CHAPTER 4

DIELECTRIC BEHAVIOUR
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4.1. Introduction

The dielectric properties of biological molecules have been the subject of experimental and theoretical studies for a long time. The study of the dielectric properties of these materials give valuable information about the physical and chemical structure of the molecules and various other properties. In particular the dielectric properties can be effectively used to identify the charge storage and transfer mechanism in case of biopolymers.

The earliest measurements of the electrical properties of the biomaterials were made by Oncley (1), Haggis (2), and Buchanan (3). Later Schwan and Pennock (4) and Schwan (5) measured the dielectric constant of hemoglobin solutions and reported three dispersions in high frequency range. They attributed these dispersions to the rotation of the protein molecule as well as its polar side chains and shell of water bound to the protein molecule. Unfortunately they found a great difficulty in working with solutions, because the dielectric constant of the bulk liquid is high, protein solution can not be made very concentrated and the effects of bound water are
not large.

The dielectric properties of water adsorbed on chicken egg white lysozyme have been investigated by Harvey and Hoekstra (6) who assigned the observed two dispersions to two different layers of bound water. The studies of several others (7-11) on biological materials suggest the existence and possible role of bound water layers in their dielectric properties.

4.2. Theoretical considerations

The relationship between dielectric constant and dielectric loss is one of the striking feature of dielectrics. Polarization and displacement vectors vary periodically when a dielectric is subjected to an alternating field, but due to absorption, they lag behind in phase with the applied field resulting in complex form of dielectric constant. This complex dielectric constant $\varepsilon$ is made of real and imaginary parts as

$$\varepsilon = \varepsilon' - i\varepsilon''$$  \hfill (4.1)
where \( \varepsilon' \) is the real dielectric constant which is observed as the change in the value of capacitance and \( \varepsilon'' \) is the dielectric loss related with the real part by the relation

\[
\tan \delta = \frac{\varepsilon'}{\varepsilon''} \tag{4.2}
\]

In an external electric field, a molecule with a permanent dipole moment may undergo orientation. In an alternating field, the orientation depends on frequency. The direction of the polarization produced by the dipole orientation in the field and the direction of the applied field may have a phase shift between them. In such cases the dielectric permittivity will be complex numbers. Debye (12) was the first to establish the relation between the complex permittivity and frequency (for gases or solutions) and this is known as Debye's dispersion equation.

According to classical equations of Debye

\[
\varepsilon = \frac{\varepsilon_0}{\omega} + \frac{(\varepsilon_0 - \varepsilon_\infty)}{1 + \omega^2 \tau^2} \tag{4.3}
\]

\[
\varepsilon'' = \left[ \frac{(\varepsilon_0 - \varepsilon_\infty)}{1 + \omega^2 \tau^2} \right] \omega \tau \tag{4.4}
\]

and
\[
\tan \phi = \varepsilon''/\varepsilon' = (\varepsilon_s - \varepsilon_\infty)\omega \tau / \varepsilon_s + \varepsilon_\infty \omega \tau^2
\]  

(4.5)

The simplest form of dielectric response is given by

\[
\varepsilon^* - \varepsilon_\infty = (\varepsilon_s - \varepsilon_\infty)/(1 + i\omega \tau_0)
\]  

(4.6)

where \(\tau_0\) is relaxation time and \(\varepsilon_s\) and \(\varepsilon_\infty\) are low and high frequency limits of the dielectric constant respectively. Although the relaxation of Debye form is often a good approximation to the behaviour of liquids or solutions containing simple polar molecules and at not too low temperatures, yet the examples for solids are relatively few.

There have been considerable difficulties in fitting an empirical distribution of Debye relaxation to available experimental data. Many empirical relations have been proposed to describe the dielectric and other relaxation processes. Some of those which are related to the polymers and especially, the biopolymers are listed here roughly in order of increasing deviations from Debye's behaviour with rather similar descriptions.
The problem of dielectric relaxation in solid state phase deviating from simple Debye behaviour, has attracted the attention of many and a number of empirical relations have been proposed. Cole(13) and Bottcher et al (14), have given a detailed description of most of them of which worth mentioning are the Cole-Davidson skewed-arc function(15), Cole-Cole circular arc function(16) and the Havriliak-Negami equation(17).

