HIGH DIELECTRIC CONSTANT MATERIALS
CONTAINING LIQUID CRYSTALS

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CHAPTER 1

Motivation and Approach

In recent years there has been increasing interest in new energy storage devices. To put this into perspective it is necessary to define a few terms. Energy storage devices are characterized by both energy density and power density. Energy density is the energy stored per unit mass or volume and power density is the power per unit mass or volume. These parameters can be plotted in what is know as a Ragone chart showing for a particular device, the specific energy parallel to the vertical axis and the specific power parallel to the horizontal axis\(^1\).

![Ragone chart](image)

Figure 1.1: A Ragone chart showing for a particular device, the amount of energy stored (energy density) and the power density. DLC are double layer capacitors. The diagonal lines show how long it would take to discharge the device. It would be desirable to be in the top right corner.
If a conventional battery, a device with a desirable high energy density, were used as a capacitor, that is discharged quickly, it would heat up and be a potential hazard. High voltage capacitors that have an energy density comparable to the best conventional batteries and power densities comparable to high performance electrolytic capacitors have many potential applications, for example in hybrid cars and defibrillators. An ideal capacitor would have the energy density of a battery, could be recharged a very large number of times (orders of magnitude more than the few hundred times that characterize batteries), would hold a charge for long periods of time, and could be discharged in a few microseconds. To enhance the energy density in a linear dielectric, one would either increase the dielectric constant and/or increase the breakdown voltage of the dielectric as shown in:

\[
\text{Energy Density} = \frac{\varepsilon_0 \varepsilon E^2}{2} \quad (1.1)
\]

Commercially available Biaxially-Oriented Poly-Propylene (BOPP) based capacitors\(^3\) with energy densities of about 1.2 Jcm\(^{-3}\) have a low dielectric constant (about 2.2) but rely on large breakdown voltages (650V/micron) to achieve the high energy densities. For reference, 1 Jcm\(^{-3}\) for a material of density near 1 gmcm\(^{-3}\) corresponds to 10\(^3\) Jkg\(^{-1}\).

Ongoing research\(^4\) with high dipole density polymers such as such poly(vinylidene fluoride) (PVDF) and Trifluuroethlene (TrFE) provide for higher energy densities of about 16 Jcm\(^{-3}\). The dielectric constant of these polymers can be enhanced (\(\varepsilon \approx 60\)) by making composites containing high dielectric constant ferroelectric ceramic powders\(^5,6\) such as PbTiO\(_3\), but lead is a potentially harmful metal. Nickel\(^7\) or Polyaniline (PANI)\(^8\)
doped PVDF composites near the percolation threshold, where many conductive particles are isolated by thin dielectrics to form microcapacitors, show an overall high dielectric constant of $\varepsilon \approx 400-1000$. The disadvantage of these systems is the low breakdown voltages near the percolation threshold.

A commercial device that provides a solution closest to the requirements is a carbon aerogel based super capacitors such as those produced by Cooper Industries under the trade name PowerStor®. Their supercapacitors obtain energy densities of about 15 J/cm$^3$ at working voltages of 2.5 V. Ideally energy densities should be as large as 100 J/cm$^3 \sim 0.1k_B T \text{nm}^3$ which is to say roughly a tenth the (room temperature) thermal energy in a cubic nanometer, therefore there is still need for significant improvement in both energy and power density. Simultaneously achieving such high energy and power densities will be a demanding task.

To help address this issue, we developed self-assembled structures that improve both energy and power density. As a benchmark consider carbon aerogel based capacitors. Work by Reynolds et al on carbon aerogels indicates that they have low densities (of order 0.03-0.06 g/cm$^3$), large specific surface areas (400-1000 m$^2$/g) and conductivities of about 10 S/cm. As a rough order of magnitude this corresponds to interconnected cylinders of radius 10 nm spaced on 150 nm centers. This clearly leads to the high area-close conductor geometry required for high capacitance.

This thesis presents studies of new types of composite dielectrics that may ultimately allow us to surpass this benchmark. Our goal is characterize and predicatively understand organic-organic composites and emulsions with very low electrical
conductivities and large specific capacitances. Initial estimates suggest a one to three orders of magnitude or greater maximum energy density than present materials may be possible. By using fluid or gel phases such these dielectrics self-healing.

Maxwell-Wagner theory suggests one may obtain large dielectric coefficients through interfacial polarizations; however, this comes at the cost of low frequency relaxations. This behavior has two requirements: (a) interfaces in the media and (b) that these materials have different conductivities and dielectric coefficients. Using liquid crystals and solvents, it is possible to use this effect to achieve a high dielectric constant low loss (conductivity) dielectric. The dielectric constant of a liquid crystal can be enhanced by the Maxwell-Wagner effect by dispersing in it an organic solvent with a higher conductivity that the liquid crystal. The use of a Fluorinated liquid crystal could further enhance the dielectric properties as the liquid crystal has a lower conductivity.

This dissertation will cover a) a brief introduction on dielectrics and the expected dielectric properties of heterogeneous systems, b) experimental measurement equipment, techniques and data analysis, c) the dielectric properties of single component systems, d) the dielectric properties of binary dispersed systems, and finally e) the dielectric properties of dispersed ternary systems.
1.1 Dielectric Materials in Electric Fields

For a given capacitor geometry and dimension, the important properties that distinguish one capacitor from another are the dielectric properties of the material(s) used to fill the space between the electrodes. These properties characterize the material’s ability to a) prevent electron transport, the higher the better and b) electrical energy storage in the media. A material with less than $10^6$ free electrons per cubic meter has a very high resistivity and is considered to be a good dielectric. However, its utility in devices also depends on its ability to store energy. Ideally one wants high resistivity and large energy storage.

To understand what affects the density of charge that can be separated by a dielectric, a short analysis of what happens to a dielectric in an electric field follows. When a dielectric is placed in an electric field it becomes polarized, that is a separation between the center of gravity of the positive and negative charges occurs. The volume density of this dipole build up is called the polarization with MKS\textsuperscript{1} units of Coulombs/meter\textsuperscript{2}. For an isotropic material, the constant that relates the polarization $\vec{P}$ to the electric field $\vec{E}$ is called the electrical susceptibility $\chi$

$$\vec{P} = \varepsilon_o \chi \vec{E}$$  \hspace{1cm} (1.2)

where $\varepsilon_o = 8.854 \times 10^{-12}$ F/m is the free space permittivity. The electric displacement $\tilde{D}$ is then defined as:

\textsuperscript{1} MKS units will be used throughout this dissertation.
\[ \vec{D} = P + \varepsilon_0 \vec{E} \] (1.3)

Defining,

\[ \varepsilon = 1 + \chi \] (1.4)

as the dielectric constant, we can write equation (1.3) as

\[ \vec{D} = \varepsilon \varepsilon_0 \vec{E} . \] (1.5)

Hence, to increase the charge stored in a capacitor of a given dimension and geometry, we need to increase the polarization and hence the dielectric constant of the material. The dielectric constant (or coefficient) is normally a complex number that accounts for charge loss due to unbound charge migration through the dielectric, i.e. the resistivity of the dielectric.

There are three mechanisms where by a homogeneous dielectric may be polarized, and these are: electronic, molecular, and dipolar. Electronic polarization occurs when electrons in a molecule tend to follow the field; the heavy nucleus stays essentially stationary while the much lighter electrons respond and follow the field. Molecular polarization occurs when the electric field stretches the bonds between atoms, thus forming a temporary dipole. Orientational polarization occurs when induced or temporary dipoles of whole molecules line up with the applied field. At the molecular and atomic levels, the local electric field is related to the dipole moment by a constant called the polarizability, \( \alpha^2 \). The relation of this microscopic property to the macroscopic

\[ \text{In this discussion we are assuming isotropic, homogeneous materials. In more complex cases } \chi \text{ and } \alpha \text{ are second rank tensors.} \]
property, the polarization per unit volume, is obtained as a product of the number of dipoles per unit volume and the induced dipole moment, \( \mu \). The Clausius-Mossotti\textsuperscript{12,13,14} relationship ties the polarizability, the dielectric constant and density together. It uses the Lorentz form of the local field

\[
\mathbf{P} = N \alpha \left( \frac{\varepsilon + 2}{3} \right) \mathbf{E}
\]  

(1.6)

and

\[
\mathbf{P} = \varepsilon_o (\varepsilon - 1) \mathbf{E}
\]

(1.7)

to obtain\textsuperscript{15}

\[
\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{N \alpha}{3 \varepsilon_o}
\]

(1.8)

The dielectric properties of homogenous mixtures were studied by the Debye\textsuperscript{16} and Onsager\textsuperscript{17}. According to Debye’s theory, neglecting intermolecular forces, the dielectric constant of a homogeneous mixture, \( \varepsilon \) is given by

\[
\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \sum N_i \left( \alpha_i + \frac{\mu_i^2}{3k_B T} \right)
\]

(1.9)

Where \( \alpha_i \) is the polarizability, and \( \mu_i \) is the dipole moment of the \( i \)th molecule, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature and \( N \) is the number of molecules per unit volume. If additivity of volumes is taken into account then, for a binary mixture equation (1.9) becomes
\[
\frac{\varepsilon - \varepsilon_a}{\varepsilon_a + 2} \Phi_a + \frac{\varepsilon - \varepsilon_b}{\varepsilon_b + 2} \Phi_b = 0
\]  

(1.10)

Where \( \Phi_a \) and \( \Phi_b \) are the volume fractions of components a and b respectively. The Onsager theory takes into account the field produced by a polar molecule on its neighbors. More advanced theories by Frohlich\textsuperscript{18} and Kirkwood\textsuperscript{19} that take into account interactions between molecules are available but they cannot be used for mixtures unless detailed information of the components are also available.

For an anisotropic liquid such as a liquid crystal, the dielectric constant has at least two components, one parallel to the long axis \( \varepsilon_\parallel \), and the other perpendicular to it \( \varepsilon_\perp \textsuperscript{20,21} \). The difference between the two is called the dielectric anisotropy. It can be calculated from the anisotropy of the polarizability \( \Delta \alpha \), the number of dipoles per unit volume \( N \), the order parameter \( S \), dipole moment \( \mu \), and the angle between the long axis and the molecular dipole moment using\textsuperscript{22}

\[
\Delta \varepsilon = \frac{NhFS}{\varepsilon_o} \left[ \Delta \alpha + \frac{F\mu^2}{2k_BT} (3\cos^2 \beta - 1) \right]
\]  

(1.11)

where \( F \) is the reaction field and \( h \) is the cavity field factor taken from Onsager relationships valid for isotropic materials, and \( k_BT \) is the Boltzmann temperature.

Sometimes there are charge carriers that migrate through the media during application of an electric field that may be stopped by interfaces; this is another source of polarization called interfacial polarization\textsuperscript{23,24,25}. This last case can lead to large scale local field disruptions that are the result of the piling up of charge at the interfaces of
dielectrics. The goal of this work is to exploit this phenomenon to make high dielectric constant, low loss dielectrics for capacitors.

