment since only one microwave experimental set-up is needed instead of several. A standard technique was employed for obtaining the relaxation time τ , using the graph of $\ln(\frac{\tau T k}{h})$ vs $\frac{1}{T}$, the relaxation time τ could be calculated at any desired temperature T . This was done for water and nitrobenzene. It is very obvious from this method of analysis for

calculating the relaxation time of a rigid spherical molecule, that τ could be evaluated at any temperature of interest without making a measurement at that very temperature.

By making measurements at several temperatures any incidental error is statistically averaged out in the straight line graph. The relaxation times calculated with this method were found to be in agreement with the literature values.

It has been observed from this experiment that as the temperature increases, the relaxation time decreases. This is reasonable in that as the temperature increases, the thermal agitation of the system also increases, and this results in lowering the frictional resistance for dipolar rotation with the values of the relaxation times decreasing. Similar results on some other polar compounds have been observed by Branin and Smyth.⁵²

In the case of ortho and meta nitrotoluene it can be seen that the relaxation time decreases from the ortho- to the meta-isomer. Ahmad and Sharma⁵³ observed similar results for these molecules and the interpretation of frictional change with temperature was supported by showing that the inner friction experienced by these compounds is of the same order on the basis of mutual and averaged mutual viscosities of the compounds. The relaxation times calculated at 20°C for weakly polar bromoform and benzene are

very small. The dielectric relaxation time here describes the decay of induced dipole moment and is of the order of the time between collisions in the liquids.⁵⁴ Water is seen to have relaxation near 10 GHz, while the other compounds studied have relaxation at lower frequencies.

In addition to relaxation times for each sample being calculated, linear regression analysis of $\ln \left(\frac{\tau T k}{h} \right)$ vs $\frac{1}{T}$ was used to calculate the enthalpy of activation and entropy of activation for water and nitrobenzene. Using these values in Equation (3.13), the free energy of activation for dipole orientation was calculated at various temperatures for these compounds. For other compounds the free energy of activation was calculated from Eyring's rate theory Equation (3.16).

In the case of water and nitrobenzene the activation energy increases from 2.4 to 10 k cal/mole and 3.2 to 10.5 k cal/mole respectively near the crystallization temperature. This increase in the activation energy near the phase change indicates the preliminary emergence of order in the arrangement of water and nitrobenzene molecules long before the crystallization point. It was shown by Stearn and Eyring²⁰ that in water the phase change from solid to liquid corresponds to an abrupt change in the free energy of activation. It was shown later by Pople⁵⁵ that this change in activation energy at phase change

is due to bending of hydrogen bonds rather than breaking of the bonds.

Thus it seems that the dielectric relaxation mechanism in polar molecules is a chemical rate process and that the solid to liquid phase change in the molecule is related to the changes in the free energy of activation for dipole orientation in the sample.

It appears that dipole relaxation plays an important role in the behavior of the dielectric response of the medium loading the cavity as phase change takes place within the sample. The method of a loaded resonant microwave cavity as applied in this work has proven to be sensitive enough to monitor small changes in phase behavior of the cavity medium. The present study could be successfully extended in monitoring the dielectric relaxation in any polar and non-polar compound with a phase change not very far from (0°C). This technique can also be applied to monitor the phase change in liquid crystals which have different ordered phases at various temperatures. Dielectric response in some biological systems can also be monitored with this technique. Perhaps a probe of the molecular systems over a broader range of frequencies will elaborate the complete phase transition mechanisms, but the present instrumentation will need improvement to conduct studies at very high frequencies. Preliminary experiments were conducted at 18 GHz to test the feasibility of using the instrument and cavity at higher frequencies. These tests

show that a new cavity must be constructed and appropriate waveguide employed to reduce spurious signals so that definitive data can be obtained.

