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# **MICROWAVE ABSORPTION IN BIOGENIC STEROIDS**

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**R. ARUNA**

**SCHOOL OF ENVIRONMENTAL SCIENCES  
JAWAHARLAL NEHRU UNIVERSITY  
NEW DELHI-110067  
1981**

CERTIFICATE

The work embodied in this thesis entitled "Microwave Absorption in Biogenic Steroids" has been carried out in the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi. The work is original and has not been submitted so far in part or full for any other degree or diploma of any university.

*R. Aruna*  
(R. ARUNA)

*J. Behari*  
(J. BEHARI)  
Supervisor

*J.M. Dave*  
(J.M. DAVE)  
Dean  
Dean

6<sup>th</sup> MAY, 1981

School of Environmental Sciences  
Jawaharlal Nehru University,  
New Delhi- 110 067.

School of Environmental Sciences  
Jawaharlal Nehru University  
New Delhi-110057.

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*R. Aruna*  
( R. ARUNA )

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## CHAPTER I

### INTRODUCTION

#### A. Importance of dielectric constant measurement

Dielectric studies of materials has been a powerful tool in assessing the structure and behavior of molecular materials<sup>1</sup>. The response of a material to an applied electromagnetic field is determined by the electrical and magnetic properties of the medium. For a non-magnetic system, the significant property which determines the impedance offered to the incidence wave is the dielectric constant of the medium. If the medium is lossy, energy is absorbed as the radiation penetrates into the material. The amplitude of the wave decreases i.e., attenuation occurs as energy is absorbed. This is accompanied by a shift in phase. The attenuation and phase shift are dependent on the dielectric properties of the medium characterized by complex permittivity  $\epsilon^*$  of the medium denoted as  $\epsilon' - j\epsilon''$ . Here  $\epsilon'$  is the real permittivity, the dielectric constant of an equivalent lossless dielectric and  $\epsilon''$  denotes the loss factor.

The complex permittivity is frequency dependent. The general behavior of polar molecules in condensed state (Fig. 1.1), may be summarised as follows:

At low frequencies,  $\epsilon'(\omega)$  is equal to the static dielectric constant and  $\epsilon''(\omega)$  is zero. As the frequency increases,  $\epsilon'(\omega)$  decreases rather slowly at first, whereas at higher frequencies of electromagnetic waves (optical frequencies) there are sharp increases followed by a decrease. The loss factor  $\epsilon''(\omega)$  has peaks in the neighbourhood of the frequencies where  $\epsilon'(\omega)$  changes. The resonance behavior at higher frequencies arises due to atomic and electronic polarizations, whereas the relaxation behavior observed at lower frequencies arises due to orientation polarization. The average energy dissipated per unit time is proportional to  $\epsilon''(\omega)$ . The absorbed energy manifests itself in the form of heat in the system.

For most condensed systems the characteristic time of the relaxation process falls in the microwave region. Thus, the study of orientation relaxation of such systems is relevant for characterisation of the effect of microwaves.



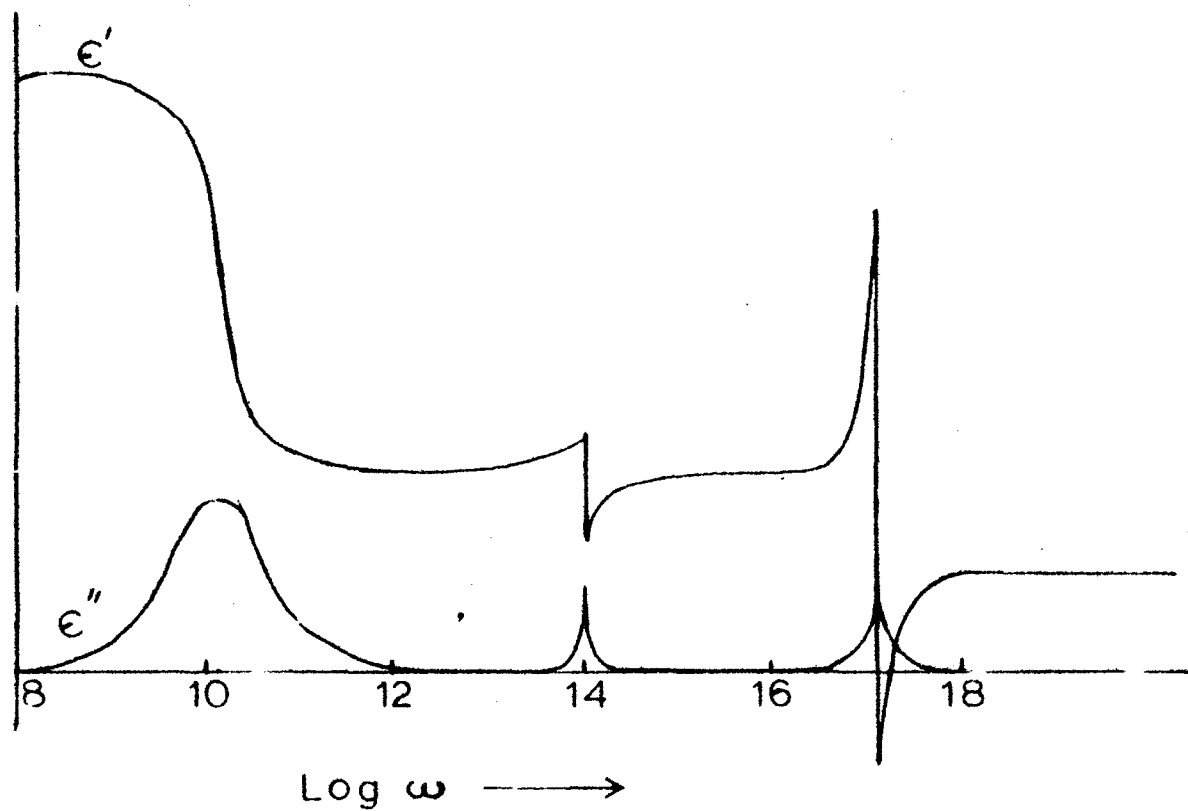


Fig 1.1 Dielectric dispersion and loss in a polar compound in condensed phase

**B. Methods of measurement of complex permittivity at microwave frequencies.**

The complex permittivity of a medium can, in principle, be evaluated by measurements on the reflection and/or transmission characteristics of the material. If an electromagnetic wave is incident on a material, part of the wave energy would be absorbed, another part would be transmitted and the remaining would be reflected back. Thus the measurement of transmission or the reflection coefficient would be sufficient for the estimation of permittivity of the medium.

A great variety of experimental procedures have been adopted for the estimation of complex permittivity of various media at microwave frequencies<sup>1-4</sup>. The suitability of any one of these methods for a particular sample is to be determined on the basis of certain criteria. The choice of the method is influenced by the type of work contemplated and the form in which the sample is available or can be put in. Apart from its form and availability, the properties of the materials determine the procedure that would be adopted.

For example, high loss materials cannot be examined by methods used for low loss materials.

The traditional methods of determining permittivity are centred around measurements in the frequency domain, the common feature of all such methods being the fact that complex permittivity is measured at various discrete frequency points. In general, the methods can be classified broadly as

- i) Free space techniques
- ii) Transmission techniques in waveguides/ coaxial lines
- iii) Reflection techniques in waveguides
- iv) Cavity and Cavity perturbation techniques.

#### Free Space Techniques:

The free space techniques are based on measurement of transmitted or reflected power from a slab of the material. Transmission methods<sup>5</sup> involve measurement of phase shift caused by the sample for computing real permittivity and measurement of attenuation for determining loss tangent,  $\tan \delta = \epsilon''/\epsilon'$ . Reflection techniques are based on standing wave measurements in free space or

comparison between direct and reflected power picked up by an antenna. If the material under test is available in the form of a large sheet, the method can be used for accurate determination of  $\epsilon'$  and  $\tan \delta$ . These methods are widely used at very high frequencies (above 40 GHz), where waveguide and cavity methods are far from successful. A different free space method involves resonance obtained in free space between two spherical microwave mirrors.<sup>6-8</sup> This method originally developed for sheets of solid dielectric can be used for high loss liquids contained in a capillary tube.

Methods depending on transmission in guides:

By confining the electromagnetic field within the enclosure of a hollow pipe or coaxial line, all boundary and stray effects disappear automatically and small amounts of any dielectric can be used for measurement with precision.

The transmission techniques are a development of the phase-amplitude balance method as described by Buchanan.<sup>9</sup> They are particularly

suitable for high loss liquids. Measurements are generally taken by varying the thickness of the liquid samples; this can be achieved by having two interfaces in the guide, one of which moves relative to the other.<sup>10</sup> An alternative method involves the direct measurement of the wavelength in the liquid and the determination of the attenuation constant by measuring the variation of amplitude with distance along the cell. For low and medium loss materials reflection techniques are preferred, as they involve lesser instrumentation problems.

#### Methods depending on reflection in guides:

The most versatile method involves measurement of the input impedance of a short circuited waveguide with and without the sample. The method proposed by Roberts and von Hippel<sup>11</sup> leads to complex permittivity on solving a transcendental equation which in general is complex reduces to a real equation for low loss materials. This method first adopted by Dakins and Works<sup>12</sup> with correction for waveguide losses gives accurate results for materials with  $\tan \delta < 0.1$ .

The dielectric parameters of a sample can also be measured when two different purely reactive terminations are available. Surber and Crouch<sup>13</sup> have described a method in which the dielectric sample is enclosed within a section of waveguide terminated by a reflecting plane, the standing wave ratio and the position of the voltage minimum are measured for both, a short circuit and an open circuit termination. This method is suitable for medium and high loss material. For low loss material, the frequency of oscillations is varied until the phase of the voltage reflection coefficient at the face of the dielectric is either zero or  $\pi$  radians. The electrical length of the sample will then be either an odd multiple of  $\lambda_d/4$  ( $\lambda_d$  being the wavelength in the dielectric) or a multiple of  $\lambda_d/2$  respectively. Though the solution is simple, the method is not as accurate as the transcendental equation method, since the sample length cannot be optimized for both reactive terminations simultaneously.

Daag and Reesor<sup>14</sup> have described a method particularly suitable for low loss liquids. They

used a specially designed long waveguide liquid cell, the real part of permittivity being derived from the change in impedance at the air-dielectric interface in the waveguide and the imaginary part from attenuation measurements on the liquid filled guide.

More recently Van Loon and Finsy<sup>15</sup> have described a single method for accurate determination of complex permittivity of low, medium and high loss liquids. The method involves computer analysis of reflected power profile. Wave propagation constant in the liquid, determined by fitting an analytical curve to reflection profile, yields the value of the complex permittivity.

#### Cavity and cavity perturbation techniques

Cavity measurement techniques are based on rigorous solutions of the electromagnetic problem. A cavity either rectangular or circular, has a natural frequency of resonance and will possess internal losses. Introduction of a dielectric into the cavity will change the natural frequency and the losses. Solution of Maxwell's equations would then lead to expression for dielectric

parameters in terms of changes in the characteristics of the cavity.

Mathematically, a completely filled resonator is the simplest situation. If the substance is highly lossy a completely filled resonant cavity will not be suitable since the quality factor  $Q$  with the dielectric will have a very low value. Under such circumstances and in case the specimen is available in small quantity, the cavity is loaded partially with the dielectric. Cavity resonators have been used by Barlow and Callen<sup>16</sup> Sinha and Brown<sup>17</sup> and others.