1.2 Dielectric Properties of Heterogeneous Systems

When two or more components are mixed they can give rise to a heterogeneous mixture if the components fail to mix at the molecular level. Materials coarsely dispersed in another media, such as emulsions, suspensions, foams, aerosols and suspensions are heterogeneous systems. Heterogeneous systems containing liquid crystals will be used to exploit the phenomena of interfacial polarization to enhance their dielectric properties over those obtainable with homogeneous systems. Much work has been done in trying to understand the dielectric properties of these types of systems. These studies range from the very simple functional forms that try to explain the measured response in terms of a certain function, to very complex mathematical forms derived from the knowledge of the type of components and how they interact when they are mixed.

A simple functional form that can take any of the forms is:

\[
f(\varepsilon) = (1 - \phi)f(\varepsilon_a) + \phi f(\varepsilon_b)
\]

(1.12)

Where \( \phi \) is the volume fraction of component \( b \), \( f(\varepsilon_a) \) and \( f(\varepsilon_b) \) are the dielectric constants of component \( a \) and \( b \) respectively, and various forms of \( f(\varepsilon) \) were proposed by Weiner (1.13), Beer (1.14), Lorentz-Lorenz (1.15), Leichtenecker (1.16)\textsuperscript{26,27,28}. 
where in (1.13) \( u \) is the function that takes into account the particles shape and structure of the disperse system. These forms do not always adequately represent real data. It was Rayleigh\textsuperscript{29}, Weiner\textsuperscript{26}, Bruggeman\textsuperscript{30}, Wagner\textsuperscript{31} and Maxwell\textsuperscript{32} who started the earliest known attempts at calculating the dielectric constant of heterogeneous systems from mathematical analysis of electric fields.

It is Maxwell’s simple explanation of dielectric dispersion of a heterogeneous system using a simple model of an infinite parallel plate capacitor filled with two parallel dielectric sheets of different dielectric permittivity and conductivity that will be described here. Here the interface is the boundary between the two dielectrics. The situation is described in Figure 1.2.

From the point of view of a boundary value problem it is clear from symmetry that the electric field is perpendicular to the electrodes. The boundary conditions are the same as those commonly encountered in textbook problems except one must include the existence of charges at the boundary between medium 1 and medium 2. This leads to a
modification of the continuity equation. The boundary conditions on $E$ and $D$ at the boundary between the dielectrics are:

$$\mathbf{n} \times (E_2 - E_1) = 0$$  \hspace{1cm} (1.17)$$

$$\mathbf{n} \cdot (D_2 - D_1) = \delta$$  \hspace{1cm} (1.18)$$

Where $\mathbf{n}$ is a unit vector perpendicular to the surface, $E$ is the electric field, $D$ the electric displacement, and $\delta$ the surface charge density. Assuming that each dielectric is homogeneous and isotropic the constitutive relationships are $D = \varepsilon E$, and $J = \sigma E$, where $\varepsilon$ is the dielectric permittivity of the media and $\sigma$ is the conductivity of the media.

![Figure 1.2: The two-layer lossy capacitor. The heavy dark lines are the plates of the capacitor. The lower section is dielectric 2 with the dielectric constant $\varepsilon_2$ and conductivity $\sigma_2$ and the upper section dielectric 1 with dielectric constant $\varepsilon_1$ and conductivity $\sigma_1$. They are of thickness $d_2$ and $d_1$ respectively, with a total thickness $d$.](image)

The equation of charge continuity is generally written as,

$$\nabla \cdot J + \frac{\partial \rho_{\text{free}}}{\partial t} = 0$$  \hspace{1cm} (1.19)$$

where $\rho_{\text{free}}$ is the free charge that contributes to conduction current. Assuming a time harmonic dependence to all quantities except $\varepsilon$ and $\sigma$ (these are assumed to be real and
non-zero at this stage) and that the time dependence is given by \(\exp(j\omega t)\), where \(j = \sqrt{-1}\), and \(\omega\) is the angular frequency. The equation of continuity for the dielectrics is written as:

\[
\nabla \cdot \sigma \mathbf{E} + j\omega \rho_{\text{free}} = 0
\]

However, the continuity of surface charge \(\delta\) must also be included. This is discussed by King\(^{33}\), and can be written as:

\[
\sigma_1 \mathbf{n} \cdot \mathbf{E}_1 - \sigma_2 \mathbf{n} \cdot \mathbf{E}_2 = j\omega \delta
\]

Equation (1.21) above is the boundary condition for continuity of charge at the dielectric boundary.

Assuming that each dielectric is homogeneous and isotropic the constitutive relationships \(\mathbf{D} = \varepsilon \mathbf{E}\) and \(\mathbf{J} = \sigma \mathbf{E}\), can be used to simplify the boundary conditions equations (1.17) and (1.18). Finally, the Maxwell equation for the electric field written in the form:

\[
\nabla \cdot \mathbf{D} = \nabla \cdot \varepsilon \mathbf{E} = \rho_{\text{free}}
\]

is required. Substituting this equation (1.22) into equation (1.20) requires that:

\[
\nabla \cdot (\sigma + j\omega \varepsilon) \mathbf{E} = 0
\]

in both dielectrics. Since \((\sigma + j\omega \varepsilon)\) is not zero this means that
\[ \nabla \cdot \mathbf{E} = 0 \quad (1.24) \]

This means that \( \mathbf{E} \) is position independent in each region. A similar substitution of the boundary equation (1.18) into (1.21) yields

\[
(\sigma_2 + j \omega \varepsilon_2) E_{2n} - (\sigma_1 + j \omega \varepsilon_1) E_{1n} = 0 \quad (1.25)
\]

Where \( E_{1n} \) is the electric field perpendicular to the conductor in dielectric material 1, \( E_{2n} \) is the same for material 2, while \( \varepsilon_1 \) and \( \varepsilon_2 \) are the dielectric constants of materials 1 and 2 respectively. The time dependence of equation (1.25) can be reduced to the DC form by at long times when \( \omega = 0 \) to give:

\[
\sigma_1 E_{1n} = \sigma_2 E_{2n} \quad (1.26)
\]

while at short times, \( \omega \to \infty \),

\[
\varepsilon_2 E_{2n} - \varepsilon_1 E_{1n} = 0 \quad (1.27)
\]

The potential difference between the plates can be written as:

\[
V = E_{1n} d_1 + E_{2n} d_2 = V_1 + V_2 \quad (1.28)
\]

Where \( V_1 \) is the potential difference on dielectric material #1, \( V_2 \) is the potential difference on dielectric material #2. Simultaneous solving equations (1.25) and (1.28) yields the solutions for \( E_{1n} \) and \( E_{2n} \) as:
\[ E_{1n} = \frac{(\sigma_2 + j \omega \varepsilon_2)V}{(\sigma_2 + j \omega \varepsilon_2)d_1 + (\sigma_1 + j \omega \varepsilon_1)d_2} \]  
\[ (1.29) \]

\[ E_{2n} = \frac{(\sigma_1 + j \omega \varepsilon_1)V}{(\sigma_2 + j \omega \varepsilon_2)d_1 + (\sigma_1 + j \omega \varepsilon_1)d_2} \]  
\[ (1.30) \]

Note that while the electric field in both regions is independent of position it is not the same.

The two dielectric slabs can easily be modeled as capacitors. Recalling that the charge is the area times the displacement and the potential difference between the ends of the region is the electric field times the distance, one obtains for capacitance:

\[ C_1 = \frac{A D_1}{V_1} = \frac{A(\varepsilon_1 + \sigma_1/j \omega)}{E_{1n} d_1} = \frac{A(\varepsilon_1 + \sigma_1/j \omega)}{d_1} \]  
\[ (1.31) \]

Similarly

\[ C_2 = \frac{A D_2}{V_2} = \frac{A(\varepsilon_2 + \sigma_2/j \omega)}{E_{2n} d_2} = \frac{A(\varepsilon_2 + \sigma_2/j \omega)}{d_2} \]  
\[ (1.32) \]

In these expressions we include the conductivity of the media to give is the effective dielectric permittivity, because the media are not conductance free dielectrics. The capacitors can then be modeled as \( C_1 \) in series with \( C_2 \). Thus, the effective capacitance, \( C \), of the capacitor shown Figure 1.2 is given by:

\[ C = \frac{C_1 C_2}{C_1 + C_2} = \frac{1}{j \omega} \left( \frac{1 + j \omega \tau_1}{1 + j \omega \tau_2} \right) \]  
\[ (1.33) \]

where,
\[
\tau_1 = \frac{\varepsilon_1}{\sigma_1} \quad (1.34)
\]
\[
\tau_2 = \frac{\varepsilon_2}{\sigma_2} \quad (1.35)
\]
\[
\tau = \frac{\varepsilon_1 d_1 + \varepsilon_2 d_2}{\sigma_1 d_1 + \sigma_2 d_2} \quad (1.36)
\]
\[
R_j = \frac{d_j}{A \sigma_i} \quad (1.37)
\]

The surface charge density can be calculated from the electric fields in both the dielectric (equations (1.29) and (1.30)) and the following boundary condition:

\[
\varepsilon_2 E_{2n} - \varepsilon_1 E_{1n} = \delta \quad (1.38)
\]
to obtain:

\[
\delta = \frac{(\varepsilon_2 \sigma_1 - \varepsilon_1 \sigma_2)V}{(\sigma_2 + j \omega \varepsilon_2) d_1 + (\sigma_1 + j \omega \varepsilon_1) d_2} \quad (1.39)
\]

This indicates that if \(\tau_1 = \tau_2\) there is no excess charge at the boundary. It also points out that regardless of the magnitude of \(\tau_1 - \tau_2\), that \(\delta \rightarrow 0\) as \(\omega \rightarrow \infty\). The importance of this fact will be explained in the next paragraph.