The mission of this investigation has been achieved in that a device was developed for monitoring dielectric response of several systems in the frequency range $7 \leq f_0 \leq 11$ GHz over various ranges of temperature which encompassed phase change for the materials studied. Data were obtained and interpreted for several samples from which physical behavior were deduced. Good correlation was found for behavior obtained using the cavity method with behavior observed using other methods.

APPENDIX A

CAVITY PERTURBATION

We know that as the sample is introduced into the cavity, it perturbs the electric and magnetic fields in the cavity and as a result of this quality factor Q of the cavity changes and there is a shift in the resonant frequency of the cavity. According to Slater's perturbation theory¹² the cavity Q changes and the resonant frequency shifts are functions of the dielectric properties of the sample producing the perturbation. In this appendix the general theory of the resonant cavities and the electromagnetic fields within them is discussed. The first problem will be to solve Maxwell's equations in a hollow cavity, subject to certain boundary conditions around the surface. Only the essential steps are developed here, the perturbation theory in detail was developed by Slater¹² and also by J. Van Bladel.⁵⁶ Since in the present investigation, the resonant cavity was operated in TE_{011} mode, the perturbation of electric field only will be discussed.

From Maxwell's equations for a hollow cavity with sample the general expression for the wave equation can be given as

$$\epsilon_0 \mu_0 \frac{d^2}{dt^2} \int \vec{E} \cdot \vec{E}_a dV + ka^2 \int \vec{E} \cdot \vec{E}_a dV$$

$$\begin{aligned}
&= -\mu_0 \frac{d}{dt} \left(\int_V \vec{J} \cdot \vec{E}_a dV - \int_{s'} (\eta \times \vec{H}) \cdot \vec{E}_a d_a \right) \\
&- k_a^2 \int_s (\eta \times \vec{E}) \cdot \vec{H}_a d_a
\end{aligned} \tag{A.1}$$

where ϵ_0 and μ_0 are the dielectric constant and the permeability in vacuum respectively. $\vec{E}$ represents the electric field applied to the cavity, $\vec{E}_a$ is the electric field of the unperturbed cavity, and k_a is the wave number. The current density of the sample is $\vec{J}$. The sample volume is v and s, s' are the surfaces of the cavity.

The microwave resonant cavity displays the same resonant characteristic as a tuned circuit and it is helpful to draw an analogy here. The differential equation for a tuned circuit containing inductance L , resistance R , and capacitance C is

$$L \frac{d^2 q}{dt^2} + R \frac{dq}{dt} + \frac{q}{C} = 0 \tag{A.2}$$

where charge q on the capacitor is used as a variable. Assuming an exponential solution, q varying as $e^{j\omega t}$, (A.2) becomes

$$(-L\omega^2 + Rj\omega + \frac{1}{C})q = 0 \tag{A.3}$$

Either in the tuned circuit or the resonant cavity, the quality factor is determined from the resonant curve shape.

Equation (A.3) can be written as

$$j \left(\frac{\omega}{\omega_0} - \frac{\omega_0}{\omega} \right) + \frac{1}{Q} = 0 \quad (\text{A.4})$$

where we used $\omega_0^2 = \frac{1}{LC}$ and $Q = \frac{L\omega_0}{R}$ is the quality factor of the cavity, ω is the driving frequency and ω_0 is the characteristic resonant frequency of the cavity.

The cavity may be treated as a resonant circuit and for small perturbation of a resonant circuit the angular frequency may be expressed as

$$\omega_0 = \omega_a + \Delta\omega_a$$

where ω_a is one of the resonant frequencies of the circuit or cavity in this experiment. Therefore, equation (A.4) becomes to a close approximation

$$j \left(\frac{\omega}{\omega_a} - \frac{\omega_a}{\omega} \right) + \Delta \left(\frac{1}{Q} \right) - 2j \frac{\Delta\omega_a}{\omega_a} = 0 \quad (\text{A.5})$$