4.2.1 Cole-Davidson skewed-arc function

Davidson and Cole(15) have described the deviations from the Debye behaviour on the high frequency side of the loss region in super cooled glycols. It has since been used more frequently for a variety of liquids and polymer solutions than for solids.

\[ \varepsilon^* - \varepsilon = \frac{(\varepsilon - \varepsilon_s)}{(1 + i\omega\tau_0)^\beta} \quad (0 < \beta < 1) \quad (4.7) \]

The frequency dependence is 'Debye-like' for \( \omega\tau_0 \ll 1 \) and for \( \omega\tau_0 \gg 1 \) a power law \( \varepsilon^* \approx (i\omega)^{-\beta} \) is frequently observed.
4.2.2 Cole-Cole circular arc function

Cole - Cole relation had its origin as a representation of electrical impedance properties of biological membranes and tissues and is widely used. This can be expressed as

\[ \varepsilon^* - \varepsilon = (\varepsilon - \varepsilon_s)/(1+i\omega\tau_o)^{1-\alpha} \quad (0<\alpha<1) \quad (4.8) \]

and the complex plane plot is the familiar circular arc with depressed center rather than the semicircle of Debye behaviour. The \( \varepsilon' \) and \( \varepsilon'' \) curves as a function of frequency are symmetric on a logarithmic scale of frequency, with the loss varying as \( (\omega\tau_o)^{-(1-\alpha)} \) for \( \omega\tau_o \gg 1 \) and as \( (\omega\tau_o)^{+(1+\alpha)} \) for \( \omega\tau_o \ll 1 \). The circular-arc function has been used to describe relaxation of many liquids and solids like crystalline substituted benzene, the hydrogen halides HBr and DBr in their ordered low temperature phases, furan and formic acid.

Though this function has been used to describe relaxation of variety of polymers in solutions and also amorphous solids but it appears that the Havriliak-Negami equation is often better suited.
4.2.3 Havriliak-Negami equation

Havriliak-Negami (17) equations were proposed to fit data on amorphous polymers and polymer solutions. Their relation for the complex permittivity is a combination of Davidson-Cole and Cole-Cole functions,

\[ \varepsilon^* - \varepsilon_\infty = (\varepsilon_s - \varepsilon_\infty) / \left[ 1 + (i\omega\tau_o)^{1-\alpha} \right]^\beta \]  \hspace{1cm} (4.9)

where \( \alpha \) and \( \beta \) ranges from 0 to 1. This results in an asymmetric complex phase locus and logarithmic frequency dependence of \( \varepsilon' \) and \( \varepsilon'' \), with the loss \( \varepsilon'' \) varying as \((\omega\tau_o)^{-(1-\alpha)}\) for \( \omega\tau_o >> 1 \) and as \((\omega\tau_o)^{-(1-\alpha)}\) for \( \omega\tau_o << 1 \).

All the above discussed functions could not fit dielectric data satisfactorily in case of biological materials, specially for the biopolymers. In recent years a considerable number of different interpretations of dielectric relaxation processes appear to show that large deviations, from exponential behaviour at both short and long times, often result from many body effects rather than as sum of physically distinct simpler processes.

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The study of frequency and temperature dependence of dielectric constant and loss factor measurements is of great importance in such cases as it allows one to isolate the contribution of one of the components of a multi-component system.

4.2.4 ac Conduction

The ac conduction $G$ can be calculated from the values of capacitance $C$ and $\tan \delta$ (loss tangent) using the equation

$$G = \omega C \tan \delta$$  \hspace{1cm} (4.10)

where $\omega$ is the frequency

4.3. Factors affecting the dielectric behaviour

(a) Frequency

The time required for ionic or electronic polarization to set in is very small as compared to the time of voltage sign change even for the highest frequencies, which find
practical use in electrical and biological processes. For this reason the polarization of the dielectrics distinguished only by a deformational mechanism of polarization completely settles itself during a very short period of time as compared with voltage half period and, therefore, hardly expect any practically essential dependence of dielectric constant on the frequency range.

But in case of dipole polarization when the frequency of the alternating voltage increases the value of $\varepsilon$ of polar dielectric at first remains constant but beginning with a certain critical frequency $f_c$, when polarization fails to settle itself completely during one half period $\varepsilon$ begins to drop approaching at very high frequencies the values typical of non-polar dielectrics.