The essential results of this analysis are equations (1.33) and (1.39). The limits of equation (1.33) in the limits as \(\omega - 0\) and \(\omega - \infty\) are now discussed. For this step it is convenient to define the frequency dependent dielectric coefficient \(\varepsilon_{eff}\) by letting
\[ C = \varepsilon_{\text{eff}} C_0 \]  

(1.40)

where \( C_0 = \frac{A}{d} \varepsilon_0 \), thus equation (1.33) can be rewritten as:

\[ \varepsilon_{\text{eff}} = \frac{1}{C_0} \frac{1}{j\omega} \frac{1}{(R_1 + R_2)\left(1 + j\omega\tau\right)} \left(1 + j\omega\tau_1\right) \left(1 + j\omega\tau_2\right) \]  

(1.41)

and upon separating the real and imaginary parts of the effective dielectric constant, one finds:

\[ \varepsilon_{\text{eff real}} = \frac{\tau_1 + \tau_2 + \omega^2 \tau_1 \tau_2 \tau - \tau}{C_0 \left(1 + \omega^2 \tau^2\right)} \]  

(1.42)

\[ \varepsilon_{\text{eff imaginary}} = \frac{\frac{1}{\omega} + \frac{\omega \tau}{\tau_1 + \tau_2} - \frac{\omega \tau_1 \tau_2}{C_0 \left(1 + \omega^2 \tau^2\right)}}{C_0 \left(1 + \omega^2 \tau^2\right)} \]  

(1.43)

The limits of \( \varepsilon_{\text{eff real}} \) at low frequencies (\( \varepsilon_s \)) and optical frequencies (\( \varepsilon_\infty \)) are:

\[ \varepsilon_s = \varepsilon_{\text{eff real}} \bigg|_{\omega \to 0} \rightarrow \frac{\tau_1 + \tau_2 - \tau}{C_0 \left(1 + \omega^2 \tau^2\right)} \]  

(1.44)

\[ \varepsilon_\infty = \varepsilon_{\text{eff real}} \bigg|_{\omega \to \infty} \rightarrow \frac{\tau_1 \tau_2}{C_0 \left(1 + \omega^2 \tau^2\right)} = \frac{\frac{1}{C_1} + \frac{1}{C_2}}{C_0} \]  

(1.45)

Thus at higher frequencies the real part of the effective dielectric response approaches that expected for two capacitors in series. This is expected because according to (1.39) the surface charge density approaches 0 as \( \omega^{-\infty} \). It is convenient to rewrite equation (1.42) as:
This indicates a smooth transition from a low frequency dielectric constant to a high frequency dielectric constant. Note that the dielectric response is higher before the transition. A similar set of operations for the imaginary part yields:

$$
\epsilon_{\text{eff, imaginary}} = \left[ \frac{\tau}{\tau_1 \tau_2 \omega} + \frac{\epsilon_s - \epsilon_\infty}{\epsilon_\infty} - \frac{\omega \tau}{1 + \omega^2 \tau^2} \right]
$$

(1.47)

Recalling that for complex dielectric permittivity we can write \( \epsilon^* = \epsilon_{\text{real}} - j \epsilon_{\text{imaginary}} \), the last two equations can simply be written as:

$$
\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + j \omega \tau} - j \epsilon_\infty \frac{\tau}{\tau_1 \tau_2 \omega}
$$

(1.48)

The last term in this equation contains the Ohmic conductivity term \( \sigma \) of the capacitor.

This can be seen by substituting equation (1.45) \( \epsilon_\infty = \epsilon_{\text{eff, real}} \bigg|_{\omega \to \infty} \rightarrow \frac{\tau_1 \tau_2}{C_0 (R_1 + R_2) \tau} \) into the term. This gives a final result for the effective dielectric response of two different dielectrics in series:
\[ \varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau} - j\frac{\sigma}{\omega} \] 

(1.49)

Again, it is important to note that the dielectric response at lower frequencies is much larger than the optical frequencies because of the contribution at lower frequencies from interfacial polarization. This contribution decreases after the relaxation frequency; which occurs when \( \omega\tau = 1 \), with a simple generalization for different values of \( \tau \) shows it is possible to have multiple “relaxations”.

There are of course modifications to Maxwell’s derivation. For example, Wagner derived expressions for dilute dispersed systems, where he obtained\(^\text{31}\),

\[ \varepsilon^* = \varepsilon^*_m + \frac{2(1-\phi)e^*_m + (1+2\phi)e^*_p}{(2-\phi)e^*_m + (1-\phi)e^*_p} \] 

(1.50)

Where \( \varepsilon^*, \varepsilon^*_m, \varepsilon^*_p \) are the complex dielectric constants of the mixture, medium, and particle respectively, and \( \phi \) is the volume fraction of the particles. Rewriting equation (1.50) in the form of equation (1.49) the following are obtained for the relaxation time (\( \tau \)) and the dielectric strength (\( \varepsilon_s - \varepsilon_\infty \)):

\[ \varepsilon_s - \varepsilon_\infty = \frac{9(\varepsilon_m\sigma_p - \varepsilon_p\sigma_m)^2\phi(1-\phi)}{[2\varepsilon_m + \varepsilon_p + \phi(\varepsilon_m - \varepsilon_p)][2\sigma_m + \sigma_p + \phi(\sigma_m - \sigma_p)]^2} \] 

(1.51)

\[ \tau = \frac{2\varepsilon_m + \varepsilon_p + \phi(\varepsilon_m - \varepsilon_p)}{2\sigma_m + \sigma_p + \phi(\sigma_m - \sigma_p)} \varepsilon_p \] 

(1.52)

Where \( \sigma_m \) and \( \sigma_p \) are the conductivities of the medium and particle respectively, and
\[ \varepsilon' = \varepsilon_m \frac{2\varepsilon_m + \varepsilon_p - 2\phi(\varepsilon_m - \varepsilon_p)}{2\varepsilon_m + \varepsilon_p + \phi(\varepsilon_m - \varepsilon_p)} \]  
\[ (1.53) \]

\[ \varepsilon_s = \varepsilon_m \frac{\sigma_s}{\sigma_m} + \frac{9(\varepsilon_p \sigma_m - \varepsilon_m \sigma_p) \sigma_m \phi}{[2\sigma_m + \sigma_p + \phi(\sigma_m - \sigma_p)]^2} \]  
\[ (1.54) \]

Note that the particle size does not enter into these calculations and that if the conductivity of the dispersing media is larger than the dispersed particles (\( \sigma_m >> \sigma_p \)), one obtains what is called oil in water system (O/W). If the conductivity of the dispersed particles is much larger than the dispersing media (\( \sigma_p >> \sigma_m \)), a water in oil (W/O) system results. This is because oils typically have a very low conductivity and water especially with impurities has a relatively high conductivity. Becher found a way of determining the type of disperse system formed by a simple d.c. resistance measurement of the sample, using the fact that the electrical conductivity of the emulsions were of the same order of magnitude as the dispersing media\textsuperscript{34}. Therefore, water in oil emulsions (\( \sigma_p >> \sigma_m \)) would be less conductive than oil in water emulsions (\( \sigma_m >> \sigma_p \)).

Becher’s finding is important when trying to determine whether a system could have contributions from an effect called electrode polarization. When a dielectric has unbound charges, they can accumulate at electrodes and obscure the dielectric response at low frequencies. If electrode polarization is suspected, when both the real and imaginary response increase rapidly at low frequencies\textsuperscript{35} then it is acceptable to eliminate this by fitting and removing from the response\textsuperscript{36, 37}. 
\[ \varepsilon_{EP} = Af^{-b} \]  

(1.55)

Where \( A \) and \( b \) are fitting parameters and \( f \) is frequency. In the field of liquid crystals, Sinha and Aleiv\(^{38,39,40} \) subtract from the dielectric response a contribution from d.c. conductivity and electrode polarization:

\[ \varepsilon_{EP,\sigma} = -j \frac{\sigma}{\varepsilon_0 \omega^n} \]  

(1.56)

Where \( \sigma \) is the DC conductivity, and \( n \) is a fitting parameter. When \( n = 1 \) the response is just from DC conductivity, but when \( n < 1 \) there is electrode polarization in addition to conductivity contributes to the dielectric response at low frequencies.

Following these findings, many began to study the effect of interfacial polarization on heterogeneous systems. Most studies were focused on water in oil systems since these would show the biggest effect from interfacial polarization. This is because equation (1.53) and equation (1.54) become almost equal in the opposite O/W system\(^41 \), unless the dielectric constant of the oil phase is much higher than the water phase. For example, Sillars measured the capacitance of a suspension of water droplets in wax, here \( \sigma_{\text{water}} >> \sigma_{\text{wax}} \), where the particle is water and the media is wax\(^42 \). Hanai prepared an emulsion of water in nujol-carbon tetrachloride, which gave a dramatic dispersion due to interfacial polarization\(^43 \). The real part of his mixtures was about 700.

O’Konski\(^44 \) and Pauly and Schwan\(^45 \) added to the theory by adding a shell to the disperse phase. They found that at higher frequencies the system behaved like a system of dispersed particles without a shell. They also found that at lower frequencies, the
dielectric constant is completely independent of the dielectric constant of the constituent phases.

He and Zhao\textsuperscript{46} working with nanoscale silica in an aqueous solution found that the relaxation time for solutions with smaller silica particles was shorter than for larger particles, while the real part of the dielectric response was larger for larger particles. They explained this in terms of counterion polarization, since the ions need a shorter time to travel the perimeter of the smaller particle to establish a dipole, a shorter relaxation time is realized. The dielectric response on the other hand arises from artificial dipoles formed when the counterions on the particles separate giving a response out of phase with the applied field. A larger particle size would give rise to a larger dipole and hence larger dielectric response.

In the field of liquid crystals, S. Kobayashi and N. Toshima\textsuperscript{47,48} working with ligand (eg 5CB) coated metal nanoparticles dispersed in liquid crystals observed Maxwell-Wagner effects in these systems due to differences in the relaxation time of the electrons in the nanoparticle and liquid crystal host. The dielectric strength $(\varepsilon(0) - \varepsilon(\infty))$ of this effect was about 100. The relaxation frequencies of these systems varied from a few to several thousands Hertz. With increasing concentration of the nanoparticles, the relaxation frequency increased. They had to add a term to the calculation of the relaxation time called the “volume occupation factor”
that accounts for the concentration of the metal nanoparticles, where $a^3$ is the volume occupied by the particle in a lattice with volume $l^3$ to give

$$\phi_2 = a^3 / l^3$$

(1.57)

Where, $\varepsilon_m$ and $\sigma_m$ are the dielectric constant and conductivity of the liquid crystal host and $\varepsilon_p$ and $\sigma_p$ are the effective dielectric constant and effective conductivity of the nanoparticle. Note that these are effective values and not bulk values. The values measured by the group are lower than the bulk values. Nevertheless, higher bulk values of $\sigma_p / \sigma_m$, the ratio of bulk values of the conductivity of the nanoparticle to the liquid crystal, give higher relaxation frequencies. This same group did not observe Maxwell-Wagner polarization in liquid crystals doped with Magnesium Oxide and observed very weak effects in semiconductor doped liquid crystal.

With all these rather complex theoretical explanations for the interfacial polarization, we will summarize contribution of interfacial polarization to the dielectric response using Hania’s simple yet effective illustration. On application of an electric field, charges are electrostatically induced in the heterogeneous system. These charges move to boundaries and remain there. If the field is held constant, conductive charges appear, these are separated according to their ability or inability to be transferred across boundaries. The amount, type and proximity of these charges to the electrodes is what separates a water in oil (W/O) from a oil on water system (O/W). In a W/O system the
conductive charges are trapped in the water phase and cannot be transferred across the boundary, what few conductive charges are there in the continuous oil phase are discharged at the electrodes. While in an O/W system, the conductive charges are in the continuous phase and the charges in the oil phase pass through the boundary, so the conductivity of this system is higher than the W/O system. The difference in the amount of charge at the interfaces immediately after applying a field (higher frequencies) and those formed after a while (lower frequencies) is what gives rise to the frequency dependent phenomena, interfacial polarization. Note that in a W/O system there will be a bigger difference and hence interfacial polarization because in an O/W system most charges are discharged.