Cavity perturbation methods<sup>18</sup> in contrast to cavity methods involve approximations in their formulation, which lead to accurate results under restricted conditions. The sample can be taken in any convenient shape like rods, discs, spheres, etc. The sample should be very small as compared with the cavity itself so that the frequency shift produced by the insertion of the sample is small in comparison with the resonant frequency of the empty cavity. Thus this method widely used by several workers<sup>19-21</sup> is highly suitable for small quantities of materials which can be put into



convenient shape.

C. Role of dielectric measurements on biological systems

The effect of microwaves on biological systems has assumed an interesting dimension in recent years.<sup>22-27</sup> This stems from the fact that microwaves are finding increasing use in medical diagnosis and therapy. Low energies such as that of microwave quanta rule out the possibility of direct effect like intermolecular bond breaking or intramolecular alterations at the molecular level, that are produced by ultraviolet and other ionizing radiations. Mechanisms of interaction of RF and microwave radiation with living systems has been reviewed by Stuchly<sup>28</sup> and Schwan.<sup>29</sup>

The possible biological effects of microwave exposure can be evaluated quantitatively by considering the probable molecular interactions with biomolecular liquids. At the molecular level, the basic mechanism underlying the interaction of microwaves with biological systems involves the effect of the field on dipoles and free charges. Exchange of energy occurs between free charges

and/or dipoles on one hand and the incident radiation on the other. The field may also produce a charge redistribution resulting in the appearance of induced dipoles. To have a feel of the situation in the real system it would be pertinent to consider the biomolecules individually in solution form. Such a system is very amenable to study by dielectric methods. The dipole absorption parameters of the molecules and mode of energy transfer would determine the mechanism of field absorption by the medium in question. Besides  $\tan \delta$ , an evaluation of relaxation time  $\tau$  and dipole moment  $\mu$  is also required. Dipole moment is a direct measure of charge asymmetry, while relaxation time provides information regarding the immediate environment of the molecule. The effect of the solvent can be isolated by determining the complex permittivity in crystalline form also.

Dielectric studies provide many other valuable information on the structure and properties of biological molecules.<sup>30</sup> The method has been used to evaluate the structure of lipoproteins.

It provides evidence in favour of lipid bilayer model and is inconsistent with the lipid core model. Helix coil transition of elongated macromolecules can be studied as a function of temperature or pH. The large changes in dipole moment and relaxation time occurring during the transition are strongly reflected in permittivity measurements. When biological molecules are present in an aqueous environment, the water molecules play an important role in determining the structure and properties of the biomolecule. Water molecules in the neighbourhood of the molecules become an integral part of a structural unit. Behavior of the structural or bound water is markedly different from that of free water molecules, termed as free water. The dielectric dispersion of bound water is expected to occur at a lower frequency than that of dispersion of free water. This principle underlies the use of dielectric methods for hydration studies.

#### D. The Present Work

Dielectric method has been widely used to investigate aqueous solution of biomolecules<sup>30-32</sup>. In contrast to a large volume of data available

on water soluble biomolecules like aminoacids, peptides and proteins, those on water insoluble ones are rather few. A number of steroids though present in traces in the living system play a vital role in the development and maintenance of the organism. These are the steroid hormones of the adrenal and gonads. The precursor for all these steroid hormones is cholesterol synthesised by the adrenal glands. Of many steroids present in living organisms, Cholesterol, Progesterone and Testosterone are soluble in simple non-polar solvents like benzene and carbon tetra chloride. Measurements on dilute solutions in non-polar, non-viscous solvents seem to be interpreted most easily, since no particular effects due to the surroundings of the polar molecules are expected for these system.

In the present work, dilute solutions of the three steroids mentioned above have been investigated and dipole moment and relaxation time have been determined by two point measurement - at 3.3 GHz and 9.4 GHz. Since the solutions are very dilute the dielectric constant and loss factor

involved are very low. Hence methods specifically designed for low loss liquids are particularly suitable. The method adopted consists of measurements on standing wave pattern in front of a column of liquid of varying length and concentration, contained in a short circuited dielectric cell. The technique was first standardised for pure solvents - benzene and carbon tetra chloride.

In addition, the permittivity of the steroids have been determined at 9.4 GHz in powder form and the crystal values have been deduced. Cavity perturbation technique was found most suitable for powders. The powder filled in a thin walled capillary tube was inserted through a small hole at the centre of a resonant cavity resonating in the  $TE_{103}$  mode. The method was standardised for bone<sup>21</sup> for which dielectric parameters are known.

The difference in  $\epsilon''$  values of the three steroids in the two phases is attributed to the difference in the mechanism of microwave absorption. However, identical values of  $\epsilon'$  are obtained. In both phases the loss is found to be high. Local energy changes due to absorption of energy may have functional implications in a biological system.

## CHAPTER II

### THEORETICAL BACKGROUND

#### A. Introduction

The dielectric response of matter to applied electromagnetic fields has been a subject of extensive investigation for many years. Our present understanding of the dielectric properties of materials is based on the Debye theory<sup>33,34</sup> of relaxing dipole interacting with an applied electric field. Early work showed that a set of exactly equivalent, non-interacting dipoles characterized by a single relaxation time  $\tau$  adequately explained the behavior of weak dipolar solutions or dipolar molecules in the gas phase, but was insufficient to account for the broader frequency range over which dispersion was observed in solids and liquids in the frequency range below  $\sim 10^{10}$  Hz. This difficulty was circumvented by a consideration of distribution of relaxation times, like Cole-Cole, Fuoss-Kirkwood, Cole-Davidson and Williams-Watts treatments<sup>35-36</sup> applied to the case of more interactive media. Such approaches involve interpretation of the experimental measurements in terms of degree

of fit to empirical functions. An empirical characterisation of loss in solids and liquids was proposed by Jonscher<sup>37</sup> and a more generalised expression was proposed by Hill.<sup>38</sup> The various types of dielectric response has been summarised by Ngai et al.<sup>39</sup> At one extreme is the case of non-interacting system characterized by Debye behavior. Increasing nearest neighbour interactions lead to behavior as postulated by Cole and Cole or Cole and Davidson.<sup>35,36</sup> Finally, as the interactions tend to be more complicated as in the case of solids and solid like substances universal dielectric response suggested by Jonscher<sup>37</sup> seems to be applicable.

#### B. The Debye Equation

When a system of dipolar molecules is placed in a static field, the polarization will be in equilibrium with the field. If the field is alternating at low frequencies, the polarization will still be in phase with the electric field. If the frequency is sufficiently large the polarization will lag behind the applied field leading to absorption of energy and fall in permittivity.

Pellat assumed that if there is a polarization in the absence of an electric field, due to the occurrence of a field in the past, the decrease of the orientation polarization depends only on the value of the orientation polarization at that instant. Assuming the rate of change of polarization to be proportional to the polarization, the differential equation for the orientation polarization in the absence of an electric field is

$$\frac{d P_{or} (t)}{dt} = - \frac{1}{\tau} P_{or} (t) \quad (2.1)$$

where,  $\tau^{-1}$  is the constant of proportionality which has dimension of a reciprocal time. The solution of eq.(2.1) leads to an exponential form

$$P_{or}(t) = P_{or}(0) e^{-t/\tau} \quad (2.2)$$

In the reverse situation when the polarization is built up due to application of a constant external field

$$P_{or}(t) = P_{or}(\infty) \left\{ 1 - e^{-t/\tau} \right\} \quad (2.3)$$



The total polarization  $P_s$  in a static field  $\vec{E}$  may be divided into two parts

$$P_s = P_\infty + P_{or} \quad (2.4)$$

where  $P_{or}$  indicates the part of  $P_s$  due to dipole orientation and  $P_\infty$  the part due to the polarizability of the particles. Neglecting the time required to establish  $P_\infty$  relative to the time required to build up  $P_{or}$ , we may consider  $P_{or}$  to be built up in the time in which  $P_\infty$  changes to  $P_s$ . The electric displacement  $D$  is related to the applied field  $E$  and polarization  $P$  by the relation

$$D = E + 4\pi P \quad (2.5)$$

Since, in the static case  $D_s = \epsilon_s E$ , where  $\epsilon_s$  is the static permittivity of the medium

$$P_s = \frac{\epsilon_s - 1}{4} E \quad (2.6)$$

Similarly, the refractive index  $n_\infty$  is defined in terms of  $P_\infty$  as

$$P_\infty = \frac{n_\infty^2 - 1}{4} E \quad (2.7)$$

with  $n_\infty^2 = \epsilon_\infty$ .

The theory of dielectric relaxation is based on the assumption that eq (2.3) is also valid for an alternating field. Representing the alternating field by  $E(t)$ , eq.(2.4) with the help of eqs.(2.6) and (2.7) becomes

$$\hat{P}_{or} = \frac{\epsilon_s - 1}{4\pi} \hat{E}(t) - \frac{\epsilon_\infty - 1}{4\pi} \hat{E}(t) \quad (2.8)$$

If the field is alternating with a frequency , it can be represented by

$$\hat{E}(t) = E_0 e^{j\omega t} \quad (2.9)$$

The differential equation for the build up of polarization would then become

$$\frac{d \hat{P}_{or}(t)}{dt} = \frac{1}{\tau} \left\{ \frac{\epsilon_s - \epsilon_\infty}{4} E_0 e^{j\omega t} - \hat{P}_{or}(t) \right\} \quad (2.10)$$

The general solution of this equation is

$$P_{or}(t) = ce^{-t/\tau} + \frac{1}{4\pi} \frac{\epsilon_s - \epsilon_\infty}{1 + j\omega\tau} E_0 e^{j\omega t} \dots (2.11)$$

The first term on the right hand side will decrease to an infinitely small value after some time and therefore, can be neglected. Thus total polarization is

$$\begin{aligned}\hat{P} &= \hat{P}_\infty + P_{or}(t) \\ &= \left\{ \frac{\epsilon_\infty - 1}{4\pi} + \frac{1}{4\pi} \frac{\epsilon_s - \epsilon_\infty}{1 + j\omega\tau} \right\} E_0 e^{j\omega t} \\ &\dots\dots (2.12)\end{aligned}$$

Thus,  $\hat{P}$  is a sinusoidal function of time with the same frequency as the applied field but lagging in phase with respect to  $\hat{E}$ . Eq. (2.5) can be generalized for alternating fields. It then leads to

$$\begin{aligned}\hat{D} &= \hat{E} + 4\pi \hat{P} \\ &= \left\{ \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + j\omega\tau} \right\} E_0 e^{j\omega t} \quad (2.13)\end{aligned}$$

Expressing complex displacement  $\hat{D}$  as  $\hat{D} = \epsilon^* \times \hat{E}$ , the complex permittivity  $\epsilon^*(\omega)$  is given by

$$\epsilon^*(\omega) = \epsilon' - j\epsilon'' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + j\omega\tau} \quad (2.14)$$



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which leads to

$$\epsilon' = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + \omega^2 \tau^2} \quad (2.15a)$$

and

$$\epsilon'' = \frac{(\epsilon_s - \epsilon_{\infty}) \omega \tau}{1 + \omega^2 \tau^2} \quad (2.15b)$$

according to eqs. (2.15)  $\epsilon'$  will decrease from  $\epsilon_s$  to  $\epsilon_{\infty}$ , where as  $\epsilon''$  will become maximum at  $\omega \tau = 1$ . A plot of  $\epsilon'$  and  $\epsilon''$  against  $\log \omega$  would be symmetrical. A method for checking eqs. (2.15) was proposed by Cole and Cole. From eqs. (2.15), it is evident that a plot of  $\epsilon''$  vs  $\epsilon'$  should be a semicircle with radius  $(\epsilon_s - \epsilon_{\infty})/2$ , and centre being on the abscissa at a distance of  $(\epsilon_s + \epsilon_{\infty})/2$  from the origin.