(B) Temperature

The temperature does not affect the processes of electronic polarization in nonpolar dielectrics and electronic polarizability of molecules does not depend on temperature. However due to the thermal expansion of the matter, the ratio of the number of molecules to the effective
length of the dielectric diminishes when the temperature increases, for which reason \( \varepsilon \) should also decrease. But when the temperature increases the ionic mechanism of polarization may also increase and in some cases the value of \( \varepsilon \) may diminish, particularly in those substances in which ionic displacement intensifies the internal field and thereby, the electronic polarization.

In case of polar dielectrics the increase in temperature facilitate the orientation of the dipoles and thereby, \( \varepsilon \) increases with increase in temperature. But as the temperature rises further, the chaotic thermal oscillations of molecules are intensified and the degree of orderliness of their orientation is diminished. This causes the curve of dependence \( \varepsilon(T) \) to pass through a maximum.

(c) Humidity

In hygroscopic dielectric with \( \varepsilon \) smaller than that of water, the permittivity is noticeably increased with moistening.
(d) **Pressure**

When the number of molecules per unit volume increases the permittivity of the dielectric increases.

**4.4. Experimental Set-up**

For the present experimental investigation a sample holding assembly designed and fabricated at Magnetism Lab, Inter University Consortium (IUC-DAEF), Indore, is used. A schematic representation of the experimental set up used for dielectric measurements is shown in Fig.(4.1) and a cross-sectional view of sample holding assembly is shown in Fig.(4.2).
FIG. 4.1: EXPERIMENTAL SET-UP:
DIELECTRIC MEASUREMENTS

MULTIMETER

POWER SUPPLY

SENSOR

SAMPLE

HEATER

HP. IMPEDENCE ANALYZER
FIG. 4.2: SAMPLE HOLDING ASSEMBLY:
DIELECTRIC MEASUREMENTS

TO IMPEDENCE ANALYZER

TO MULTIMETER
TO POWER SUPPLY

TEFLON INSULATION

SAMPLE

TEMPERATURE SENSOR
HEATER

TEFLON INSULATION
The sample whose both sides are coated with silver paints could be placed between two copper blocks of diameter 0.9 cm. The upper block is movable and exerts a slight pressure on the pellets. Both the blocks are efficiently insulated with teflon from the body of the cell. A heater connected to a dc power supply is used to increase the temperature of the sample. To measure the temperature, a temperature sensor (PRT) calibrated to a Keithley’s multi meter is placed near the sample as shown in the figure. The whole cell could be placed in a cryostat in which liquid nitrogen is used to reduce the temperature to 80K.

To measure the capacitance and loss tangent in the temperature range 100K to 373K Hewlett-Packard low frequency impedance analyzer (model no HP 4192A) is used. The measured capacitance and loss tangent are converted to dielectric constant and dielectric loss respectively to identify the dielectric behaviour of the samples.
4.5. Results

The results obtained for the present investigations are presented in two parts, part A and part B. In part A the dielectric behaviour and the variation of ac conduction of Dextrin with respect to temperature and frequency is discussed. The dielectric behaviour and ac conduction of Folic acid is discussed in part B.

Part A

The measured capacitance and loss tangent is converted to dimensionally independent values of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$). Both the dielectric constant and loss were found to be independent of temperature and frequency below 273K, therefore, the variation from 275K is reported.

Fig (4.3) and (4.4) represent the temperature dependence of dielectric constant and dielectric loss from 275K to 363K in the frequency range 10 kHz to 1 MHz. The frequency dependence is shown in fig (4.5) and (4.6) respectively. The calculated ac conduction with respect to temperature and
frequency is depicted in Fig (4.7) and (4.8).

A.1 Effect of Temperature on dielectric constant and dielectric loss

Temperature dependence of dielectric constant and loss from 275K to 363K at different frequency ranges is presented in Fig. (4.3) and Fig. (4.4). It has been observed that both dielectric constant and loss increase initially with temperature up to 323K and then decrease at higher temperatures for all the frequency ranges.