An instrument that measures the dielectric response, like the one described in the next section, cannot distinguish between the induced and conductive trapped charges. Therefore, the instrument will measure these charges as a sum of the two, while the conductive or free charges will be measured as conductivity. The conductivity disappears at higher frequencies.

In this dissertation, results of attempts to control the magnitude of the dielectric response, the conductivity, and the relaxation frequency of heterogeneous systems containing liquid crystals will be presented.
1.3 Measurement Equipment

1.3.1 Schlumberger 1260 Gain-Phase Analyzer

The dielectric properties of the materials were determined from measurements of the impedance of samples contained in parallel plate geometries. The impedance was measured using a Schlumberger® (Solarton) SI 1260 impedance/gain-phase analyzer. The SI 1260 is capable of producing a single sine wave to a device under test over a frequency range of 10µHz to 32MHz. It is also capable of sweeping frequency, amplitude or bias. The applied wave produces a current through the device under test that is of the same frequency but generally of different phase and amplitude than the applied voltage (Figure 1.3). However, there will be no phase shift for pure resistances.

![Figure 1.3: The current produced through the device under test (dashed) in response to the applied voltage (solid line).](image)

The complex impedance ($Z^*$) is then obtained from measuring the ratio of the applied voltage to the resultant current.
\[ Z^* = \frac{V \sin(\omega t)}{I \sin(\omega t + \theta)} \]  

(1.59)

Where \( V \) is the applied voltage, \( I \) is the resultant current, \( \omega \) is the applied frequency in radians/sec (\( \omega = 2\pi f \)), and \( \theta \) is the phase shift. The complex impedance can be separated to give us the real and imaginary parts if the impedance from which the conductance (\( G \)) and the capacitance (\( C \)) can be calculated.

\[ Z^* = Z' + Z'' = R + jX = a \cos(\theta) + ja \sin(\theta) \]

(1.60)

\[ = \frac{1}{G} + \frac{1}{j\omega C} \]

here \( R \), is the resistance, \( X \), the reactance, \( a \), the magnitude of the impedance and \( \theta \) the phase shift.

Figure 1.4: The relationship between the resistance (\( R \)) and the reactance (\( X \)) to the magnitude (\( a \)) and phase \( \theta \) of the complex impedance \( Z^* \)

In practice the resulting waveform does not look like Figure 1.3, because in real devices there is generally a non-linear relationship between current and voltage. This means when the current can be expanded in a Taylor series about \( V=0 \) and there will be
terms beyond first order in the voltage; viz. \( I = a + bV + cV^2 + \ldots \). For sufficiently small voltage the current will be linearly dependent on the voltage; of course how small is small enough is not known a priori, and often the signal to noise ratio decreases as the input voltage is decreased because of thermal noise, etc that do not depend on current. Thus it is common experimental practice always to use the minimum voltage consistent with good signal to noise ratio.

If this fails, the SI1260 uses a method called sine correlation to obtain the response waveform\(^{50}\). If the response of the test item is \( y(t) \) to an input \( v(t) \), then the real \( R(t) \) and imaginary \( I(t) \) components of the response can be obtained by multiplication of \( y(t) \) by \( \sin(\omega t) \) and \( \cos(\omega t) \) respectively (Figure 1.5). The results are then fed into two identical integrators, where they are averaged over time. As the averaging time \( T \) increases, the contributions of all the other unwanted harmonics go to zero and we obtain \( R(T) \) and \( I(T) \), the real and imaginary responses with the same frequency as \( v(t) \). It is desirable for the integration time \( (T) \) to be an integer multiple of the test frequency so as to reduce non-linear harmonic distortions. In practice, averaging is better over integer multiples of complete cycles so as to avoid certain measurement errors from offsets of the system output\(^{51}\). This system can be thought of as a system whose input \( v(t) \) is fed into a transfer function \( G(j\omega) \) with an output \( y(t) \). This transfer function acts as a band pass filter with the center frequency set at \( \omega_1 \), whose bandwidth becomes narrower as the average time \( T \) increases (Equation (1.61))\(^{51}\).
Figure 1.5: Schematic of the SI1260’s method of obtaining the response with the same frequency as the generators’ from the response $y(t)$. Note that this method not only rejects other harmonics, it also rejects noise.

In order to choose the correct wave form to measure the impedance, the limits of the SI 1260 have to be taken into account. The voltage output range for this device is between 0 to 3V. The current measurement limits are 6µA to 6mA. For example, using a 1V drive to measure the impedance of a 15 Ohm component will produce a current drain on the generator of over 66mA, which is well beyond the capability of the instrument which are impedance ranges for capacitance are from 1pf to 10mF with 5 digit resolution and resistance from 10mΩ to 100MΩ.

In order to ease and automate the collection of impedance data over a range of frequencies and amplitudes, the SI1260 was connected via a National Instruments GPIB USB interface to a PC. The instrument was controlled using Solarton’s SMaRT®
software. The procedure and setting for all measurements are the same and are discussed in the appendix. Initially the two leads to the device under test were connected to the SI1260 using a Schlumberger 12603 in-circuit test module. This module and the device are connected to the front BNC terminals as shown schematically below.

![Schematic showing connections of the Schlumberger 12603 in circuit test module to the SI 1260’s front BNC terminals and the device under test. The generator produces a sine wave that drives a current into I, the voltage developed is measured by V1.](image)

**Figure 1.6**

1.3.2 **Solartron® 1296 Dielectric Interface**

When studying dielectrics using an impedance analyzer like the SI 1260, one soon approaches its limits of current measurement, especially at lower frequencies where impedances can get very high. The Solartron® Dielectric interface is an attachment to the SI1296 that extends the impedance analyzer’s current measurement capability downwards from 6mA to 100fA (Figure 1.7). Another added bonus is the built in power supply that increases the SI1260’s voltage range from 3V to 7V.
The interface also can be used to get very accurate measurements of capacitances when measurements by referencing either a built in or external calibrated standard capacitor. Any “noise” from the reference capacitor measurements are used to “cleanup” the sample measurements. This method was only used on a second run after analyzing and finding reasonable samples, because it doubled the measurement time and also required matching the reference capacitors with the sample.

An air capacitor with an area of $1\text{cm}^2$, and thickness of 10 microns was used to compare the impedance measurements using the 12603 in circuit test models and the 1260 dielectric interface (Figure 1.7)

![Figure 1.7: Schematic of the connections to the Solartron® 1296 Dielectric Interface to the Schlumberger SI 1260 Gain/ Phase analyzer.](image)
Figure 1.8: Comparing the measurements taken by using either the 12603 in circuit test module or the 1296 dielectric interface for impedance measurements. The plots shown are frequency responses of the Impedance magnitude and phase, shown on the left and right graphs respectively. The measurements are taken without the use of a reference capacitor.
1.4 Dielectric Measurement Analysis

The use of dielectric measurements to characterize materials is not new, and two recent books that discuss this area in great detail are readily available\textsuperscript{52,53}. The fundamental goal of such measurements is to characterize the dielectric material and its interfaces. A flow diagram describing the measurement and characterization of a material using dielectric spectroscopy is shown in Figure 1.9 (adapted with changes from reference 52).

![Flow diagram for dielectric property measurement and characterization.](image)

Previous sections have discussed the dielectric system and the measurement system. This section will discuss the four blocks in this flow chart that are centered on theory: models, equivalent circuits, theory and curve fitting. Two caveats are in order at this point. First, the equivalent circuit that yields a given impedance response is not
unique. Thus a natural question is which equivalent circuit does one pick? This requires varying external parameters and physical insight. Similarly models may fit the data extremely well, but often appear to be more of a numerical, best fit game than based on physical models. The second caveat this chapter will deal with macroscopic models; the detailed microscopic models still need to await further research and discovery.

The basic idea of the equivalent circuit approach is to model the response as a combination of *ideal* circuit elements. This means the model capacitor is a point capacitor and has no resistance or inductance, similarly a resistance (or conductance) is a point conductor lacking capacitance and inductance. An infinite number of series, parallel, series-parallel, and other combinations can be constructed to fit the data. Here physical insight is an essential guide. We expect our dielectric system to consist of electrodes and the bulk dielectric. Thus two capacitors will probably be needed to fit the data. Similarly we know the dielectric is not lossless so a conductance in parallel with the capacitor representing the bulk dielectric will be required. A difficulty arises very quickly in such an approach. The point-ideal device model ignores distributed elements that are part of every real device. This is generally taken care of by adding distributed impedance devices such as the constant phase element that we will discuss later, and terms to account for diffusion and other non-idealities.

In the present context, by models it is meant functional forms, generally with some physical basis, that represent the dielectric response of the material over a range of frequencies and generally through temperature dependent parameters the temperature dependence of the system as well. This would seem to be a fairly simple matter:
establish which of the models fits best and the values and uncertainty of the best-fit parameters. However, this is not the case. Havariliak and Havriliak\textsuperscript{54} point out that there appears to be a theoretical preference amongst some scientists and there is some ambiguity in the discussion of dielectric relaxation.

This section will first discuss equivalent circuit models. This section will also introduce two common elements that are used to model distributed model elements. The next section will discuss various models that are used to parameterize the response of materials to varying frequency electric fields. The final section will very briefly discuss the fitting programs that were used.

1.4.1 Equivalent Circuit Models

As discussed earlier there are an infinite number of possible equivalent circuit models that can represent the dielectric frequency response. Typically Occam’s principle is invoked to remove all unnecessary elements from the model. Thus we will discuss in this section two simple models: the Debye model and the Cole-Cole model. The Cole-Cole model will introduce the constant phase element that will be discussed in some detail at that stage. The Warburg elements, another group of distributed elements will then be discussed.
1.4.2 The Debye Equivalent Circuit

This simple model was proposed by Debye in 1929\textsuperscript{16}, and has been a staple of dielectric relaxation analysis since that time. It assumes that the polarization relaxes from its short time to long time value after application of a unit step voltage following first order kinetics. This behavior can be modeled using the circuit below.

![Figure 1.10: The Debye equivalent circuit.](image)

Through the use of standard expressions from AC circuit theory this circuit can be shown to have the following equivalent complex capacitance, $C^*(\omega)$

$$C^*(\omega) = C_1 + \frac{C_2}{1 + \omega^2 \tau^2} - \frac{j \omega \tau C_2}{1 + \omega^2 \tau^2}$$

(1.62)

where $\tau = RC_2$, and the * on $C$ indicates that it is a complex quantity. The limiting values of this equivalent capacitance are shown below:

Table 1: The limiting values and definitions of the Debye equivalent circuit

<table>
<thead>
<tr>
<th>Frequency Limit</th>
<th>Value of C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega \rightarrow 0$</td>
<td>$C \rightarrow C_1 + C_2 = C_0$</td>
</tr>
<tr>
<td>$\omega \rightarrow \infty$</td>
<td>$C \rightarrow C_1 = C_\infty$</td>
</tr>
</tbody>
</table>
Since the capacitance is proportional to the dielectric constant equation (1.62) is equivalent to:

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

(1.63)

where the subscripts zero and infinity refer to the frequency limits discussed above. Although this form looks like that derived by Maxwell for interfacial polarization, the polarization of polar molecules in electric fields was the mechanism Debye used to derive this expression. Graphs of the real and imaginary response as a function of \( \omega \tau \) are shown below.