### C. Departure from Debye Behavior

Although eqs.(2.15) give an adequate description of the behavior of the orientation polarization for a large number of condensed systems, for many other systems marked deviations occur. This is

evident from the occurrence of more than one maximum in  $\epsilon''$  as a function of frequency, or from a broader peak in the graphical representation of  $\epsilon''$  as a function of frequency. The deviations occur due to a distribution of relaxation times either distinct from each other or closely spaced such that they are not directly evident. Cole-Cole suggested the following empirical modifications to eq.(2.14).

$$\epsilon^*(\omega) = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + (j\omega\tau)^{1-h}} \quad (2.16)$$

This leads to depressed semicircular arc plot of  $\epsilon''$  against  $\epsilon'$ . The factor  $h$  being related to the depression of the centre from  $\epsilon'$  axis. Another generalised expression was given by Davidson and Cole

$$\epsilon^*(\omega) = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{(1 + j\omega\tau)^{\beta}} \quad (2.17)$$

Cole-Cole plot for the above equation is asymmetric and is often called skewed arc. At low frequencies the plot cuts the  $\epsilon'$  axis perpendicularly, whereas, on the high frequency side at an angle  $\pi\beta/2$ .

The maximum of  $\epsilon''(\omega)$  is found for a value of  $\omega > \tau^{-1}$ . Some of the descriptions of relaxation behavior have been proposed for experimentally measurable functions other than  $\epsilon^*(\omega)$ . Expressions for loss factor  $\epsilon''(\omega)$  were suggested by Fuoss and Kirkwood, and Jonscher, and for step response function was proposed by Williams and Watts. Dotcher and Bordewijk<sup>36</sup> and Hill et al.<sup>35</sup> have given a detailed description of the various functions proposed for explaining the departure from pure Debye behavior.

D. Dielectric relaxation in dilute solutions of polar compounds in non-polar solvents

To characterize the dielectric relaxation in the case of dilute solution of polar compounds in non-polar solvents in terms of molecular parameters, we start with molar polarization  $[\hat{P}]$  given by

$$[\hat{P}] = \frac{M}{d} \frac{\epsilon^* - 1}{\epsilon^* + 2} \quad (2.18)$$

where  $M$  is the average molecular weight of the mixture and  $d$  its density. Intrinsic relaxation time  $\tau^*$  of molar polarization in alternating fields

is defined by the equation

$$[\hat{P}] = [P]_{\infty} + \frac{[P]_s - [P]_{\infty}}{1 + j\omega\tau^*} \quad (2.19)$$

$$\text{with } [P]_{\infty} = \frac{M}{d} \frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} \quad (2.20)$$

$$\text{and } [P]_s = \frac{M}{d} \frac{\epsilon_s - 1}{\epsilon_s + 2} \quad (2.21)$$

Combining eqs. (2.18) to (2.21)

$$\frac{\epsilon^* - 1}{\epsilon^* + 2} = \frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} + \left\{ \frac{\epsilon_s - 1}{\epsilon_s + 2} - \frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} \right\} \frac{1}{1 + j\omega\tau^*} \quad (2.22)$$

Eq. (2.22) on simplification, leads to

$$\epsilon^*(\omega) = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + j\omega\tau^* \frac{\epsilon_s + 2}{\epsilon_{\infty} + 2}} \quad (2.23)$$

Comparison of eq.(2.23) with eq. (2.14) leads to

$$\tau = \tau^* \frac{\epsilon_s + 2}{\epsilon_{\infty} + 2} \quad (2.24)$$

Since the solution is very dilute and the solvent is non-polar the difference between  $\epsilon_s$  and  $\epsilon_\infty$  is very small. Hence  $\tau^*$  in eq.(2.22) can be replaced by  $\tau$ . The derivation of eq.(2.22) is based on the Lorentz formula for internal field with the inherent assumption that the molecules can be considered to be spheres. Assuming that Debye equation for static fields is valid

$$\frac{\epsilon_s - 1}{\epsilon_s + 2} = \frac{4\pi}{3} \sum_i N_i \left( \alpha_i + \frac{\mu_i^2}{3kT} \right) \quad (2.25)$$

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi}{3} \sum_i N_i \alpha_i \quad (2.26)$$

where,  $\alpha_i$  and  $\mu_i$  are the polarisability and dipole moment of the  $i$ th particle, the summation being carried over all particles of the medium. For a dilute solution of a polar solute in a non-polar solvent eqs. (2.24) to (2.26) give

$$\frac{\epsilon^* - 1}{\epsilon^* + 2} = \frac{4\pi}{3} \left\{ \sum_i N_i \alpha_i + N \frac{\mu^2}{3kT} \frac{1}{1 + j\omega\tau} \right\} \quad (2.27)$$



where  $N$  is the number of dipoles per  $\text{cm}^3$ . On splitting eq.(2.27) into real and imaginary parts, the imaginary part yields

$$\frac{3\epsilon''}{(\epsilon'+2)^2 + \epsilon''^2} = \frac{4\pi N\mu^2}{9kT} \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (2.28)$$

When the solution is very dilute this equation can be further simplified. In that case  $\epsilon'$  differs only slightly from the static value  $\epsilon_s$  of the pure solvent, while  $\epsilon'' \ll \epsilon_s$ . Using these assumptions eq.(2.28) leads to

$$\frac{\tan \delta}{c} = \frac{(\epsilon_s+2)^2}{\epsilon_s} \frac{\pi N_A \mu^2}{6750 kT} \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (2.29)$$

where  $C$  is the number of gram molecules of the polar compounds per litre and  $N_A$  is the Avagadro number.  $\tan \delta / C$  is called the molar loss tangent. Eq.(2.29) can be rearranged to give

$$\frac{\tan \delta}{c} = S \left\{ \frac{1}{\tau} + \omega^2\tau \right\} \quad (2.30)$$

$$\text{where, } S = \frac{6750 \text{ kT } \epsilon_s}{(\epsilon_s + 2)^2 N_A \pi \mu^2 c} \quad (2.31)$$

Thus,  $\tau$  and  $\mu$  can be evaluated from a plot of  $\omega / \tan \delta$  vs  $\omega^2$ . This treatment neglects the frequency dependence of  $\epsilon'$ , which is permissible at very low concentrations. The solution can be considered to be sufficiently dilute if the weight fraction of the solute in the solution is less than 0.01.

For two point measurement eq.(2.30) yields

$$S\tau = \frac{(\omega_1 / \tan \delta_1 - \omega_2 / \tan \delta_2)}{\omega_1^2 - \omega_2^2} \quad (2.32)$$

$$\text{and, } S/\tau = \frac{\omega_1 \omega_2 (\omega_2 / \tan \delta_1 - \omega_1 / \tan \delta_2)}{\omega_1^2 - \omega_2^2} \quad (2.33)$$

where, subscripts 1 and 2 denote the two points of measurement. Thus  $\tau$  and  $\mu$  are evaluated using eqs.(2.31) and (2.33). Though theoretically the loss in non-polar solvent is zero, in practice they do exhibit small but finite loss. Hence the contribution of the solute is obtained as  $\Delta \tan \delta = \tan \delta_{\text{soln}} - \tan \delta_{\text{solv}}$  ( $\Delta$  shall be dropped from now on).

### E. Theoretical calculation of Relaxation Time

Attempts have been made to explain the dynamic behavior of molecular systems in time dependent fields in terms of molecular properties and interactions. In the earliest attempt by Debye, the molecules were considered to be spheres, say of radius  $a$ , with a dipole at its centre immersed in a uniform medium of viscosity  $\eta$ . The torque  $M$  applied to the dipole by the electric field was assumed to be counterbalanced by the frictional forces which were proportional to the angular velocity of the dipole molecule at steady state condition. Thus application of Stoke's Law for a rotating sphere leads to the following expression for relaxation time<sup>34,35</sup>

$$\tau = \frac{4 \pi \eta a^3}{kT} \quad (2.34)$$

The Debye equation has been modified in two directions, first to account for the deviation of molecular shape from spherical symmetry and second to refine the viscosity in terms of both the solute molecule and the medium. When molecules are far

from spherical it is necessary to take their shape into account. As a first approximation such molecules may be considered to be ellipsoids of revolution, which includes both the prolate ellipsoid ( $a > b$ ) and the oblate ellipsoid ( $a < b$ ). Here  $a$  and  $b$  are the axis lengths of the ellipsoid which is considered to rotate about the  $a$  axis to give the 3-dimensional model for the molecule. Two relaxation times should be found for a solution of such molecules, corresponding to relaxation of the  $a$  and the  $b$  axes. The relationship between the two relaxation times and the molecular shape and size has been calculated by Perrin and is given by the equations<sup>40</sup>

$$\frac{\tau_a}{\tau_0} = \frac{4}{3} \frac{a^4 - b^4}{b^2 (2a^2 - b^2) aS - 2a^2 b^2} \quad (2.35)$$

$$\frac{\tau_b}{\tau_0} = \frac{8}{3} \frac{a^4 - b^4}{b^2 (2b^2 - a^2) aS + 2a^4} \quad (2.36)$$

$$\text{where, } S = \frac{2}{(a^2 - b^2)^{1/2}} \ln \left\{ \frac{a + (a^2 - b^2)^{1/2}}{b} \right\}$$

$$\text{if } a > b \quad (2.37)$$

$$S = \frac{2}{(b^2 - a^2)^{1/2}} \tan^{-1} \left\{ \frac{(b^2 - a^2)^{1/2}}{a} \right\} \text{ if } a < b \quad (2.38)$$

and  $\tau_0$  is the relaxation time of a sphere of the same volume as the ellipsoid, i.e.  $\frac{4}{3} \pi \eta ab^2/kT$ .

Only in the limiting condition that the solvent medium surrounding an absorbing polar molecule represents a uniform field is it possible to define a viscosity coefficient  $\eta$  as a property of the medium alone. Wirtz considered a model in which the solute molecule and the cluster of solvent molecules which surround it are considered to be acting as a unit in rotational response to the field. A different expression for the frictional coefficient was given by Hill.<sup>35</sup> The formulation based on Andrade's theory of viscosity considers the resistance to rotation which a molecule experiences as a result of the loss of angular momentum which occurs in collisions with its neighbours.

Apart from the formulations discussed; several empirical approaches have been made. A review is given by Illinger.<sup>41</sup>

F. The dielectric properties of Heterogeneous Systems

The static permittivity of a two-component heterogeneous system must lie somewhere between the two extremes corresponding to a capacitance whose plates are filled with (a) mixed fibres stretching from plate to plate, and (b) interleaved sheets parallel to the plates. The mixture relations are based on the assumption that a system of spherical or ellipsoidal particles of random orientation are uniformly dispersed within a continuous medium. An extensive review is given by Van Beek<sup>42</sup>. Of the different mixture formulae, Bottchers formula and Landau-Lifshitz formula which was also independently proposed by Looyenga are found to provide better agreement between calculated and experimental values.