A.2 Effect of Frequency on dielectric constant and dielectric loss

The frequency dependence of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) from 10 kHz to 1 MHz at all the different temperatures from 275K to 363K with a gap of 10 K is presented in Fig. (4.5) and Fig. (4.6). For all temperatures both the dielectric constant and loss decrease very rapidly initially with increasing frequency and appear to settle to a more or less constant value at high frequencies.
Figure 4.3
Temp. dependence of dielectric constant
(Dextrin)

Dielectric constant

Low Freq.

High Freq.

Temperature(K)
Figure 4.4
Temp. dependence of Dielectric Loss
(Dextrin)
Figure 4.5
Freq dependence of Dielectric constant
(Dextrin)
Figure 4.6
Freq dependence of Dielectric Loss
(Dextrin)

dielectric loss

\[ \begin{align*}
323K & \quad \bullet \\
313K & \quad \bullet \\
333K & \quad \bullet \\
303K & \quad \bullet \\
343K & \quad \bullet \\
353K & \quad \bullet \\
363K & \quad \bullet \\
275K & \quad \bullet
\end{align*} \]

\[ \begin{align*}
\ln(\text{frequency}) & \quad 1 \quad 3 \quad 5 \quad 7
\end{align*} \]
Figure 4.7
Temp. dependence of ac conductivity (Dextrin)
Figure 4.8
Freq. dependence of ac conductivity (Dextrin)

\[ \text{In(conductivity)} \]

\[ \begin{align*}
\text{Low Temp} \\
\text{High Temp.}
\end{align*} \]

\[ \begin{align*}
\text{In(frequency)} \\
1 & \quad 3 & \quad 5 & \quad 7
\end{align*} \]
A.3 Effect of temperature on ac conduction

The ac conduction is calculated and its dependence with respect to temperature is depicted in fig (4.7) in the form of ln(conductance) versus inverse absolute temperature. The figure clearly indicates that the ac conduction decreases with increase in temperature for all the frequency ranges.

A.4 Effect of frequency on ac conduction

The frequency dependence of ac conduction in the form of ln(conductance) versus ln(frequency) is plotted in fig (4.8). In all the temperature range the conductance is found to be increasing.

A.5 Discussion

The bound water molecules have been found to contribute strongly to the polarization in case of biological molecules and biopolymers. The thermally stimulated pressure and current studies of bound water in lysozyme, have been reported by S. Mascarenhas and S. Celaschi(18). The dielectric
relaxation spectra of water adsorbed on lysozyme has been studied by S.C. Harvey and P. Hoekstra (19). The effect of bound water on DNA and RNA bioelectrets (20) has also been studied by S. Mascarenhas et al (21). The role of bound water for dielectric properties has been studied by Tomaselli and Shamos (22) in case of collagen and by Freeman for bone (23) and in glucose by Pissis (24).

The similar behaviour obtained in case of Dextrin also indicates the importance of bound water molecules for the dielectric behaviour of the system, in the temperature range studied. The temperature dependence of dielectric behaviour may be explained in terms of a diffusion controlled process. As the temperature increases from 275K, \( \varepsilon' \) increases steadily as more water molecules undergo transition from bound to free (mobile) states and contribute to the total polarization. The total number of water molecules in the sample may not have been altered appreciably till the temperature 323K, but for \( T > 323K \) a diffusion process enhanced by the elevated temperature appears to dominate and \( \varepsilon' \) decreases as the number of water dipoles, contributing to polarization, decreases.
The occurrence of maximum at temperature $T = 323K$ represents the superposition of the two processes:

(i) transition of water molecule from bound state to free state
and
(ii) diffusion of water molecules out of the system.

The dielectric loss dependence could also be explained in the same manner as no relaxation phenomena is being observed in the frequency region studied.

The observed behaviour could be directly traceable to the bound water in the system most probably through the Maxwell-Wagner type space charge polarization as also suggested by the observed frequency dependence of dielectric constant and loss. It appears, therefore, that the observed polarization in the temperature range studied, is primarily due to bound water molecules present in the biomolecule, Dextrin.

The observed behaviour of ac conduction is in accordance with the theory of hopping conduction. The electronic hopping mechanism for ac conduction is the
characteristic of the strong frequency dependence tending towards the square law at higher frequencies. This type of behaviour is observed in insulating dielectric materials (25-30).