![figure](image)

**Figure 1.11:** The real and imaginary and dielectric responses as modeled by the Debye equivalent circuit. Note that the real response decreases from a larger response \( \varepsilon_0 \) to a lower response \( \varepsilon_\infty \) when \( \omega \tau = 1 \), where the imaginary response shows a maxima with a magnitude half of the difference of the lower and higher response.
A weakness of this model is that it assumes there is only one relaxation time. In real materials there is often a range of relaxation times, thus making it a poor model to parameterize the behavior of real dielectrics. However, it does demonstrate a number of significant points such as in the real dielectric constant is smaller above a relaxation (where $\omega \tau \approx 1$) than at frequencies well below the relaxation, and the loss tends to be a maximum near the region where $\omega \tau \approx 1$.

### 1.4.3 The Cole-Cole Equivalent Circuit

Not surprisingly, there has been much work to correct the single relaxation time problem. One of the more successful models was developed by Cole and Cole. This seems to describe the behavior of a wide range of polar liquid and solids. This equivalent circuit introduces a new element, that at the time of their work was purely empirical, but has in recent years has been obtained from theoretical models. This element is the constant-phase element, CPE. Its physical origins will be discussed in the next section. For now it may be though of a circuit element that has its impedance, $Z_{\text{CPE}}$ given by the following expression:

$$Z_{\text{CPE}} = A(j\omega)^{-n}$$  \hspace{1cm} (1.64)

where the coefficient $A$ and the exponent $n$ are an empirically determined parameter that are picked to obtain the best fit. The Cole-Cole equivalent circuit has the following circuit diagram:
Figure 1.12: The Cole-Cole equivalent circuit. Here the resistor from the Debye model is replaced by the constant phase element (CPE)

The complex equivalent capacitance obtained for this circuit is given by the following expression after setting $C_1 + C_2 = C_0$ and $C_1 = C_\infty$:

$$C^*(\omega) = C_\infty + \frac{(C_0 - C_\infty)}{1 + (C_0 - C_\infty)A(j\omega)^{1-\alpha}} = C_\infty + \frac{(C_0 - C_\infty)}{1 + (j\omega\tau)^{1-\alpha}}$$  \hspace{1cm} (1.65)

Where

$$\tau = \left(A(C_0 - C_\infty)\right)^{1+\alpha}$$ \hspace{1cm} (1.66)

Clearly finding the real and imaginary parts of this expression is more complex than in the Debye circuit, except when $\alpha=0$ or 1 when it reduces to the Debye model or a constant capacitance respectively.

By expanding this expression one finds: $^{56}$

$$\varepsilon^* - \varepsilon_\infty = (\varepsilon_0 - \varepsilon_\infty) \left[ \frac{1 + (\omega\tau)^{1-\alpha} \left( \sin \frac{1}{2} \alpha \pi - j \cos \frac{1}{2} \alpha \pi \right)}{1 + 2*(\omega\tau)^{1-\alpha} * \sin \frac{1}{2} \alpha \pi + (\omega\tau)^{2(1-\alpha)}} \right]$$ \hspace{1cm} (1.67)
The use of standard definitions of hyperbolic functions and simple algebra allows this to be rewritten as:

\[
\epsilon^* - \epsilon_\infty = \frac{1}{2} (\epsilon_0 - \epsilon_\infty) \left[1 - \frac{\sinh (1 - \alpha) x - j \cos \frac{1}{2} \alpha \pi}{\cosh (1 - \alpha) x + \sin (\frac{1}{2} \alpha \pi)}\right], \quad \text{where } x = \ln(\omega \tau) \quad (1.68)
\]

Cole and Cole make the following statement about the constant phase element, “It must be understood the use of the complex impedance $Z$ is merely one way of expressing the experimental facts and that it and its real and imaginary parts have no conventional meaning.” Graphs of the Cole-Cole form will be shown as a limiting case of the Havriliak-Negami theoretical model later.

### 1.4.4 Distributed Circuit Elements

The models that have been discussed above employ ideal, point components. In practice such devices are theoretical abstractions that do not exist. The actual test cells used in these experiments have a finite expanse in three dimensions and this leads to a dielectric response that can only be modeled through an equivalent circuit that includes distributed elements. A common example of a distributed circuit element is a transmission line. While the transmission line can very adequately be modeled using Maxwell’s equations, the connection to standard low-frequency electronics is better seen through a distributed circuit model, where the wires are assumed to have impedance and
the model assumes so much capacitance/unit length, resistance/unit length, etc.- that is the impedance has spatial extent and can not be modeled as an ideal impedance at a point.

The finite spatial extent of the test cells and dielectric materials used in all experiments leads to two generic types of distributed response. The first type of effect occurs even if the electrodes are perfectly flat, and the system is spatially uniform, and consists of diffusion of defects, ions, etc. in the dielectric. Diffusion leads to a response that can be modeled as a distributed circuit element that is analogous to a transmission line. The second will occur because the systems we study are not homogeneous and the electrodes are not point electrodes. In this case, the macroscopic current may be thought of as the sum of a very large number of microscopic currents that because of electrode roughness, dielectric inhomogeneities and the like are not all the same. This leads to a distributed response once more.

1.4.5 Models for Diffusion

The simplest of the diffusion elements is called the Warburg element\textsuperscript{57}, which models linear diffusion in an infinite length. More practical forms that model diffusion in a finite length are available\textsuperscript{58}. The “\textit{O}” element models the diffusing species in parallel with the capacitor, while the “\textit{T}” element models the diffusing species in series with the capacitor\textsuperscript{59}. The impedance for the “\textit{O}” element is written as\textsuperscript{52}: 
\[ Z_{WO} = R_{RD} \left[ \tanh \sqrt{js} \right] \]  
(1.69)

Where \( R_{RD} \) is the resistance to diffusion,

\[ s \equiv l_e^2 (\omega/D) \]  
(1.70)

and \( D \) is the diffusion coefficient of the diffusing particle, \( l_e \) is the finite length region of diffusion. At low frequencies, \( s \) is small and the hyperbolic tangent may be expanded to yield:

\[ Z_{WO} = R_{RD} \left[ \sqrt{js} \right] = \frac{R_{RD}}{\sqrt{js}} \left[ \sqrt{js} - \frac{js^2}{2} \right] = R_{RD} \left[ 1 - j \frac{l_e^2 \omega}{3D} \right] \]  
(1.71)

The impedance, \( Z_{(RC)} \) of a resistor (R) in parallel with a capacitor (C) is given by:

\[ Z_{(RC)} = \frac{R}{1 + j \omega RC} = \frac{R - j \omega R^2 C}{1 + (\omega RC)^2} \approx R \left[ 1 - j \omega RC \right] \text{ when } \omega RC << 1 \]  
(1.72)

Comparing these two expressions it is clear that at very low frequencies, the Warburg “O” element is to a good approximation a resistor, \( R_{RD} \) in parallel with a capacitor of value \( C = \frac{l_e^2}{3DR_{RD}} \), with the resistor being the bigger contributor to the impedance.

The impedance for the series arrangement \( Z_{WT} \) is written as:

\[ Z_{WT} = R_{RD} \left[ \coth \sqrt{js} \right] \]  
(1.73)

where \( s \) and \( R_{RD} \) have the same definitions as in equation (1.69) above. At low frequencies, \( s \) is small and the hyperbolic cotangent may be expanded to yield:
The impedance of a resistor (R) in series with a capacitor (C) is given by:

$$Z_{RC} = R + \frac{1}{j\omega C} \quad (1.75)$$

Again, comparing these two expressions, it is clear that the T element at low frequencies is a resistor $\frac{R_{RD}}{3}$ in series with a capacitor of value $C = \frac{l_{e}^2}{D R_{RD}}$. Note here the capacitor has the bigger contribution to the impedance and if the value if this capacitor becomes too big a situation results where the field is “blocked” from the rest of the dielectric.

For both these elements, O and T, at very high frequencies $\coth x \to 1$ and $\tanh x \to 1$, and $Z_{WO} = Z_{WT} = Z_{W\infty}$:

$$Z_{W\infty} = \frac{R_{D0}}{\sqrt{j\omega}} \quad (1.76)$$

Substituting for the definition of s and knowing $\frac{1}{\sqrt{j}} = \frac{1}{\sqrt{2}}(1-j)$ equation (1.76) becomes:

$$Z_{W\infty} = \frac{R_{D0}}{l_{e}} \sqrt{\frac{D}{2\omega}}(1-j) \quad (1.77)$$

This is the infinite length Warburg element, this can be explained because one can define a frequency dependent diffusion length, $l_{D} = \sqrt{\frac{D}{\omega}}$. At high frequencies the diffusion length is so small that the diffusing species does not see the film is of finite thickness.
This effect can occur at all frequencies if the diffusion length is infinite giving us the infinite Warburg element. The magnitude of this element, both the real and imaginary parts, at all frequencies are equal and depend upon $1/\sqrt{\omega}$. Defining

$$\sigma = \frac{R_{RD}}{l_e} \sqrt{\frac{D}{2}}$$

(1.78)

the impedance of this element may also be written as:

$$Z(\omega) = \frac{\sigma(1-j)}{\sqrt{\omega}}$$

(1.79)

The Warburg diffusion coefficient, $\sigma$, can be determined from the magnitude of the impedance, $|Z| = \sqrt{\frac{2}{\omega}}\sigma$, at $\omega = 1 \text{rad/s} \sim 0.16 \text{Hz}$ using:

$$\sigma = \frac{|Z|}{\sqrt{2}}$$

(1.80)

The following term is commonly defined in simulations; $B = \frac{l_e}{\sqrt{D}}$, where $l_e$ is the diffusion length, $D$ is the diffusion coefficient. B defines a characteristic time for the particle to diffuse; its units are $s^{1/2}$, when B becomes large either by long diffusion lengths or a low diffusion coefficient, the O and T elements reduce to the infinite Warburg element ($W_\infty$). Using this definition of B, and equations (1.78) and (1.80) the magnitude of the admittance $Y_0 = (1/Z)$ at $\omega = 1 \text{rad/s} \sim 0.16 \text{Hz}$ can be defined as

$$Y_o = \frac{B}{R_{RD}}$$. Using the definitions, the O, T, and infinite Warburg elements and their
frequency limits are shown in Table 2, while characteristic impedance plots of these elements when \( Y_o = 0.001 \text{ S. s}^{1/2} \) and \( B = 0.1 \text{ s}^{1/2} \) are shown in Figure 1.13.