Bottcher's formula is based on the assumption that the field within each component of the heterogeneous mixture is taken equal to the field in a sphere with the dielectric constant of that component in a medium with the apparent dielectric constant of the heterogeneous mixture. This leads to an expression for apparent permittivity  $\epsilon_m$  of the mixture, which

is symmetric with respect to both components of the mixture, namely,

$$\frac{\epsilon_m - \epsilon_1}{3 \epsilon_m} = y_1 \frac{\epsilon_2 - \epsilon_1}{2 \epsilon_m + \epsilon_2} \quad (2.39)$$

where  $y_2$  refers to the volume fraction of the component 2. The Landau-Lifshitz - Looyenga's formula (2.40) is also symmetric with respect to the two components, but does not involve the particle shape in its deviation.

$$\epsilon_m^{1/3} = y_1 \epsilon_1^{1/3} + y_2 \epsilon_2^{1/3} \quad (2.40)$$

Attempts made to generalize mixture relations for complex permittivity has provided success only under restricted conditions.<sup>43,44</sup> For small volume fraction of polar solutes in non-polar solvents, eq.(2.40) holds for real permittivity. The crystal and powder values of the complex permittivity are related by the expressions

$$\epsilon_p'^{1/3} - 1 = y (\epsilon_s'^{1/3} - 1) \quad (2.41a)$$

$$\epsilon_p'' = y \epsilon_s'' \left( \frac{\epsilon_p'}{\epsilon_s'} \right)^{2/3} \quad (2.41b)$$

where subscript p and s refer to powder and crystal respectively and y is the volume fraction occupied by the molecules in powder form.



CHAPTER III

MATERIALS AND METHOD

A. Theoretical background of the method for  
Solutions

The method using standing wave measurements in front of a column of dielectric is based on the relation derived by Roberts and vonHippel.<sup>11</sup> The technique consists of reflecting the wave at normal incidence from a column of the liquid backed by a perfectly reflecting surface, which is enclosed in a waveguide cell. Standing waves are set up in the region in front of the sample as a result of the superposition of the incident and the reflected waves, propagating in the TE<sub>10</sub> mode.

The transverse field components  $E(x)_1$  and  $H(x)_1$  in air (medium 1) at a distance  $x$  from the dielectric surface along the axis of the wave guide are

$$\begin{aligned} E(x)_1 &= A_{11} \exp(\gamma_1 x) + A_{r1} \exp(-\gamma_1 x) \\ &= A_{11} \left\{ \exp(\gamma_1 x) + \Gamma_0 \exp(-\gamma_1 x) \right\} \quad (3.1a) \end{aligned}$$

$$\begin{aligned}
 H(x)_1 &= \frac{A_{11}}{Z_1} \exp(\gamma_1 x) - \frac{A_{r1}}{Z_1} \exp(-\gamma_1 x) \\
 &= \frac{A_{11}}{Z_1} \left\{ \exp(\gamma_1 x) - r_0 \exp(-\gamma_1 x) \right\} \quad (3.1b)
 \end{aligned}$$

where,  $A_{11}$  and  $A_{r1}$  are the amplitudes of the incident and reflected wave at the dielectric surface.  $r_0$  is then  $A_{r1}/A_{11}$  and defines the reflection coefficient which characterizes the section of the waveguide containing the medium 2. In terms of a complex quantity  $\phi = \xi + j\eta$ ,  $r_0$  is defined as

$$r_0 = A_{r1}/A_{11} = e^{-2\phi} \quad (3.2)$$

The wave impedance  $Z(o)$  of the dielectric filled section is given by the ratio of the electric to the magnetic field intensities at the dielectric surface,

$$\begin{aligned}
 Z(o) &= \frac{E(o)}{H(o)} = Z_1 \frac{1 + r_0}{1 - r_0} = Z_1 \frac{1 + e^{-2\phi}}{1 - e^{-2\phi}} \\
 &= Z_1 \coth \phi \quad (3.3)
 \end{aligned}$$

Neglecting the attenuation in the air filled guide, the complex propagation factor  $\gamma_1 = \alpha_1 + j\beta_1$  reduces to

$$\gamma_1 = j\beta_1 = j 2\pi / \lambda_1 \quad (3.4)$$

where,  $\lambda_1$  is the wavelength in air inside the waveguide. Eq.(3.1a) leads to maximum and minimum field amplitudes of the standing wave

$$E_{\max} = |A_1| (1 + |R_0|) = |A_1| (1 + e^{-2\xi}) \quad \dots \quad (3.5a)$$

$$E_{\min} = |A_1| (1 - |R_0|) = |A_1| (1 - e^{-2\xi}) \quad \dots \quad (3.5b)$$

Hence,

$$\frac{E_{\min}}{E_{\max}} = \frac{1 - e^{-2\xi}}{1 + e^{-2\xi}} = \tan h \xi \quad (3.6)$$

If  $X_0$  is the separation of the first minimum from the front face of the sample, then  $\psi$  is given by

$$\frac{2\pi X_0}{\lambda_1} = -2\psi - \frac{2\pi X_0}{\lambda_1} + \pi \quad (3.7a)$$

or, 
$$\psi = \frac{\pi}{2} - \frac{2\pi x_0}{\lambda_1} \quad (3.7b)$$

Thus,  $\xi$  and  $\psi$ , and hence, input impedance  $Z(o)$  can be expressed in terms of measurable quantities,  $x_0$ , and  $E_{\min}/E_{\max}$ . Eq.(3.3) yields

$$Z(o) = Z_1 \frac{\tanh \xi - j \cot \psi}{1 - j \tanh \xi \cot \psi} = Z_1 \frac{\frac{E_{\min}}{E_{\max}} - j \tan \frac{2\pi x_0}{\lambda_1}}{1 - j \frac{E_{\min}}{E_{\max}} \tan \frac{2\pi x_0}{\lambda_1}} \quad \dots\dots(3.8)$$

The standing wave in the dielectric is represented by

$$E(x_2) = A_{12} \exp(\gamma_2 x) + A_{r2} \exp(-\gamma_2 x) \quad (3.9a)$$

and

$$H(x_2) = \frac{A_{12}}{Z_2} \exp(\gamma_2 x) - \frac{A_{r2}}{Z_2} \exp(-\gamma_2 x) \quad (3.9b)$$

At the short circuit,  $x = -d$ , introducing the boundary condition  $E(x_2) = 0$  at  $x = -d$ , eq. (3.9a) leads to

$$0 = A_{12} \exp(-\gamma_2 d) + A_{r2} \exp(\gamma_2 d) \quad (3.10)$$

From eq.(3.9) impedance at the interface is

$$Z(o) = \frac{E(o)_2}{H(o)_2} = Z_2 \frac{1 - \exp(-2 \gamma_2 d)}{1 + \exp(-2 \gamma_2 d)}$$

which by virtue of eq.(3.10) becomes

$$Z(o) = Z_2 \tanh \gamma_2 d \quad (3.11)$$

The product of the characteristic impedance and the propagation constant of the wave are related as

$$\gamma_2 Z_2 = j \omega \mu_2 \quad (3.12a)$$

where  $\mu_2$  is the permeability of the medium 2.

Since the medium is non-magnetic  $\mu_2 = \mu_0$  of free space, hence,

$$\gamma_2 Z_2 = j \omega \mu_0 = \gamma_1 Z_1 \quad (3.12b)$$

Substituting for  $Z_2$  in terms of  $Z_1$ , and in (3.12)

$$Z(o) = Z_1 \frac{\gamma_1}{\gamma_2} \tanh \gamma_2 d \quad (3.13)$$

Eqs.(8) and (13) then lead to

$$\frac{\frac{E_{min}}{E_{max}} - j \tan \frac{2\pi x_0}{\lambda_1}}{1 - j \frac{E_{min}}{E_{max}} \tan \frac{2\pi x_0}{\lambda_1}} \cdot \frac{\lambda_1}{2\pi d j} = \frac{\tanh \gamma_2 d}{\gamma_2 d} \quad (3.14)$$

The most general procedure is to solve this complex transcendental equation for  $\gamma_2 d$  after the measured values of  $E_{\min}/E_{\max}$ ,  $\lambda_1$ ,  $d$  and  $X_0$  are obtained. When the dissipation factor  $\tan$  of the dielectric is very small, eq.(3.14) can be separated into real and imaginary parts.<sup>12</sup> Denoting  $E_{\max}/E_{\min}$  as  $\rho$ , the real part of eq.(3.14) gives

$$\frac{-\lambda_1 \left( \tan \frac{2\pi X_0}{\lambda_1} \right) \cdot (1 - 1/\rho^2)}{2\pi d \left( 1 + 1/\rho^2 \cdot \tan^2 \frac{2\pi X_0}{\lambda_1} \right)} = \frac{\beta_2 d (1 - \tanh^2 \alpha_2 d) \tan \beta_2 d + \alpha_2 d (1 + \tan \beta_2 d) \tanh \alpha_2 d}{(\alpha_2^2 d^2 + \beta_2^2 d^2) (1 + \tanh^2 \alpha_2 d \tan^2 \beta_2 d)} \quad (3.15)$$

When  $\alpha_2 d$  and  $1/\rho$  are small, eq. (3.15) reduces to

$$\frac{-\lambda_1 \tan \frac{2\pi X_0}{\lambda_1}}{2\pi d} = \frac{\tan \beta_2 d}{\beta_2 d} \quad (3.16)$$

Eq.(3.16) contains measurable quantities on the left hand side and hence, can be solved for  $\beta_2 d$ .

The complex propagation factor  $\gamma_2 d$  can be expressed in terms of the permittivity  $\epsilon'$  and loss factor  $\epsilon''$  of the dielectric as

$$\begin{aligned} \gamma_2 d &= \alpha_2 d + j \beta_2 d \\ &= \frac{\pi \epsilon'' d}{\lambda [\epsilon' - (c\lambda/\lambda_c)^2]^{1/2}} + j \frac{2\pi d}{\lambda} [\epsilon' - (c\lambda/\lambda_c)^2]^{1/2} \end{aligned} \quad (3.17)$$

where,  $\lambda_c$  is the cut off wavelength of the guide and  $\lambda$  is the free space wavelength. Since  $\lambda$ ,  $\lambda_c$  and  $\lambda_g$  are connected by the relation

$$1/\lambda^2 = 1/\lambda_c^2 + 1/\lambda_g^2 \quad (3.18)$$

imaginary part of eq.(3.17) gives

$$\epsilon' = \frac{1/\lambda_c^2 + (\beta_2 d / 2\pi d)^2}{1/\lambda_c^2 + 1/\lambda_g^2} \quad (3.19)$$

The solution of eq.(3.16) for  $\beta_2 d$  is multi-valued. The correct value can be chosen since the expected value of  $\epsilon'$  is known.