Part B

The measured capacitance and loss tangent of Folic acid are converted to dimensionally independent values of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$). In low temperature both the dielectric constant and loss were found to be appreciably less and independent on temperature or frequency below 273K. Therefore, the variation from 275K is only reported here.

The temperature dependence of dielectric constant and dielectric loss from 275K to 363K in the frequency range 10 kHz to 1 MHz is represented in fig (4.9) and fig (4.10). The frequency dependence is shown in fig (4.11) and (4.12) respectively. The calculated ac conduction with respect to temperature and frequency is shown in Fig (4.13) and (4.14).
B.1 Effect of temperature on dielectric constant and dielectric loss

Temperature dependence of dielectric constant and loss from 275K to 353K at different frequency ranges is presented in fig. (4.9) and fig (4.10). It has been observed that both dielectric constant and loss increase initially with temperature up to 313K and then decrease at higher temperatures for all the frequency ranges.

B.2 Effect of frequency on dielectric constant and dielectric loss

The frequency dependence of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) from 10 kHz to 1 MHz at all the different temperatures from 275K to 363K with an interval of 10 K is presented in fig (4.11) and fig (4.12). For all temperatures both the dielectric constant and loss decrease very rapidly initially with increasing frequency and appear to settle to a more or less constant value at high frequencies.
Figure 4.9
Temp. dependence of dielectric constant
(Folic acid)

Dielectric constant

10KHz
50K
100K
200K
300K
400K
500K
1MHz

Temperature(K)
Figure 4.10
Temp. dependence of Dielectric Loss
(Folic acid)
Figure 4.11
Freq dependence of Dielectric constant
(Folic acid)

Dielectric constant

\[ \ln(\text{frequency}) \]
Figure 4.12
Freq dependence of Dielectric Loss
(Folic acid)
Figure 4.13
Temp. dependence of ac conductivity
(Folic acid)

\[ \ln(\text{conductivity}) \]

1000/T

High Freq.
Low Freq.
Figure 4.14
Freq. dependence of ac conductivity
(Folic acid)
B.3 Effect of temperature on ac conduction

The ac conduction is calculated and its dependence with respect to temperature is depicted in fig (4.13) in the form of $\ln(\text{conductance})$ versus inverse absolute temperature. The figure clearly indicate that the ac conduction decreases with increase in temperature for all the frequency ranges.

B.4 Effect of frequency on ac conduction

The frequency dependence of ac conduction in the form of $\ln(\text{conductance})$ versus $\ln(\text{frequency})$ is plotted in fig (4.14). In all the temperature range the conductance is found to be increasing.

B.5 Discussion

The dielectric behaviour of Folic acid similar to that of Dextrin and other biomaterials (31-34) also indicate the importance of bound water molecules in the temperature range studied. The temperature dependence of
dielectric behaviour may be explained in terms of a diffusion controlled process. With the rise in temperature from 275K, as more water molecules undergo transition from bound to free (mobile) states contributing to the total polarization and increasing $\varepsilon''$ steadily. The total number of water molecules in the sample may not alter appreciably till the temperature 313K, and for $T > 313K$ a diffusion process enhanced by the elevated temperature may dominate so that the number of water dipoles, contributing to polarization, decreases, and $\varepsilon$ reduces.

The occurrence of maximum at temperature $T = 323K$ represents the superposition of the two processes:

(i) transition of water molecule from bound state to free state and

(ii) diffusion of water molecules out of the system.

As no relaxation phenomena is being observed in the frequency range studied, the dielectric loss dependence could also be explained in the same manner.

The observed behaviour could be directly traceable to the bound water in the system most probably
through the Maxwell-Wagner type space charge polarization as also suggested by the observed frequency dependence of dielectric constant and loss. It appears, therefore, that the observed polarization in the temperature range studied, is primarily due to bound water molecules present in Folic acid.

The ac conduction behaviour observed in case of Folic acid is similar to that obtained for Dextrin and, therefore, could be explained similarly. Such behaviour is also reported by different investigators[35-37]

4.6. Conclusion

The dielectric behaviour and the ac conduction studies of both the materials reveal the role of bound water in them. In both the materials the observed polarization is directly traceable to the bound water in the system, through a Maxwell-Wagner type of polarization. The observed ac conduction behaviour suggest that the conductance is due to electronic hopping(26-28) through the localized levels caused under the influence of water molecules.
4.7. References


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