For a time-dependent solution varying as $j\omega t$, equations (A.1) and (A.5) combine to give

$$\begin{aligned} \Delta \left(\frac{1}{Q} \right) - 2j \frac{\Delta\omega_a}{\omega_a} &= \frac{-j}{\omega_a \epsilon_0 \mu_0} \frac{\int (\hat{n} \cdot \vec{E}) \cdot \vec{H}_a ds}{\int \vec{E} \cdot \vec{E}_a dV} \\ &- \frac{1}{\epsilon_0 \omega_a} \frac{\int (\hat{n} \times \vec{H}) \cdot \vec{E}_a ds' - \int \vec{J} \cdot \vec{E}_a dV}{\int \vec{E} \cdot \vec{E}_a dV} \end{aligned} \quad (\text{A.6})$$

For the particular situation in which the perturbation is one of currents produced within the cavity by the introduction of sample, perfectly conducting walls are assumed, thereby eliminating the surface integrals from equation (A.6), because relative changes in Q and ω for the cavity were monitored. Therefore, the resulting equation of interest is given by

$$\Delta\left(\frac{1}{Q}\right) - 2j \frac{\Delta\omega_a}{\omega_a} = \frac{\int \vec{J} \cdot \vec{E}_a dv}{\epsilon_0 \omega_a \int \vec{E} \cdot \vec{E}_a dV} \quad (A.7)$$

The currents in the sample are related to its polarization $\vec{P}$ by

$$\vec{P} = (\epsilon - \epsilon_0) \vec{E}_s = \epsilon_0 (\epsilon' - j\epsilon'' - 1) \vec{E}_s \quad (A.8)$$

where E_s is the local field of the sample. It can be seen from Maxwell's equation that

$$\nabla \times \vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t} \quad (A.9)$$

But

$$\vec{D} = \epsilon_0 \vec{E}_s + \vec{P} \quad (A.10)$$

Therefore equation (A.9) becomes

$$\nabla \times \vec{H} = \vec{J} + \frac{\partial}{\partial t} [\epsilon_0 \vec{E}_s + \vec{P}] = \vec{J} + j\omega [\epsilon_0 \vec{E}_s + \vec{P}] \quad (A.11)$$

Equations (A.7), (A.8) and (A.11) simplify to

$$\Delta\left(\frac{1}{Q}\right) - 2j \frac{\Delta\omega_a}{\omega_a} = j[(\epsilon' - 1) - j\epsilon''] \frac{\int \vec{E}_s \cdot \vec{E} dv}{\int \vec{E} \cdot \vec{E}_a dV} \quad (\text{A.12})$$

Hence the equations for perturbation of the cavity can be written as

$$\frac{\Delta\omega}{\omega} = - \frac{\epsilon' - 1}{2} \frac{\int \vec{E}_s \cdot \vec{E} dv}{\int \vec{E} \cdot \vec{E}_a dV} \quad (\text{A.13})$$

$$\Delta\left(\frac{1}{Q}\right) = \epsilon'' \frac{\int \vec{E}_s \cdot \vec{E} dv}{\int \vec{E} \cdot \vec{E}_a dV} \quad (\text{A.14})$$

where ω represents the resonant frequency of the cavity and the other parameters have been defined earlier.

Equations (A.13) and (A.14) were used to determine the relative behavior of ϵ' and ϵ'' for each sample monitored as it underwent phase change from liquid to solid phase.

APPENDIX B

In this section a discussion is given to show how the dielectric relaxation for each compound varies at different frequencies.

A constant volume V_c of the sample was employed at three different frequencies of 7.2, 9.2 and 10.1 GHz and Δf , ΔW were recorded at different temperatures for each compound of interest. The number of molecules in constant volume V_c of each compound as given in Table XIII were calculated as follows.

From the density of each compound the mass for a constant volume V_c is calculated

$$m = d \cdot V_c \quad (B.1)$$

The number of molecules n in mass m is given by

$$n = \frac{N_A}{M} \times m \quad (B.2)$$

where N_A is the Avogadro's number ($N_A = 6.023 \times 10^{23}$ molecules/g-mole) and M is the molecular weight.