Equating the imaginary parts of eq.(3.14)

$$\frac{-\lambda_1 / \rho \left( 1 + \tan^2 \frac{2\pi x_0}{\lambda_1} \right)}{2\pi d \left( 1 + \frac{1}{\rho_2} \tan^2 \frac{2\pi x_0}{\lambda_1} \right)} \quad (3.20)$$

$$= \frac{\alpha_2 d \tan \beta_2 d - \alpha_2 d \tanh^2 \alpha_2 d - \beta_2 d \tanh \alpha_2 d - \beta_2 d \tanh \alpha_2 d \tan^2 \beta_2 d}{(1 + \tanh^2 \alpha_2 d \tan^2 \beta_2 d) (\alpha_2^2 d^2 + \beta_2^2 d^2)}$$

When  $\alpha_2 d$  and  $1/\rho$  are small, eq.(3.20) reduces to

$$\alpha_2 d \approx \frac{(\beta_2 d)^2 \lambda_1}{2\pi d \rho} \frac{1 + \tan^2 \frac{2\pi x_0}{\lambda_1}}{\beta_2 d (1 + \tan^2 \beta_2 d) - \tan \beta_2 d} \quad (3.21)$$

Eqs.(3.17) and (3.21) lead to the following expression for  $\tan \delta_2$ .

$$\tan \delta_2 = \frac{\lambda_1}{\pi d \rho} \left[ 1 - (\lambda/\lambda_c)^2 / \epsilon' \right] \frac{1 + \tan^2 \frac{2\pi x_0}{\lambda_1}}{(1 + \tan^2 \beta_2 d) - \frac{\tan \beta_2 d}{\beta_2 d}} \quad (3.22)$$



The experimentally determined values of the voltage standing wave ratio,  $K_0$ ,  $\lambda_1$ ,  $d$ , together with the solution  $\beta_2 d$  of eq. (3.16) give the value of the loss tangent  $\tan \delta$ .

Since there is always some finite loss in the walls of the waveguide,  $\rho$  includes those losses together with the dielectric losses. The wall losses can be eliminated using the dissipation factor of the empty waveguide

$$\tan \delta_w = \frac{\Delta x}{d} \frac{1}{1 + \lambda_1^2 / \lambda_c^2} \quad (3.23)$$

where  $\Delta x$  is the width of the minimum of the standing wave at double power points in the air filled guide. Loss tangent of the dielectric is then obtained as

$$\tan \delta = \tan \delta_2 - \tan \delta_w \quad (3.24)$$

B. Theoretical background of the cavity  
Perturbation Technique

A perturbation theory which gives the change in the resonant frequency ( $f$ ) and loaded Quality factor ( $Q$ ) of a cavity due to small changes in the cavity was developed by Bethe and Schwinger.<sup>16</sup> Consider two cavities denoted by subscripts 1 and 2, which are 'almost' alike. The small difference between the two cavities is assumed to be in the permittivity or the permeability of the material it contains. The cavity walls are assumed to be lossless. Maxwell's equations for these cavities then are:

$$\begin{aligned} \nabla \times \bar{E}_j &= -j \omega_j \mu_j \bar{H}_j \quad ; \quad \nabla \times \bar{H}_j = j \omega_j \epsilon_j \bar{E}_j \\ j &= 1, 2 \end{aligned} \quad (3.25)$$

where, the angular frequencies  $\omega_j$  are complex and are understood to reflect all losses, so that losses through the coupling mechanism are included. The four equations represented by eq.(3.25) lead to

$$\begin{aligned}
& \int_{V_c} \left\{ \bar{E}_2 \cdot (\nabla \times \bar{H}_1) - \bar{E}_1 \cdot (\nabla \times \bar{H}_2) + \bar{H}_2 \cdot (\nabla \times \bar{E}_1) - \bar{H}_1 \cdot (\nabla \times \bar{E}_2) \right\} dV \\
& = j \int_{V_c} \left\{ (\omega_1 \epsilon_1 - \omega_2 \epsilon_2) \bar{E}_1 \cdot \bar{E}_2 - (\omega_1 \mu_1 - \omega_2 \mu_2) \bar{H}_1 \cdot \bar{H}_2 \right\} dV \\
& \dots (3.26)
\end{aligned}$$

On application of Gauss's divergence theorem, left hand side of eq. (3.26) becomes

$$\begin{aligned}
& \int_{S_c} (\bar{H}_1 \cdot \bar{E}_2) \cdot d\bar{S} - \int_{S_c} (\bar{H}_2 \times \bar{E}_1) \cdot d\bar{S} \\
& = \int_{S_c} \left\{ (\bar{H}_1 \times \bar{E}_2)_n - (\bar{H}_2 \times \bar{E}_1)_n \right\} dS \quad (3.27)
\end{aligned}$$

Since the walls are perfectly conducting, the tangential component of  $\bar{E}$  is zero. Hence,  $\bar{H}_1 \times \bar{H}_2$  cannot have a component normal to  $S_c$ , consequently the left hand side of eq. (3.26) is zero. Eq. (3.26) on rearrangement then gives

$$\begin{aligned} & \omega_1 \int_{V_c} (C \epsilon_1 \bar{E}_1 \cdot \bar{E}_2 - \mu_1 \bar{H}_1 \cdot \bar{H}_2) dV \\ &= \omega_2 \int_{V_c} (C \epsilon_2 \bar{E}_1 \cdot \bar{E}_2 - \mu_2 \bar{H}_1 \cdot \bar{H}_2) dV \end{aligned} \quad (3.28)$$

subtracting each side of eq.(3.28) from the integral

$$\omega_2 \int_{V_c} (C \epsilon_1 \bar{E}_1 \cdot \bar{E}_2 - \mu_1 \bar{H}_1 \cdot \bar{H}_2) dV$$

leads to the following equation on rearrangement.

$$\frac{\omega_2 - \omega_1}{\omega_2} = \frac{\int_{V_c} [(C \mu_2 - \mu_1) \bar{H}_1 \cdot \bar{H}_2 - (C \epsilon_1 - \epsilon_2) \bar{E}_1 \cdot \bar{E}_2] dV}{\int_{V_c} (C \epsilon_1 \bar{E}_1 \cdot \bar{E}_2 - \mu_1 \bar{H}_1 \cdot \bar{H}_2) dV} \quad (3.29)$$

Assuming cavity 1 to be empty,  $\epsilon_1 = \epsilon_0$  and  $\mu_1 = \mu_0$ . The cavity is assumed to be perturbed by a non-magnetic material of permittivity  $\epsilon_2$ . The volume of the sample  $V_s$  is assumed to be small as compared to  $V_c$ . Under these conditions eq. (3.29) becomes

$$\frac{\omega_2 - \omega_1}{\omega_2} = - \frac{\epsilon^* - 1}{2} \frac{\int_{V_s} \bar{E}_1 \cdot \bar{E}_2 dV}{\int_{V_c} |\bar{E}_1|^2 dV} \quad (3.30)$$

where,  $\epsilon^*$  is the relative complex permittivity of the sample in cavity 2.

The complex angular frequencies  $\omega_1$  and  $\omega_2$  in eq. (3.30) are related to measurable quantities. The complex angular frequency  $\omega$  associated with a dissipative system can be written as

$$\omega = \omega_R + j \omega_i \quad (3.31)$$

when the time variation is taken as  $e^{j\omega t}$ . The real part  $\omega_R$  is related to real frequency  $f$  by

$$\omega_R = 2 \pi f \quad (3.32)$$

Since energy involves square of field quantities,  $e^{j2\omega t}$  will be associated with energy. Hence, energy decreases as  $e^{-2\omega_i t}$  and the energy loss per unit energy is  $(1 - e^{-2\omega_i t})$  or  $2\omega_i t$ . Power loss per unit energy is then  $2\omega_i$  so that total average power loss in the system is  $2\omega_i U_T$  where  $U_T$  is the total average energy of the system.  $Q$  is defined as

$$Q = \frac{\omega_R \text{ (stored energy in cavity)}}{\text{(average power loss)}} \quad (3.33)$$

Using (3.32), (3.33) now becomes

$$Q = \frac{2 \pi f V_T}{2 \omega_i V_T} = \frac{\omega_R}{2 \omega_i} \quad (3.34)$$

Now eq.  $\frac{\omega_2 - \omega_1}{\omega_2} \approx \frac{(\omega_{R2} - \omega_{R1}) + j(\omega_{i2} - \omega_{i1})}{\omega_{R2} (1 + j \omega_{i2} / \omega_{R2})}$   
on application of eqs. (3.32) and (3.34) gives

$$\frac{\omega_2 - \omega_1}{\omega_2} \approx \left\{ \frac{f_2 - f_1}{f_2} + j \left( \frac{1}{2Q_2} - \frac{1}{2Q_1} \right) \right\} \left( 1 - j \frac{1}{2Q_2} \right) \quad \dots\dots(3.35)$$

Since  $(1/2Q_2)$  can be neglected as compared to unity,

$$\frac{\omega_2 - \omega_1}{\omega_2} \approx \frac{f_2 - f_1}{f_2} + \frac{j}{2} \left( \frac{1}{Q_2} - \frac{1}{Q_1} \right) \quad (3.36)$$

Eqs. (3.30) and (3.36) then lead to

$$2 \frac{f_1 - f_2}{f_2} - j \left( \frac{1}{Q_1} - \frac{1}{Q_2} \right) = e^{-1} V_s \frac{\int \bar{E}_1 \cdot \bar{E}_2 dV}{\int_V |\bar{E}_1|^2 dV} \quad (3.37)$$

Here, the field  $\bar{E}_1$  in the empty cavity is presumed to be known and only the perturbed field  $\bar{E}_2$  in the sample volume  $V_s$  remains as an unknown. For

a cylindrical specimen placed with its axis parallel to the  $\vec{E}$  field in the cavity,  $\vec{E}_2$  will be everywhere tangent to the unperturbed electric field lines in the cavity. When the sample ends with field lines on the cavity walls, the tangential electric field will be continuous over the boundary of the specimen. Hence  $\vec{E}_2 = \vec{E}_1$ .

In the present arrangement, the sample is placed to  $\vec{E}$  by inserting it through a small hole in the wider wall of a rectangular cavity operating in  $TE_{10}$  mode. The electric field is then given by

$$E_y = E_0 \sin \frac{\pi x}{a} \sin \frac{2\pi z}{d} \quad (3.38)$$

where  $a$  and  $d$  are the width and length of the cavity respectively. Then

$$\int_{V_c} |\vec{E}_1|^2 dV = \frac{V_0 E_0^2}{4} \quad (3.39)$$

Assuming that the sample is placed where  $\vec{E}_2$  is maximum,

$$\int_{V_s} \vec{E}_1 \cdot \vec{E}_2 dV = E_0^2 V_s \quad (3.40)$$

Separating eq.(3.37) into real and imaginary parts and substituting for the integrals using (3.39) and (3.40).

$$\epsilon' = 1 + \frac{1}{2} \frac{V_0}{V_s} \left\{ \frac{f_1 - f_2}{f_2} \right\} \quad (3.41)$$

$$\epsilon'' = \frac{1}{4} \frac{V_0}{V_s} \left\{ \frac{1}{Q_2} - \frac{1}{Q_1} \right\} \quad (3.42)$$

The relative error in putting  $\bar{E}_2 = \bar{E}_1$  and other approximations is of the order of  $((f_1 - f_2)/f_2) + (1/Q_2)$ .

In the present study the powder was filled in a thin walled capillary tube. Assuming that the empty cavity is not significantly affected by the empty tube, cavity 1 is taken to be the cavity perturbed by the tube alone and cavity 2 as the cavity perturbed by the sample filled tube.

### C. Materials used

The chemicals used in the study were commercially available and were of sufficient purity. The source of the chemicals is indicated Table 3.1.



Table 3.1

Chemical	Source
Cholesterol	Sigma
Progesterone	C.S.I.R. Centre for Biochemicals, India.
Testosterone	"
Benzene	B.D.H. Analar
Carbon tetra Chloride	"

The molecular weight, dimensions and density of the steroids is given below.