![Impedance Graph](image)

**Figure 1.13:** The impedance of the “O”, “T” and “W\(\infty\)” elements, when \( Y_o = 0.001 \) and \( B = 0.1 \). Note that they all behave like the \( W\infty \) element for frequencies \( > 2/B^2 = 100 \text{Hz} \). The limiting values at lower frequencies are shown in the table below.

<table>
<thead>
<tr>
<th>Element</th>
<th>Impedance</th>
<th>Admittance</th>
<th>( Z(\omega \to 0) )</th>
<th>( Z(\omega \to \infty) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>( \frac{1}{Y_o \sqrt{j\omega}} ) tanh( B\sqrt{j\omega} )</td>
<td>( Y_o \sqrt{j\omega} ) coth( B\sqrt{j\omega} )</td>
<td>( Z = \frac{B}{Y_o} - j\frac{B\omega}{3Y_o} )</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>( \frac{1}{Y_o \sqrt{j\omega}} ) coth( B\sqrt{j\omega} )</td>
<td>( Y_o \sqrt{j\omega} ) tanh( B\sqrt{j\omega} )</td>
<td>( Z = \frac{B}{3Y_o} - j\frac{1}{B\omega Y_o} )</td>
<td>( Z = \frac{1}{Y_o \sqrt{j\omega}} )</td>
</tr>
<tr>
<td>( W\infty )</td>
<td>( \frac{1}{Y_o \sqrt{j\omega}} )</td>
<td>( Y_o \sqrt{j\omega} )</td>
<td>N/A</td>
<td></td>
</tr>
</tbody>
</table>
1.4.6 The Constant Phase Element

The second generic feature that leads to distributed component type behavior is inhomogeneities in the dielectric cell and the dielectric. This is modeled by a constant phase element that has an impedance given by: $Z_{CPE} = A(j\omega)^{-n}$ where both A and n are frequency independent terms. The phase angle of the CPE is frequency independent and has a value of $-90^\circ n$ degrees, hence the name Constant Phase Element. Generally $n \neq 0.5$, since when $n = 0.5$, this corresponds to an infinite Warburg element. While it is rarely used in the limits, it should be noted that $n = 1$ corresponds to an ideal capacitor, and $n = 0$ corresponds to an ideal resistor. Due to this fact it has been also named “recap” by some.

It is generally thought to arise from inhomogeneities in the electrode-dielectric system or non-uniform diffusion. Varying thickness and composition of a dielectric can also provide a CPE response. About 20 years ago there was a great deal of interest in the impedance of rough surfaces, and it was found that CPE can be caused by inhomogeneities in the potential field that are often found at the dielectric-electrode interface with porous, rough and irregular electrodes - in essence all real world electrodes. By using fractal models for the interface, CPE behavior was explained.

Graphs of the real and imaginary impedance for various exponents $n$ and $A = 1 \times 10^{-5}$ are shown below.
Figure 1.14: Simulation of the real and imaginary response of the constant phase element as the value of the exponent changes from 0 (corresponding to a resistor) to 1 (capacitor = $1 \times 10^{-5}$ F) plotted as a function of frequency. The bottom curve is the Cole-Cole plot of the same. Note that the angle between the curve and the x axis increases with increasing $n$, but stays the same (constant phase).
1.4.7 Theoretical models

Obviously the above, can be considered theoretical models. What makes these models different than those discussed above is that they have no simple physical model to explain the theoretical form; rather they all assume a very specific form for the distribution of relaxation times. This section will be limited to one theoretical form, that of Havriliak-Negami.\textsuperscript{68} This theoretical form fits a broad range of experimental data in many materials. The capacitance as a function of frequency for a dielectric modeled by this theoretical form is given by:

\[
C^*(\omega) = C_\infty + \frac{(C_0 - C_\infty)}{\left(1 + (j\omega\tau_0)^\mu\right)^\phi}
\]  

(1.81)

where \(C_0\) and \(C_\infty\) are the low frequency and high frequency capacitances respectively, \(\tau_0\) is the mean relaxation time, and the exponents \(\mu\) and \(\phi\) are empirical parameters that are varied to obtain the best fit to the data. This equation reduces to those seen above and others in appropriate limits. In the limit \(\mu\to1\) and \(\phi\to1\), this expression reduces to:

\[
C^*(\omega) = C_\infty + \frac{(C_0 - C_\infty)}{1 + j\omega\tau_0}
\]  

(1.82)

This is just the Debye model. In the limit \(\phi\to1\), but \(\mu\) is unspecified this expression reduces to:
This is the Cole-Cole form when the correspondence between \( \alpha \) and \( \mu \) is made, that is \( \mu = 1 - \alpha \). Finally, when \( \mu \to 1 \) and \( \phi \) is unspecified, this reduces to the Davidson-Cole\(^{69}\) model:

\[
C^*(\omega) = C_\infty + \frac{(C_0 - C_\infty)}{1+(j\omega \tau_0)^\mu}
\] (1.83)

The Davidson-Cole model implicitly assumes a range of dielectric relaxation times\(^{70}\), as opposed to the Debye model which assumes a single relaxation time. To see how this might occur, assume there is a distribution of relaxation times, \( G(\tau) \), where the distribution of relaxation times is normalized such that:

\[
\int_{-\infty}^{\infty} G(\tau)d\tau = 1
\] (1.85)

If one assumes a Debye relaxation at every frequency, then the Davidson-Cole equation (1.84) becomes\(^{71}\):

\[
\frac{C^*(\omega) - C_\infty}{C_0 - C_\infty} = \frac{1}{(1+j\omega \tau_0)^\phi} = \int_{-\infty}^{\infty} \frac{1}{1+j\omega \tau} G(\tau)d\tau
\] (1.86)

Solution of this equation leads to the following form for \( G(\tau) \):
Thus, the Davidson-Cole form is consistent with the above distribution of relaxation times and a Debye relaxation at all allowed relaxation times. The physical basis of this distribution function is certainly not obvious.

The previous paragraph suggests a rather general formalism; the complex dielectric response is related to the integral of the Debye response over a distribution of times:

$$
\int C^*(\omega) - \frac{C_0}{\omega} = \int_{\omega}^{1+\omega} G(\tau)d\tau
$$

This is an integral equation, and experience suggests that integral transformations may allow one to extract $G(\tau)$. In fact, this is the case. Defining $j\omega=p$, and the Laplace transform as:

$$
F(p) = L(\tau) = \int e^{-p\tau} f(\tau) d\tau
$$

it becomes apparent that $G(\tau) = L^{-1}L^{-1}(F(p))$, where $L^{-1}$ denotes the inverse transformation. This allows us to construct the following table of $G(\tau)$ for the various models discussed.72
Table 3: A table showing the distribution of relaxation times $G(\tau)$ for the Debye, Cole-Cole, Davidson-Cole and Havriliak-Negami models.\(^{72}\)

<table>
<thead>
<tr>
<th>Type of relaxation</th>
<th>$f(\omega)$</th>
<th>$G(\tau); \ t = \frac{\tau}{\tau_0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Debye</td>
<td>$f(\omega) = \frac{1}{1 + j\omega\tau_0}$</td>
<td>$G(\tau) = \delta(\tau - \tau_0)$</td>
</tr>
<tr>
<td>Cole-Cole</td>
<td>$f(\omega) = \frac{1}{1 + (j\omega\tau_0)^\mu}$</td>
<td>$G(\tau) = \frac{1}{2\pi \tau_0} \frac{\sin(1-\mu)\pi}{\cosh(\mu \ln t) - \cos(1-\mu)\pi}$</td>
</tr>
<tr>
<td>Davidson-Cole</td>
<td>$f(\omega) = \frac{1}{(1 + j\omega\tau_0)^\phi}$</td>
<td>$G(\tau) = \begin{cases} \sin \pi \phi \left( \frac{\tau}{\tau_0 - \tau} \right)^\phi &amp; \text{if } \tau &lt; \tau_0 \ 0 &amp; \text{if } \tau \geq \tau_0 \end{cases}$</td>
</tr>
</tbody>
</table>
| Havriliak-Negami   | $f(\omega) = \frac{1}{(1 + (j\omega\tau_0)^\mu)^\phi}$ | $G(t) = \left(\frac{1}{\pi}\right)\frac{t^{\mu\phi-1} \sin(\phi\Theta)}{(t^{2\mu} + 2t^\mu \cos \pi\mu + 1)^{\phi/2}}$  

$\Theta = \arctan\left(\frac{\sin \mu\pi}{t^\mu + \cos \mu\pi}\right), \ 0 \leq \mu; \mu\phi \leq 1$
Using the distribution of relaxation times $G(\tau)$ found for the Cole-Cole distribution and using $\tau_0 = 1$, a plot of various values of $\mu$ as a function of $t$ is shown in Figure 1.15a below. The plot for $\mu = 0.9999$ was an attempt to obtain the Debye distribution, showing a delta function for the distribution of relaxation times, $G(\tau)$ at $\tau_0 = 1$. It is often useful to look at $tG(\tau)$, the integral of this is the average relaxation time. A plot of this is shown in Figure 1.15b. Note that the distribution broadens as the value of $\mu$ decreases.

For illustration, a simulation showing the real and imaginary response of a dielectric with a dielectric with Cole-Cole distribution with $C_0 - C_\infty = 200$ and $\tau_0 = 0.001 \sim 160\text{Hz}$ with various values of $\mu$ are shown in Figure 1.16. Note the depression of the center of the semicircle in the Cole-Cole plot and the increased width of the imaginary plot as the value of $\mu$ decreases. All this shows that for increasing $\mu$ the relaxations tends toward the most probable value $\tau_0$. 
Figure 1.15: A plot showing the distribution of relaxation times for the Cole-Cole distribution for various values of $\mu$. The distribution about the most probable time broadens as $\mu$ decreases.
Figure 1.16: A simulation using the Cole-Cole circuit showing (a) the real and imaginary response of for various values of $\mu$, $\tau_0=0.001 \sim 160$Hz and $C_0-C_\infty=200$ and (b) the same but plotted in a Cole-Cole plot. Note the depression of the center of the semicircle as $\mu$ gets smaller.
Doing the same for the Davidson Cole distribution, the plots of $G(\tau)$ and $tG(\tau)$ for various values of $\phi$ are shown below. Note that the distribution function is highly asymmetric, thus the distribution of relaxation times is the same.