The constant volume used for different frequencies can be calculated by

$$V_c = \pi r^2 l \quad (B.3)$$

where r is the radius of the sample holder and l is the length of the sample holder into the cavity.

The values of dW per molecule for each compound under investigation were plotted against the dipole moment of each compound at different frequencies. Figure (19) shows such plots. It is seen from this figure that dW per molecule for each compound except water has a maximum value at 7.2 GHz showing that these compounds have relaxation towards lower frequencies. On the other hand water seems to have relaxation at higher frequency. This is also evident from the relaxation times of each compound. Nitrobenzene, Ortho and Meta nitrotoluenes have higher relaxation times than water and since relaxation frequency ω_c is inverse of the relaxation time τ , therefore water has relaxation at higher frequency than the other compounds mentioned earlier.

Fig. 19--Net change in width of a resonant cavity between solid and liquid phases as a function of dipole moment for various compounds studied in this investigation.

APPENDIX C

The experimental data tables for the microwave parameters calculated in this investigation are listed in the following pages.

TABLE XIII

DATA TABLE FOR ΔW IN MHZ FOR DIFFERENT COMPOUNDS AT DIFFERENT FREQUENCIES AND NUMBER OF MOLECULES FOR EACH COMPOUND FOR A CONSTANT VOLUME $V_C = 0.027928 \text{ cm}^3$

COMPOUND	DENSITY g/cm ³	#MOLE- CULES IN V_C	ΔW (MHz)		
			7.2GHz	9.2GHz	10.1GHz
WATER	1.0	9.345*	0.5083	1.0	1.385
NITROBENZENE	1.2037	1.6446*	0.7133	0.4129	0.3876
BENZENE SUL- FONYL CHLORIDE	1.3842	1.318*	0.546	0.313	0.2853
O-NITROTOLUENE	1.163	1.426*	0.6253	0.36	0.345
M-NITROTOLUENE	1.157	1.419*	0.605	0.3485	0.325
BROMOFORM	2.89	1.923*	0.2836	0.164	0.1564
BENZENE	0.879	1.896*	0.0	0.0	0.0

* TO BE MULTIPLIED BY 10^{20}

TABLE XIV
DATA TABLE FOR $F(E)$ FOR DIFFERENT
COMPOUNDS AT MICROWAVE FREQUENCIES

COMPOUND	$F(E) \cdot 10^6$		
	7.2 GHz	9.2 GHz	10.1 GHz
WATER	2.9	4.7	6.15
NITROBENZENE	-	-	5.80
BENZENE SULFONYL CHLORIDE	-	-	6.10
O-NITROTOLUENE	-	-	5.30
M-NITROTOLUENE	-	-	5.60
BROMOFORM	-	-	9.85

TABLES XV - XX

The following are the experimental data tables of frequency shifts Δf and width changes ΔW in MHz as a function of temperature for various compounds used in this investigation at microwave frequencies.

TABLE XV

WATER

$f_0 = 7.2$ GHz			$f_0 = 9.2$ GHz			$f_0 = 10.1$ GHz		
T (K)	Δf	ΔW	T (K)	Δf	ΔW	T (K)	Δf	ΔW
250	0.0227	0.0	252.5	0.045	0.0	252.5	0.0559	0.0
262	0.0229	0.0	262.2	0.0449	0.0	262.2	0.0560	0.0
272.9	0.0227	1.18*	272.9	0.045	1.53*	272.9	0.0546	2.19*
275.8	0.261	0.1242	275.5	0.42	0.49	275.5	0.5497	0.6441
276.5	0.3998	0.3255	276.5	0.64	0.707	276.5	0.7578	0.8707
278	0.6034	0.5093	278	1.07	1.037	278	1.4094	1.393
283	0.6379	0.4993	283	1.16	1.0175	283	1.6057	1.3247
288	0.6577	0.4675	288	1.22	0.8868	288	1.6625	1.248
293	0.6922	0.3721	293	1.325	0.79	293	1.775	1.1716
298	0.7102	0.2792	298	1.378	0.696	298	1.853	1.077
303	0.738	0.1911	303	1.4	0.6471	303	1.9457	0.998

*TO BE MULTIPLIED BY 10^{-6} .