Table 3.2

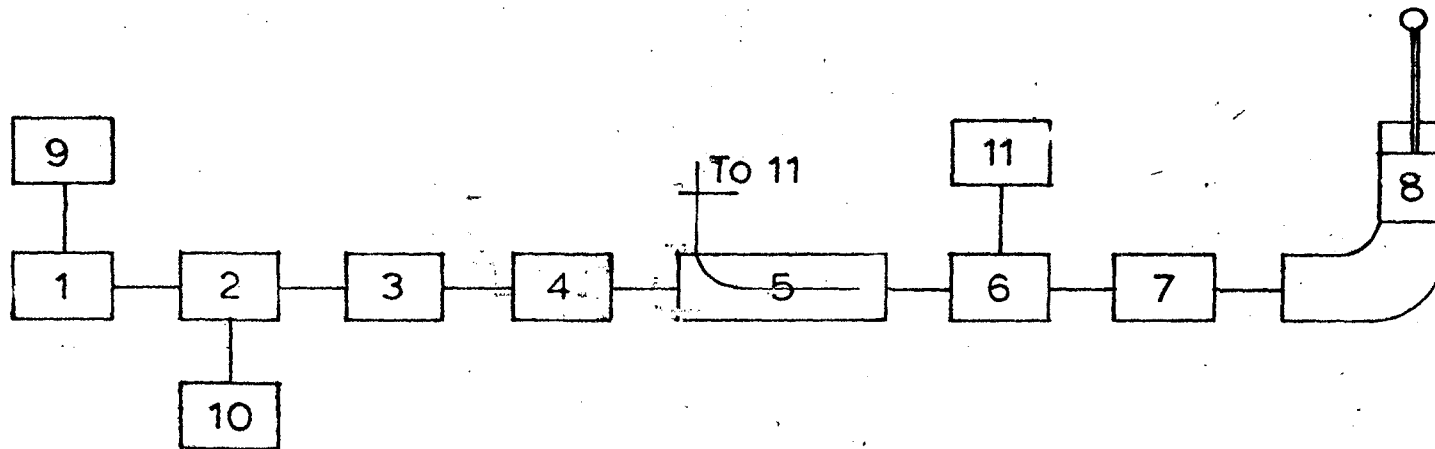
Molecular Dimensions<sup>45</sup> and Density<sup>46</sup> of the steroids

Name	Mol. wt.	Molecular Dimensions	Density
Cholesterol	386.7	20 Å <sup>o</sup> x 7.2 Å <sup>o</sup> x 5.0 Å <sup>o</sup>	1.067
Progesterone	314.4.	12.31Å <sup>o</sup> x 6.94Å <sup>o</sup> x 5.14Å <sup>o</sup>	1.166
Testosterone	288.4	11.01Å <sup>o</sup> x 6.03Å <sup>o</sup> x 5.59Å <sup>o</sup>	1.27*

\*Estimated value.

#### D. Experimental Procedure.

(1) **Measurement on Solutions:** The complete electrical system is shown in schematic form in the block diagram, Fig. 3.1. Measurements were carried out at two frequencies, one in the S-band (3.3 GHz) and the other in the X-band (9.4 GHz), under identical conditions. Microwave power supplied by a klystron, passes an isolator, frequency meter, tuner, directional coupler, slotted section, second tuner and finally impinges on the liquid cell. A packaged signal generator was used in the S-band. The liquid cell is a section of a waveguide with a thin mica window. A perfectly reflecting flat plate plunger is used to vary the length of the dielectric filled in the cell. Initially, with the liquid cell terminated by a matched load, the system is tuned such that the standing wave ratio observed on the slotted section is less than 1.02. Replacing the short circuiting plunger, the positions of the minima are noted with and without the liquid. The travelling probe is then removed from the slotted section, and the reflected power with and without the sample is noted. If  $A$  is the attenuation of



- |                        |                          |
|------------------------|--------------------------|
| 1 Generator (Klystron) | 7 E-H. Tuner             |
| 2 Isolator             | 8 Liquid cell            |
| 3 Frequency meter      | 9 Klystron. power supply |
| 4 Slide Screw Tuner    | 10 Matched load          |
| 5 Directional coupler  | 11 V.S.W.R. meter        |
| 6 Slotted section      |                          |

Fig 3-1 Schematic diagram of set up for measurements on liquids

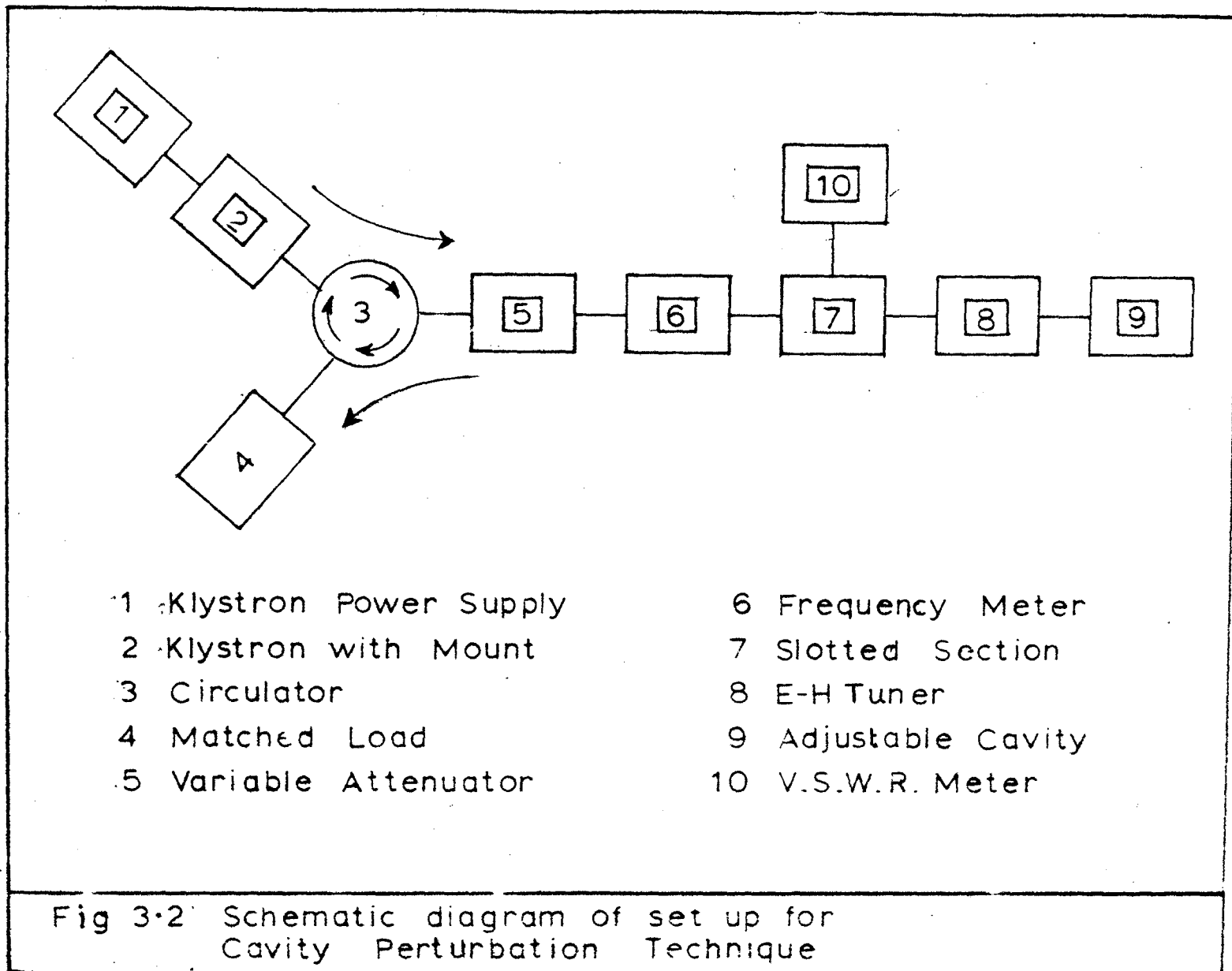
the reflected wave, the VSWR is then given by

$$\rho = \frac{\text{antilog}(A/20) + 1}{\text{antilog}(A/20) - 1} \quad (3.43)$$

The permittivity and loss tangent were computed using the relation discussed before.

The method was first standardized for pure solvents. A number of observations were taken for different lengths of liquid column that are roughly odd multiples of  $\lambda_d / 4$ . Solutions of varying concentration were then investigated, the maximum weight fraction in each case being 0.01. Loss tangent due to the solute,  $\tan \delta$  was plotted against concentration in moles/litre, and mean molar loss tangent was determined. The dipole absorption parameters were then computed as outlined in Chapter II.

(11) Measurement on Powders: The schematic diagram of the experimental set up for measurement of complex permittivity of the powders is shown in fig. 3.2. In this case the power from the source was fed into a line consisting of an isolator,



variable attenuator, frequency meter, slotted section, tuner and terminated by a waveguide cavity. The cavity is designed to resonate at 9.4 GHz in  $TE_{103}$  mode. A small hole is drilled at the centre of the wider wall of the cavity such that a specimen, introduced through the hole will be parallel to the electric field and will be in the maximum field. The resonant frequency and Q of the cavity are determined before and after loading the cavity. The set up was first standardized for bone which dielectric parameters are known.

The powders were packed in a thin walled glass capillary tube by gentle tapping and the density was noted. Care was taken to maintain the packing fraction constant for a particular steroid. The complex permittivity of the powders were determined as described above. The crystal values were determined using Landau-Lifshitz-Looyenga's formula for mixtures generalized for complex permittivities.

CHAPTER IVRESULTS AND DISCUSSIONA. Analysis of Experimental Data

The loss tangents of the solutes observed in different solutions at 3.3 GHz and 9.4 GHz are tabulated below:

Table 4.1I. Cholesterol in Benzene:

Conc. in gm/ml.	$\tan \delta \times 10^3$ at 3.3 GHz	$\tan \delta \times 10^3$ at 9.4 GHz
.00225	1.31 $\pm$ .04	0.46 $\pm$ .03
.00450	2.61 $\pm$ .03	0.94 $\pm$ .03
.00675	4.04 $\pm$ .04	1.46 $\pm$ .05
.00900	5.29 $\pm$ .04	1.94 $\pm$ .04

II. Progesterone in Benzene:

Conc. in gm/ml.	$\tan \delta \times 10^3$ at 3.3 GHz	$\tan \delta \times 10^3$ at 9.4 GHz
.00225	1.48 $\pm$ .06	0.56 $\pm$ .04
.00450	2.92 $\pm$ .05	1.21 $\pm$ .03
.00675	4.39 $\pm$ .04	1.82 $\pm$ .05
.00900	5.84 $\pm$ .05	2.41 $\pm$ .04

## III. Testosterone in Benzene

Conc. in gm/ml.	$\tan \delta \times 10^3$ at 3.3 GHz	$\tan \delta \times 10^3$ at 9.4 GHz
.00225	2.49 $\pm$ .04	1.12 $\pm$ .06
.00450	5.05 $\pm$ .03	2.21 $\pm$ .03
.00675	7.47 $\pm$ .06	3.31 $\pm$ .04
.00900	9.98 $\pm$ .05	4.48 $\pm$ .05