Figure 1.17: A plot showing the distribution of relaxation times for the Davidson-Cole distribution for various values of $\phi$. Note the two peaks at $t=0$ and at $\tau=\tau_0$. 
Note that there is a peak at a relaxation time of zero, and at \( \tau = \tau_0 \). Numerical analysis of \( \int_0^{0.5} G(t)dt \) indicates that for \( \phi < 0.5 \) a larger integral is obtained than for those of \( \phi > 0.5 \) (Table 4). This means that the relaxation times are closer to zero when \( \phi < 0.5 \) and closer to \( \tau_0 \) for \( \phi > 0.5 \). Further analysis shows that the mean relaxation time is given by \( \langle \tau \rangle = \phi \tau_0 \). Experimental \( \phi \)'s tend to be greater than 0.5, Davidson and Cole found \( \phi \) between 0.5 and 0.7.

A simulation showing the real and imaginary response of a dielectric with a Davidson-Cole distribution with \( C_0 - C_\infty = 200 \) and \( \tau_0 = 0.001 \sim 160 \text{Hz} \) with various values of \( \phi \) are shown in Figure 1.18. Note the skewing from a semicircle of the Cole-Cole plot as the value of \( \phi \) is decreased.

**Table 4: The value of \( \int_0^{0.5} G(t)dt \) of the Davidson-Cole distribution for various values of \( \phi \).**

<table>
<thead>
<tr>
<th>( \phi )</th>
<th>( \int_0^{0.5} G(t)dt )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.92</td>
</tr>
<tr>
<td>0.2</td>
<td>0.83</td>
</tr>
<tr>
<td>0.3</td>
<td>0.73</td>
</tr>
<tr>
<td>0.4</td>
<td>0.62</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>0.6</td>
<td>0.38</td>
</tr>
<tr>
<td>0.7</td>
<td>0.27</td>
</tr>
<tr>
<td>0.8</td>
<td>0.17</td>
</tr>
<tr>
<td>0.9</td>
<td>0.78</td>
</tr>
</tbody>
</table>
Figure 1.18: A simulation using the Davidson-Cole circuit showing (a) the real and imaginary response of for various values of $\phi$, $\tau_d=0.001 \sim 160$Hz and $C_0-\infty=200$ and (b) the same but plotted in a Cole-Cole plot.
The Havriliak-Negami relaxation time distribution is more complex since it depends on two exponents and has the constraints \(0 \leq \mu \leq 1\) and \(\mu \phi \leq 1\). The following graphs of \(G(\tau)\) and \(tG(\tau)\) illustrate some results when \(\mu = 1\) (Figure 1.19) and \(\mu = 0.5\) (Figure 1.20). From these plots the similarity to the Cole-Cole distribution when \(\mu > 1\) and \(\phi = 1\) is clear. Also, larger values of \(\phi\) have a greater asymmetry towards larger normalized times and a peak at higher normalized times. The real and imaginary responses and the Cole-Cole plot for various values of \(\phi\) when \(\mu = 0.5\) is shown in Figure 1.21. The Debye circuit \(\phi = 1\) and \(\mu = 1\) is shown for reference. Note the initial depression of the Cole – Cole plot as \(\mu \to 0.5\) followed by the skewing as \(\phi\) increases.

Thus as a rule of thumb \(\mu\) near 1 corresponds to a sharper distribution and for a given \(\mu\), larger \(\phi\) leads to a more skewness towards higher normalized times.
Figure 1.19: The plots of (a) $\log G(\tau)$ vs $t$ and (b) $tG(\tau)$ vs $t$ for $\mu=1$ and $\phi=.5$ and 1. The similarity to the Cole-Cole Distribution when $\mu \rightarrow 1$ and $\phi=1$ is clear.
Figure 1.20: The plots of (a) logG(τ) vs t and (b) tG(τ) vs t for μ = 0.5 and φ = 0.5, 1, 1.5 and 2. Note that larger values of φ have a greater asymmetry towards larger normalized times and peak at higher normalized times.
Figure 1.21: A simulation using the Havriliak-Negami circuit showing (a) the real and imaginary response of for \( \mu = 0.5 \) and various values \( \phi \) and of \( \tau_0 = 0.001 \sim 160 \text{Hz} \) and \( C_0 - C_{\infty} = 1 \times 10^{-5} \text{F} \) and (b) the same but plotted in a Cole-Cole plot. The Debye circuit response is shown for reference, not e the initial depression of the Cole-Cole plot when \( \mu \to >0.5 \) followed by the skewing as \( \phi \) increases.
1.5 Curve Fitting

The goal of this study is to create heterogeneous systems with high dielectric constants using liquid crystals. When the mixture is made and placed in a sample holder, its impedance is measured using the impedance analyzer. From these measurements the dielectric response of the sample can be determined if the impedance of the empty sample holder is know (discussed in the next chapter). This calculated dielectric response will have some characteristic features which together with some physical knowledge of the sample, a model made of circuit elements discussed above can be made to fit these data. That is, the data can be parameterized using equations of circuits that best model the data. The model chosen can simply be one that is used to parameterize the data for easy comparison across data samples or it can be a model chosen to specifically determine a physical quantity. For example, if the measured dielectric response looks like a Debye response, then using a curve fitting program, one could fit the data to equation (1.63),

$$
\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2 \tau^2} - \frac{j\omega \tau (\varepsilon_0 - \varepsilon_\infty)}{1 + \omega^2 \tau^2},
$$

to obtain $\varepsilon_0 - \varepsilon_\infty$, $\tau$ and $\varepsilon_\infty$. Alternatively the same data could be fitted to obtain a resistance and a capacitance if the equation

$$
C^*(\omega) = \frac{C}{1 + (\omega RC)^2} - j\frac{\omega RC^2}{1 + (\omega RC)^2}
$$

for the complex capacitance of a resistor in series with a capacitor is used to fit the data.

In this work, maximizing the magnitude of the dielectric response (real response), while keeping losses (imaginary response) to a minimum is the goal. It would seem that a model containing a capacitor is parallel with a resistor would be sufficient, but due
multiple relaxation frequencies, non-Debye responses and other effects that can be modeled by the constant phase element, the circuits used in this dissertation contain a combination of Havriliak-Negami element, the constant phase element, resistance and capacitors. The exact choice of circuits used to fit data will be discussed as they are used.

Initially the curve fitting was done using a program written in Mathematica, which used Mathematica’s nonlinear regression routine to fit the experimental data to equations corresponding to the model used. This process required changing the equation and initial parameters every time a new model was needed. To avoid this, a commercial program zSim® from echem software was used to fit the data. This program takes dielectric response data and the equivalent circuit represented using Boukamp’s code as inputs to fit the data. Boukamp’s code is a method of representing an equivalent circuit using predetermined circuit element symbols (Table 5) nested in parentheses of several levels. Examples of codes for a few select circuit elements are shown in Table 6. The outputs of the program are parameters of the model that best fits the data.

<table>
<thead>
<tr>
<th>Circuit Element</th>
<th>Boukamp Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistor</td>
<td>R</td>
</tr>
<tr>
<td>Capacitor</td>
<td>C</td>
</tr>
<tr>
<td>Inductor</td>
<td>L</td>
</tr>
<tr>
<td>Warburg</td>
<td>W</td>
</tr>
<tr>
<td>Havriliak-Negami</td>
<td>H</td>
</tr>
</tbody>
</table>
Table 6: Sample Boukamp code for some circuit elements

<table>
<thead>
<tr>
<th>Circuit</th>
<th>Boukamp CODE</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>RC</td>
</tr>
<tr>
<td>C</td>
<td>(RC)</td>
</tr>
<tr>
<td>R</td>
<td>R(HC)</td>
</tr>
</tbody>
</table>

ZSimp uses the Down-Hill simplex method for optimizing the chi squared value of the fit. Minimizing the value of chi squared involves minimizing:

\[
\chi^2 = \sum_{i=1}^{n} \left[ \frac{\left( a_i - \varepsilon'\left( \omega_i; \bar{p} \right) \right)^2 + \left( b_i - \varepsilon''\left( \omega_i; \bar{p} \right) \right)^2}{\sigma_i^2} \right]
\]

(1.91)

where the numerator is the distance between the experimental \((\omega_i, a_i, b_i)\) and calculated \((\omega_i, \varepsilon'\left( \omega_i; \bar{p} \right)\text{ and } \varepsilon''\left( \omega_i; \bar{p} \right))\) points, \(\bar{p}\) are the fitting parameters and \(\sigma_i\) is the standard deviation. The implementation does not need starting points as the method is based on evaluating the function to be fitted using random parameters (trial and error) and
comparing it to the data and until the best fit is determined. Using this method it is fit can
be done quickly as not further input is needed from the user. The results of the fit are
graphically and parametrically represented in a window. The program also allows to
model circuits, that is, the program can output a dielectric spectrum for a given circuit.
This can be useful when deciding on the model to be used to fit the data.

With this tool and good knowledge of the dielectric mixtures it was possible to
correctly compare and evaluate the mixtures that were prepared.
CHAPTER 2

The Dielectric Sample Holder

The impedance of the mixtures was measured in capillary filled cells whose conductors were of known separation and area. Briefly, these cells were made of two pieces of soda lime float glass coated with a transparent conductive layer of Indium Tin Oxide (ITO) (supplied by Colorado Concepts Coatings with sheet resistance of 100 Ω/□) separated by spacers. The spacing between the plates was controlled using cylindrical glass spacers of known diameter. Finally, the electrode area was controlled by etching a pattern on the layer of ITO using photolithography techniques. The manufacturer of the ITO glass placed a barrier layer made of silicon dioxide between the glass and ITO layers, to prevent ionic diffusion from the glass. After patterning the ITO, a thin layer of polyamic acid (PAA) dissolved in N-Methyl Pyrrolidinone (NMP) is spun coated then hard baked (or imidized) to form a layer of polyimide. This layer when rubbed in a single direction with a velvet cloth defines the alignment direction for the liquid crystals in the mixtures. In this section we present the results of the study of the effect that the alignment and conductive layers have on our measurements.
2.1 The Apparent Dielectric Response

The goal of the measurements is to compare the dielectric response of a series of mixtures. The previous chapter explained how the Schlumberger Impedance analyzer measured the complex impedance of the sample; here, the techniques for obtaining the dielectric response from this data will be discussed. This measured response is called the apparent dielectric response because even after this first analysis step, the response still contains responses from interfacial polarization, conductivity and electrode polarization. Therefore, the response for the same mixture may be different in different cells of differing cell properties. This section will discuss the important effects that the cells have on the measurements.

Two methods were initially used to extract the apparent dielectric response from the measured cell impedance. One of the methods assumed that the cells were ideal infinite area parallel plate capacitors. With this assumption we can use equations (2.1) and (2.2) can be used to calculate the apparent real and imaginary dielectric response respectively.
\[ \varepsilon' = \frac{dZ}{A\varepsilon_0\omega(Z^2 + Z')^2} \] (2.1)

\[ \varepsilon'' = \frac{dZ'}{A\varepsilon_0\omega(Z^2 + Z')^2} \] (2.2)

where, \( \varepsilon' \) and \( \varepsilon'' \) are the apparent real and imaginary dielectric response respectively, \( A \) is the electrode area, \( d \) is the spacing between the electrodes, \( \varepsilon_0 \) is the permittivity of vacuum, \( \omega \) is the angular frequency, \( Z \) and \( Z' \) are the measured real and imaginary impedance respectively. The thickness of the cell was measured after cell construction, but prior to filling using a spectrometer to study the interference fringes formed by the air gap in the cell. The area of the electrode is obtained by calculating the dimensions of the patterned ITO area.