TABLE XVI
NITROBENZENE

$f_O = 7.2 \text{ GHz}$			$f_O = 9.2 \text{ GHz}$			$f_O = 10.1 \text{ GHz}$		
T (K)	Δf	ΔW	T (K)	Δf	ΔW	T (K)	Δf	ΔW
268	0.01	0	268	0.0098	0	268	0.0379	0
271	0.0103	1.3×10^{-5}	271	0.011	0	271	0.03807	0.336×10^{-6}
273	0.009	$\sim 10^{-5}$	273	0.0103	0	273	0.038	$\sim 10^{-6}$
280	0.0515	0.1256	278.9	0.047	0.00767	277.8	0.085	0.1523
282	0.165	0.257	280	0.0748	0.151	278	0.1561	0.3189
282.5	0.2174	0.3341	281	0.198	0.4136	279.5	0.1664	0.3382
283	0.3498	0.7147	283	0.2123	0.412	283	0.1681	0.3957
288	0.3913	0.7038	288	0.2371	0.3911	288	0.1751	0.3947
293	0.4247	0.6896	293	0.2628	0.3743	293	0.1772	0.3879
298	0.4503	0.6653	298	0.2873	0.3274	298	0.185	0.3743

TABLE XVII
BENZENE SULFONYL CHLORIDE

$f_O = 7.2 \text{ GHz}$			$f_O = 9.2 \text{ GHz}$			$f_O = 10.1 \text{ GHz}$		
T(K)	Δf	ΔW	T(K)	Δf	ΔW	T(K)	Δf	ΔW
283	0.0198	0	283	0.01	0	283	0.0123	0
285	0.0203	0	285	0.0103	0	285	0.0115	3.6×10^{-5}
289.85	0.0765	0.1995	289.9	0.0331	0.087	288.9	0.0293	0.0897
290.3	0.1375	0.3803	290.6	0.0937	0.1385	289.7	0.0467	0.1398
291	0.2497	0.5516	291	0.145	0.3193	290.5	0.1134	0.287
292	0.2633	0.5509	292	0.1507	0.3165	292	0.1192	0.2806
295	0.2758	0.5488	295	0.1611	0.3105	295	0.1266	0.2742
296	0.325	0.5479	296	0.1687	0.3055	296.5	0.1303	0.2629
298	0.3301	0.5468	298	0.1738	0.3011	298	0.1372	0.2524
303	0.3516	0.5353	303	0.1815	0.2893	300	0.1429	0.2507
						303	0.15	0.2415

TABLE XVIII
ORTHO-NITROTOLUENE

$f_O = 7.2 \text{ GHz}$			$f_O = 9.2 \text{ GHz}$			$f_O = 10.1 \text{ GHz}$		
T (K)	Δf	ΔW	T (K)	Δf	ΔW	T (K)	Δf	ΔW
255	0.01	0	255	0.0095	0	255	0.01078	0
258	0.0101	0	258	0.0098	0	258	0.01053	0
260	0.0098	0	260	0.0107	0.0017	260	0.01017	0
265.7	0.1251	0.265	264.5	0.0267	0.125	265.5	0.0885	0.2017
266	0.2895	0.6301	265	0.1409	0.3651	266	0.1378	0.3508
273	0.3248	0.6165	266	0.1598	0.3601	273	0.1517	0.3492
283	0.374	0.5838	273	0.1747	0.3565	283	0.1542	0.3449
288	0.411	0.546	283	0.2001	0.3387	288	0.1614	0.3353
293	0.4293	0.5337	288	0.2137	0.3298	293	0.1748	0.3319
296	0.438	0.5199	293	0.2198	0.3145	295.75	0.1758	0.3304
298	0.4571	0.5148	296	0.2247	0.3124	298	0.1788	0.3283
			298	0.2259	0.3065			