## IV. Cholesterol in Carbon tetra Chloride

Conc. in gm/ml	$\tan \delta \times 10^3$ at 3.3 GHz	$\tan \delta \times 10^3$ at 9.4 GHz
.004	1.74 $\pm$ .06	0.62 $\pm$ .05
.008	3.49 $\pm$ .04	1.24 $\pm$ .06
.012	5.30 $\pm$ .05	1.88 $\pm$ .04
.016	7.02 $\pm$ .06	2.50 $\pm$ .04

## V. Progesterone in Carbon tetra Chloride

Conc. in gm/ml	$\tan \delta \times 10^3$ at 3.3 GHz	$\tan \delta \times 10^3$ at 9.4 GHz
.004	2.08 $\pm$ .05	0.77 $\pm$ .04
.008	4.09 $\pm$ .06	1.58 $\pm$ .05
.012	6.24 $\pm$ .06	2.34 $\pm$ .04
.016	8.29 $\pm$ .04	3.14 $\pm$ .03



Variation of Loss tangent with concentration in benzene

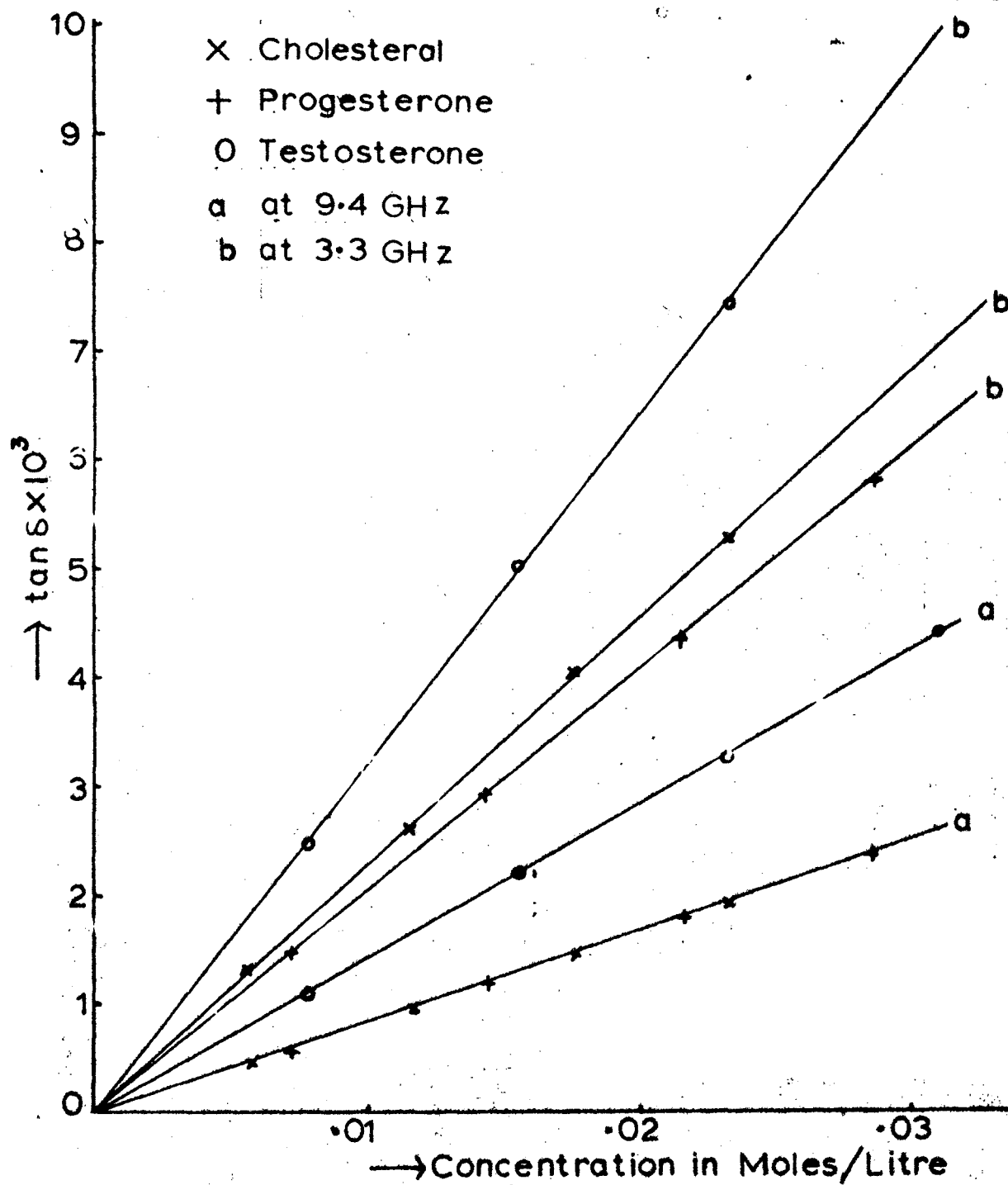


Fig 4.1

Variation of loss tangent with concentration  
In carbon tetra chloride

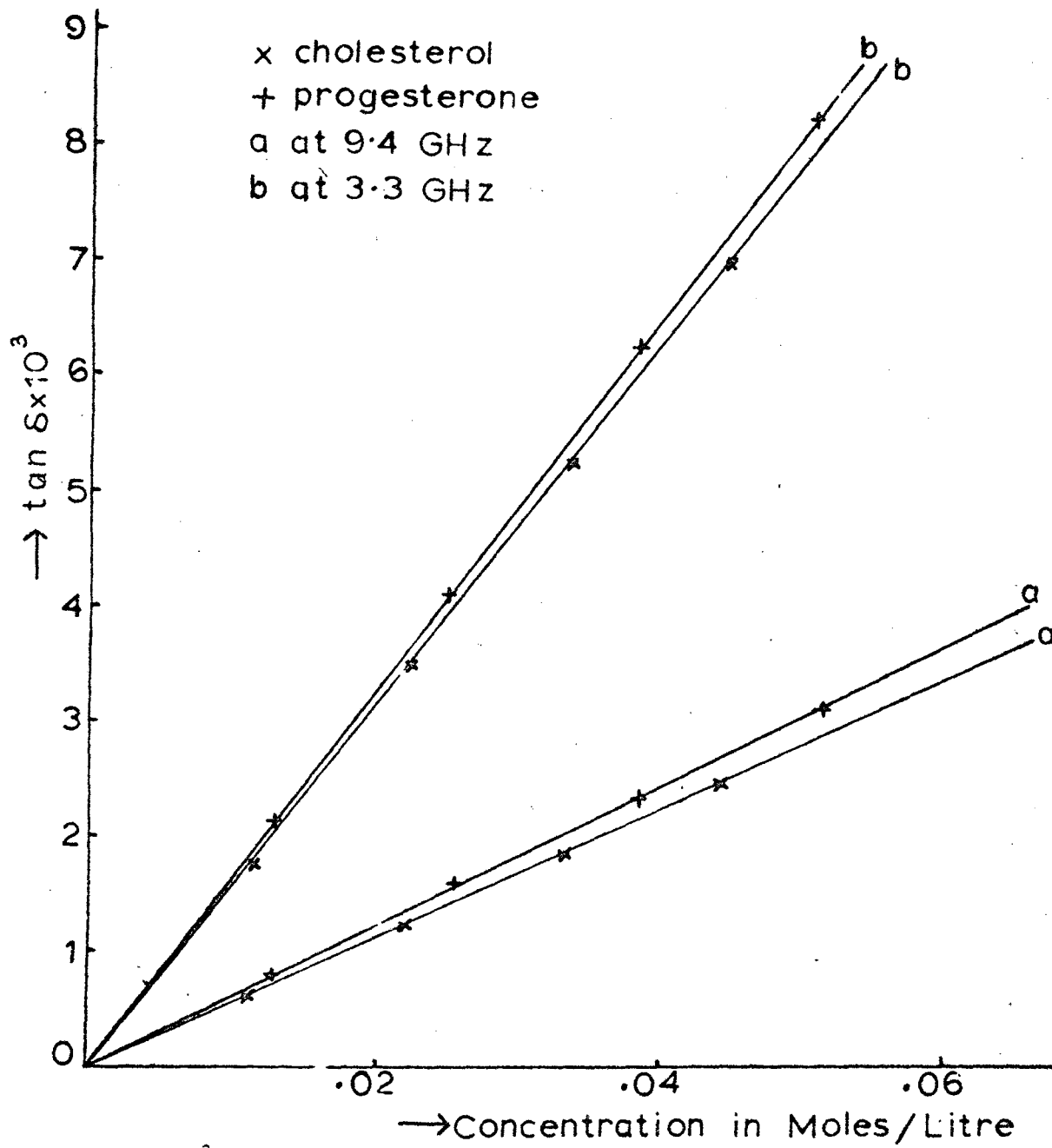


Fig 4.2

Plots of  $\tan \delta$  vs. molar concentration for different solutions are shown in figs. 4.1 and 4.2. All measurements were carried out at 30°C. The values of dipole moment and relaxation time computed from the data presented are tabulated in Table 4.2. The values of relaxation time calculated using the Debye equation (2.34) are given alongwith the observed values.

Table 4.2

Relaxation time\* and apparent Dipole Moment of the solutes\*

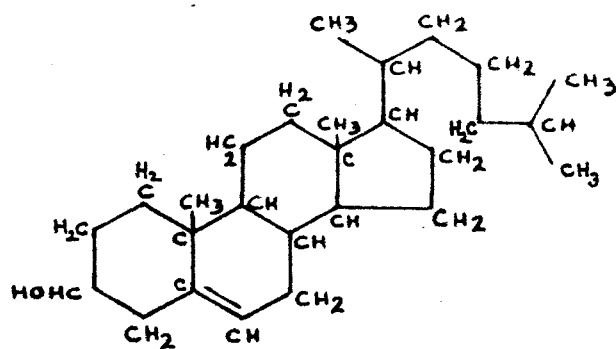
Solute	Solvent	$\tau_{\text{obs}} \times 10^{12} \text{ sec}$	$\mu \text{ in D}$	$\tau_{\text{D}} \times 10^{12} \text{ sec}$
Cholesterol	Benzene	252.3	4.79	152.4
Progesterone	Benzene	108.7	3.23	93.0
Testosterone	Benzene	85.7	3.74	77.8
Cholesterol	$\text{CCl}_4$	376.1	4.87	227.8
Progesterone	$\text{CCl}_4$	162.1	3.28	139.0

\* at 30°C.

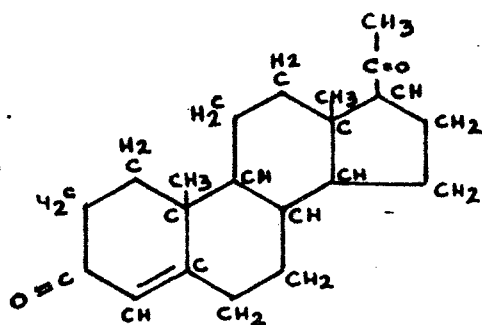
The observed relaxation times of Progesterone and Testosterone agree fairly well with the values calculated using Debye's theory of microscopic relaxation time. Since the molecules are comparatively

large with respect to the solvent molecules, it is expected that the observed values should be close to the Debye values.<sup>47,48</sup> The difference between the observed values and the calculated values of Cholesterol in both solvents can be attributed to the longer axial ratio in this case (Table 3.2). For prolate ellipsoids, the difference between the relaxation times about the two axes increases sharply as the axial ratio becomes increasingly greater than 2. All the molecules are prolate ellipsoids, the axial ratio of Cholesterol being greater than 2.  $\tau_{obs}$  for Cholesterol lies between the relaxation times of the long and short axes calculated using Perrin's equations (2.35) to (2.37) -  $325.2 \times 10^{-12}$  sec and  $164.6 \times 10^{-12}$  sec in Benzene and  $486.1 \times 10^{-12}$  sec and  $246.0 \times 10^{-12}$  sec in Carbon tetra chloride. However, the ratio of  $\tau_{obs}$  in Carbon tetra Chloride and Benzene is in the ratio of the viscosities of the two solvents as predicted by Debye's theory.

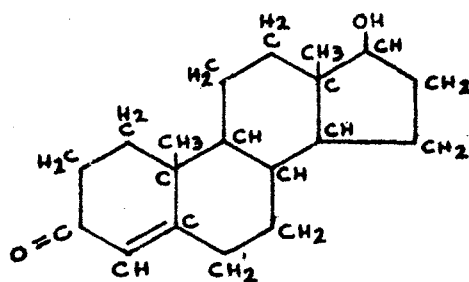
In this context, it may be mentioned that in many cases dielectric absorption of the intramolecular processes is not readily separated from the



cholesterol



progesterone



testosterone

Fig 4.3 Structure of Cholesterol , Progesterone & Testosterone

overall rotation of the molecules and hence interpretation of the dielectric data solely on the basis of overall relaxation of the molecules may not be valid. All solutes used in the present study possess a rotating group. Smyth<sup>49</sup> observes that the dielectric absorption in most aromatic compounds having a rotatable polar group is characterized by two discrete relaxation processes - an intramolecular having a small relaxation time and a molecular with relatively large relaxation time. The characteristic time for group reorientations falls in the far infrared region the value usually being of the order of a few picoseconds or less.<sup>50</sup> The Debye value for overall relaxation being about two orders of magnitude greater than that for group reorientations, the contribution of the latter process to the loss factor can be neglected at frequencies less than a few GHz. Thus, it may be concluded that the three steroids - Cholesterol, Progesterone and Testosterone show a near Debye type behavior in a non-polar environment.

In order to deduce the permittivity of the solute  $\epsilon'_{sol}$  from the solution data more

concentrated solutions were studied. The data is presented in Table 4.3. The  $\epsilon'_{sol}$  values were computed using equations (2.40).

Table 4.3

I. Cholesterol in Benzene

Conc. in gm/ml.	Volume fraction $\times 10^2$	$\epsilon'_{soln}$	$\epsilon'_{sol}$
0	0	$2.250 \pm .013$	-
.016	3.37	$2.296 \pm .008$	3.894
.020	4.22	$2.308 \pm .009$	3.908
.024	5.06	$2.317 \pm .009$	3.832
.028	5.90	$2.327 \pm .008$	3.802
.032	6.75	$2.340 \pm .008$	3.840

$$\epsilon'_{sol} (\text{Cholesterol}) = 3.86 \pm .04$$

II. Progesterone in Benzene

Conc. in gm/ml	Volume fraction $\times 10^2$	$\epsilon'_{soln}$	$\epsilon'_{sol.}$
0	0	$2.250 \pm .013$	-
.016	3.09	$2.263 \pm .010$	2.697
.020	3.86	$2.267 \pm .008$	2.718
.024	4.63	$2.271 \pm .009$	2.733
.028	5.40	$2.274 \pm .008$	2.722
.032	6.18	$2.277 \pm .009$	2.714

$$\epsilon'_{sol} (\text{Progesterone}) = 2.72 \pm .01$$

### III. Testosterone in Benzene

Conc. in gm/ml	volume fraction $\times 10^2$	$\epsilon'$ soln	$\epsilon'$ sol.
0	0	2.250 $\pm$ .013	-
.016	2.83	2.274 $\pm$ .008	3.203
.020	3.54	2.279 $\pm$ .009	3.167
.024	4.25	2.285 $\pm$ .007	3.172
.028	4.96	2.291 $\pm$ .008	3.176
.032	5.67	2.296 $\pm$ .009	3.156

$$\epsilon'_{\text{sol.}} (\text{Testosterone}) = 3.18 \pm .02$$

The powder data for the solutes and the corresponding crystal values deduced using eq. (2.41) are given below in Table 4.4.

Table 4.4

Permittivity and Loss factor of the solutes in solid state  
at 9.4 GHz

Solute	$\epsilon'_P$	$\epsilon''_P$	Packing fraction	$\epsilon'_S$	$\epsilon''_S$	$\tan \delta$
Cholesterol	1.828 $\pm$ .009	0.129 $\pm$ .004	.398	3.83	.549	.143
Progesterone	1.589 $\pm$ .008	0.144 $\pm$ .004	.424	2.70	.492	.182
Testosterone	1.709 $\pm$ .011	0.227 $\pm$ .006	.411	3.20	.864	.270



It is found that the permittivity increases with increasing dipole moment (progesterone  $\rightarrow$  testosterone  $\rightarrow$  cholesterol). The small difference in dipole moment of Cholesterol and Progesterone in the two solvents may be attributed to solvent effect. The permittivity of the solute obtained from powder data agrees fairly well with the values deduced from solution data. Hence, we can assume that the contribution of these molecules to permittivity in any medium will be the same as in non-polar media.

The loss factor in the solid phase shows wide divergence from the loss in solution. This is to be expected since the mechanism of absorption is different in the two phases. Dipole relaxation accounts for loss in solution form. Since dilute solutions in non-polar solvents behave like non-interacting systems eq. (2.29) shows that the maximum loss which is observed at the relaxation frequency is determined by the dipole moment of the polar molecules and their concentration. The loss at a particular frequency would depend also on the molecular environment. The dependence on the

molecular environment comes through the relaxation time which is determined by the viscosity of the solvent. In contrast, loss in the solid phase would exhibit very little dispersion at frequencies between a few MHz to a few GHz. Since dipoles are not free to rotate, dipole reorientation cannot contribute to loss in the solid state. Constrained vibrational and rotational states of molecular segments may be altered by absorption of microwave quanta, thereby contributing to the loss.<sup>51</sup> Only if tunneling is important, vibrational motion would contribute in the microwave region. The rotational states are more important in this context since their characteristic time falls in the microwave region. Parts of the molecules from the size of -OH groups to large side chains are often free to rotate, constrained by existing covalent bonds. The relative orientation of these molecular segments to the remainder of the molecule is determined by the weak electrostatic interaction potential between the segment and its environment. The potentials are in general multiwell functions, the relative depths of the minima, the distance between them and heights of the barriers being determined by the

segment and its chemical environment. The potential may be more than one dimensional. The absorption of energy would then change the state from one well to another, either during reemission of a micro-wave photon or cause rotational tunneling.

Though the permittivity of all the steroids that have been investigated is small, they exhibit high loss both in the solid phase and in solution. Loss in Testosterone is distinctly higher than the loss in Cholesterol and Progesterone.

#### B. Concluding Remarks

The interactions of microwaves with a living system may be classified as primary or secondary. The mechanism of absorption of microwave energy in a living system may be considered as the main part of primary interaction. Schwan and Piersol<sup>52</sup> term the overall heating produced in the system due to absorption of energy as primary heating. According to them selective heating of biological media is possible for short periods of time. Thermoregulatory mechanisms do not permit such selective heating at molecular and cellular levels, unless special irradiation techniques are used. Nevertheless,

changes in subcellular structures due to heating, either volume or selective, may have profound consequences on biological functions affecting biochemical reactions.

The primary interaction of the incident radiation with a living system will evoke a response from it, the effect being influenced by a number of physical and physiological parameters. The thermal effect would involve a rise in temperature. This in turn will affect the metabolic rate. Thermal stimulation or the impairment of the function of various organs is to be expected. Local temperature rises in organs exerting controlling functions are expected to affect the metabolism and/or function of the whole organism. A wide range of experimental data on biological effects of microwaves has been reviewed by Baranski and Czerski.<sup>23</sup> A detailed description of cardiovascular effects, effects on central nervous system, endocrine glands, male and female reproduction systems, blood and blood forming systems is presented. According to Michaelson et al.<sup>33</sup>, since the temperature influences the metabolism, microwave heating may lead to displacement of

mineral equilibrium. Many isolated reports on various metabolic effects exist. Several authors have reported changes in blood serum proteins following microwave exposure. Reported variation in the albumin-globulin index in the blood serum following exposure, has been explained as a result of interference with liver or adrenal function. Michaelson et al.<sup>54</sup> have reported changes in endocrine function and hormone levels in animals on exposure. Changes in plasma corticosterone, growth hormone and thyroid hormone levels has been attributed to temperature increase.

Gorden and Schwan<sup>55</sup> have pointed out that an apparent discrepancy exists between the theoretical explanations available, known effects on molecules and isolated components and the effects observed in complex biosystems. To bridge the gap, proper understanding of interaction of microwaves with biological systems at various levels of organization should be acquired through extensive biological, medical and biophysical studies. Apart from the analysis of the cumulative and delayed effects,

intensity effects and estimation of threshold values, spatial distribution of absorbed energy, effects occurring at the molecular level requires attention.

Returning to the present study, the two phases considered exhibit nearly the two extremes of the various types of dielectric response in condensed matter mentioned in section IIA. It is apparent that the behavior of these molecules under physiological conditions would be determined by various factors including the state of the molecule and its immediate environment. The dielectric behavior will be significantly affected by dipolar interactions with the surroundings.

Cholesterol occurs in all animal organs and tissues and, alongwith phospholipids, is concentrated in the membrane fraction of the cell.<sup>56</sup> It is mainly found in the plasma, liver, adrenal gland and some other endocrine organs largely as esters of long chain fatty acids. Several tissues have the capacity to synthesize it. Liver contributes predominantly to the level of serum cholesterol. Bile salts are synthesized from Cholesterol

and during the process some free Cholesterol also gains entrance into the bile. Plasma lipoproteins constitute a heterogeneous group of lipid complex consisting of Cholesterol and its esters along with other constituents. Skin too contains fatty acids esterified with Cholesterol as well as free Cholesterol.

Progesterone, and Testosterone are directly secreted into the blood by the synthesizing tissues.<sup>56</sup> Through circulation the hormones reach their target organs, where the hormone is metabolized or inactivated. The steroids are transported in blood stream in association with proteins. They bind to albumin in blood non-specifically, while there are also specific binding proteins for some steroids. A certain fraction of the molecules is also found in the native state.

The esterified Cholesterol and protein bound steroid molecules would exhibit a different dielectric behavior compared to the native molecules. The steroid protein complex would relax at considerably lower frequencies. The relaxation frequency of the native molecules would not be very much different from the value in non-polar environments, but

the loss would be modified by intermolecular interactions. The binding of steroid to plasma proteins plays an important physiological role, since it is only the unbound fraction which is freely exchangeable with the extravascular and intracellular compartments and has biological activity. Rabinowitz et al.<sup>57</sup> observe that though the macroscopic dielectric properties of biological systems can be understood in terms of the molecular structure of water and the amount of free (and bound) water present in the system, the interaction of the field with numerically minor but functionally significant biomolecules will have negligible input into the dielectric constant but may have important functional implications.

In view of the foregoing comments, the parameters determined in the present study and the observation that the real permittivity is the same in the solid phase and in solution may help in identifying the state of these molecules under physiological conditions and to ascertain the nature of interactions.



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