TABLE XIX

META-NITROTOLUENE

$f_O = 7.2 \text{ GHz}$			$f_O = 9.2 \text{ GHz}$			$f_O = 10.1 \text{ GHz}$		
T (K)	Δf	ΔW	T (K)	Δf	ΔW	T (K)	Δf	ΔW
280	0.0123	0	280	0.0097	0	280	0.0082	0
283	0.011	0	283	0.0098	0	283	0.0085	0
285	0.0243	0	285	0.0089	0	285	0.0079	0
288	0.0933	0.051	288.5	0.0335	0.0783	288.8	0.0317	0.093
289.5	0.1497	0.3017	289.65	0.0759	0.1903	289.3	0.0856	0.1733
290	0.2855	0.6131	290	0.1458	0.3497	290	0.1391	0.3288
291	0.291	0.6043	291	0.1538	0.3483	291	0.1485	0.321
292	0.2993	0.6017	292	0.1597	0.3436	292	0.1536	0.3187
293	0.3097	0.5985	293	0.1623	0.34	293	0.1578	0.3151
298	0.3261	0.5874	298	0.174	0.3292	298	0.1618	0.3079
303	0.3503	0.5729	303	0.1993	0.3115	303	0.1677	0.2978

TABLE XX
BROMOFORM

$f_O = 7.2 \text{ GHz}$			$f_O = 9.2 \text{ GHz}$			$f_O = 10.1 \text{ GHz}$		
$T(^{\circ}\text{K})$	Δf	ΔW	$T(^{\circ}\text{K})$	Δf	ΔW	$T(^{\circ}\text{K})$	Δf	ΔW
275	0.00365	0.00505	276	0.00398	0.005	273	0.00323	.00506
279	0.0036	0.005	278.5	0.00387	0.0055	278	0.00398	.0053
281.5	0.1255	0.135	281	0.0653	0.093	282.5	0.0413	0.0757
282	0.2498	0.2843	281.6	0.1356	0.1647	283	0.1273	0.1573
285	0.2576	0.2750	284	0.1458	0.1615	285	0.1338	0.1476
288	0.2673	0.2553	287.5	0.1583	0.1433	287	0.1383	0.1363
290	0.2719	0.2449	290	0.1675	0.1275	290	0.1467	0.1129
292	0.2765	0.2297	291	0.1703	0.1206	293	0.1532	0.0923
295	0.2843	0.2078	295	0.1798	0.0938	295	0.1587	0.0753
296	0.2853	0.1996	295.8	0.1838	0.085	296.5	0.1631	0.0626
298	0.2903	0.1850	298	0.1865	0.0705	298	0.1656	0.0533

TABLE XXI

DATA TABLE FOR $\ln(\tau Tk/h)$ AS A FUNCTION OF $1/T$ FOR WATER AND NITROBENZENE

$1/T$ (1/K)	$\tau \times 10^{12}$ (sec) WATER	$\tau \times 10^{12}$ (sec) NITROBENZENE	$\ln(\tau Tk/h)$	
			WATER	NITROBENZENE
0.003597	15.03	54.09	4.46616	5.74677
0.003533	12.54	41.83	4.30287	5.50756
0.003472	11.59	-	4.2416	-
0.003413	10.0	39.6	4.11125	5.4875
0.003356	8.62	38.5	3.97967	5.47625
0.0033	6.94	-	3.77953	-

 $k = 1.38 \times 10^{-23} \text{ J/K} , \quad h = 6.626 \times 10^{-34} \text{ J-sec} .$

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