The second method consisted of measuring the impedance of both the empty and the filled cells. Taking the ratio of the empty impedance to the filled impedance should give us the apparent dielectric response of the mixtures without any lead resistance or other frequency dependant cell properties as shown in equation (2.3)

\[ \frac{Z_{\text{empty}}}{Z_{\text{full}}} = \frac{j\omega\varepsilon_0\varepsilon_{\text{full}}^* A}{d} \] (2.3)

where \( Z_{\text{empty}} \) and \( Z_{\text{full}} \) are the measured complex real and impedance of the empty and filled cell respectively, \( j \) is \( \sqrt{-1} \), \( A \) is the electrode area, \( d \) is the spacing between the electrodes, \( \varepsilon_0 \) is the permittivity of vacuum, \( \omega \) is the angular frequency, and \( \varepsilon_{\text{full}}^* \) and \( \varepsilon_{\text{empty}}^* \) are the complex relative dielectric constants. This ratio is a complex ratio that
gives us equations (2.4) and (2.5) for the apparent real ($\varepsilon'$) and imaginary ($\varepsilon''$) responses of the mixtures respectively

$$
\varepsilon' = \frac{C_{\text{filled}}' + C_{\text{empty}}'}{C_{\text{empty}}' + C_{\text{empty}}''} \quad (2.4)
$$

$$
\varepsilon'' = \frac{C_{\text{filled}}'' - C_{\text{empty}}''}{C_{\text{empty}}' + C_{\text{empty}}''} \quad (2.5)
$$

where, $C_{\text{filled}}'$ and $C_{\text{empty}}'$ are the real capacitances of the filled and empty cells, respectively, and the double primed superscripts symbolize the imaginary response. A LabView routine was written to step through the data and calculate the apparent real and imaginary responses. This routine is shown in the appendix. This method has the potential advantage that the fringe fields and other non-idealities are approximately taken into account.

### 2.2 Cell Properties affecting the Apparent Dielectric Response

By comparing the two methods discussed in section 2.1, it was found that the second method, where the empty cell parameters were measured as a function of frequency was necessary. The assumption that the empty cell was an ideal, perfect capacitor caused the calculated apparent real dielectric response between $10^5$ to $10^6$ Hz to be less than one (Figure 2.1). This result is nonphysical, and the reason for this error is seen on studying the capacitance of an empty cell (Figure 2.2), which shows that the cell has a frequency dependent dielectric response.
Figure 2.1: Graphs showing the apparent dielectric response of a cell obtained using two methods. The first method uses the empty cell impedance (solid data), while the second uses the empty cell dimensions (open squares). Both methods were described earlier.
Figure 2.2: The typical frequency response of the empty test cells. Note that the cell has a small frequency dependence that is apparent at high and low frequencies in both the imaginary and real responses.

The empty cell data shown in Figure 2.2 was modeled as the equivalent circuit shown in Figure 2.3 below. Feeding this data and the Boukamp code for the circuit, R(RC)(RC), to the ZSimp program, the following results were obtained. The combined lead and ITO resistance of both electrodes was 420 Ω, the combined capacitance and resistance of the polyimide were $1.78 \times 10^{-9}$ F and $1.26 \times 10^9$ Ω respectively, while the air gap capacitance and resistance were $9.8 \times 10^{-11}$ F and $3.21 \times 10^{12}$ Ω respectively. Using these values as a starting point, the simulation function in the modeling software ZSimp® was used to vary the resistance of the leads and ITO and study its effect on the frequency response of this system. On increasing this value dispersion starts to occur at lower frequencies (Figure 2.4).
Figure 2.3: An equivalent circuit for modeling the Impedance of the empty cell. $R_{ITO}$ is the resistance of ITO and $R_{lead}$ is the resistance of the lead, $R_{p}$ is the resistance of polyimide, $C_{p}$ is the resistance of polyimide, $R_{Gap}$ is the resistance of the air gap, and $C_{gap}$ is the capacitance of the air gap.

Figure 2.4: Results of a simulation showing the real and imaginary capacitive response of an empty cell as the resistance of the leads and electrode (ITO) are increased. The starting point of the simulation is the values from a fit to a real empty cell with a lead and ITO resistance of 420 Ohms (solid line). Note that as this resistance is increased so does the dispersion at these frequencies ($10^{4} - 10^{6}$ Hz).
In light of these findings, experiments were done to see the effects of cell construction, polyimide coatings and different ITO surface resistances. Glass coated with ITO at Delta Technologies Inc. was used to make the cells as described above. The sheet resistances of ITO used were $6 \pm 2 \ \Omega/\square$ (part no.CG-41IN-S207), $10 \pm 2 \ \Omega/\square$ (part no.CG-51IN-S115), $20 \pm 5 \ \Omega/\square$ (part no.CG-61IN-S115), $45 \pm 15 \ \Omega/\square$ (part no.CG-81IN-S215), $80 \pm 10 \ \Omega/\square$ (part no.CG-90IN-S215) and the Colorado Concepts Coatings (LCI stock) $100 \pm 5 \ \Omega/\square$. To further enhance this effect we filled the cells with liquid crystal E7. The impedance of these cells was measured and the results show the same trend as the simulation with some experimental error.
Figure 2.5: The apparent dielectric response of E7 in cells of varying ITO sheet resistance. The top graphs show the real and imaginary responses, while the bottom graph shows the start of the high frequency relaxation as the resistance is increased. Note that, as expected the dispersion starts at lower frequencies as the resistance increases.
The presence and the properties of the polyimide film was another factor that had an impact on the apparent dielectric response. The presence of polyimide defines the alignment of a liquid crystal in the cell, hence determining which part of the dielectric tensor gets measured by the impedance analyzer. For example, ITO coated with rubbed polyimide 2555 from Dupont® aligns the molecule with its long axis parallel to the substrate and rub direction, this is called planar alignment. While coating the ITO glass with Nissan’s 7511 orients the long molecular axis perpendicular to the substrate, called homeotropic alignment. In some cases, uncoated ITO can promote homeotropic alignment. In the measurements of the liquid crystals E7 (Figure 2.7) and E31 (Figure 2.8) from Merck®, the cells coated with Dupont’s 2555 enabled us to measure the perpendicular component of the molecules dielectric response, while the cells coated with Nissan’s 7511 and the bare glass cell enabled us to measure the parallel component.

The alignment layer and orientation of the liquid crystal also has a big impact on the electrode polarization and conductivity of the mixture\textsuperscript{74}. This is apparent when we fit the equivalent circuit shown in Figure 2.6 to the dielectric measurements of the liquid crystals E7 (Figure 2.7) and E31 (Figure 2.8). The constant phase element, Q, models electrode polarization. Under homeotropic alignment with E7, the value of $n$ in the constant phase element, Q is 0.8571 as opposed to the planar alignment’s 0.9602 (Table 7). When there is no alignment layer as in the case with the E31 measurements $n$ is 0.7171, while the planar aligned cell $n=1$ (Table 8). This indicated that we get the biggest effect is from electrode polarization from the cell with no alignment followed by the cell with Nissan’s 7511 (homeotropic alignment). The increased electrode
polarization can be explained by higher conductivity in the homeotropic alignment as there is anisotropy in conductivity in liquid crystals due to higher easier mobility of ions in the homeotropic state. This higher conductivity provides more ions to polarize the electrode\textsuperscript{75}.

![Figure 2.6: Equivalent circuit used to model E31 and E7 filled in planar and homeotropic cells. R\textsubscript{ITO} is the resistance of the ITO, Q is a constant phase element that models any electrode polarization, C\textsubscript{LC} is the capacitance of the liquid crystal at intermediate frequencies, and R\textsubscript{LC} is the resistance of the liquid crystal.](image_url)
Figure 2.7: The apparent dielectric response of the liquid crystal E7 as measured using cells that align its long axis either parallel to the substrate (P) or perpendicular to the substrate (H). The cell with polyimide 2555 enabled us to measure the dielectric component perpendicular to the long molecular axis ($\varepsilon_\perp$), while Nissan 7511 cell measured the parallel component ($\varepsilon_\parallel$).

Table 7: Results from the fit of the circuit in Figure 2.6 to the dielectric measurements of E7 Figure 2.7. Q and $C_{LC}$ are reported as dielectric constants because the circuit was fit to the apparent dielectric constant measurements above. $n$ is the exponent of the constant phase element.

<table>
<thead>
<tr>
<th>Polyimide Coating</th>
<th>$R_{ITO}$</th>
<th>A</th>
<th>n</th>
<th>$R_{LC}$</th>
<th>$\varepsilon_{LC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dupont® 2555</td>
<td>278.64</td>
<td>793</td>
<td>0.9602</td>
<td>3.05E+6</td>
<td>5.31</td>
</tr>
<tr>
<td>Nissan® 7511</td>
<td>245.08</td>
<td>708</td>
<td>0.8571</td>
<td>9.10E+7</td>
<td>21.90</td>
</tr>
</tbody>
</table>
Figure 2.8: The apparent dielectric response of the liquid crystal E31 as measured using cells that align its long axis either parallel to the substrate (P) or perpendicular to the substrate (triangle data). The cell with polyimide 2555 enabled us to measure the dielectric component perpendicular ($\varepsilon_\perp$) to the long molecular axis, while the bare glass cell measured the parallel component ($\varepsilon_\parallel$).

Table 8: Results from the fit of the circuit in Figure 2.6 to the dielectric measurements of E3 in Figure 2.8. $Q$ and $C_{LC}$ are reported as dielectric constants because the circuit was fit to the apparent dielectric constant measurements above. $n$ is the exponent of the constant phase element.

<table>
<thead>
<tr>
<th>Polyimide Coating</th>
<th>$R_{ITO}$</th>
<th>$A$</th>
<th>$n$</th>
<th>$R_{LC}$</th>
<th>$\varepsilon_{LC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dupont® 2555</td>
<td>505.08</td>
<td>125</td>
<td>1</td>
<td>3.92E+05</td>
<td>5.98</td>
</tr>
<tr>
<td>NO Coating</td>
<td>203.38</td>
<td>25000</td>
<td>0.7171</td>
<td>4.32E+05</td>
<td>21.75</td>
</tr>
</tbody>
</table>
Another polyimide property that affected the apparent dielectric response is the coating spin speed and polyamic acid (PAA) concentration. These parameters affect the polyimide film thickness, which was measured using a variable angle spectrometric ellipsometer. The ellipsometric measurements will be discussed in a later section. When the same mixture was filled into cells with similar construction but with different coating spin speed and PAA concentration, the measured apparent dielectric responses were different. To better understand the effect of the polyimide coating on the measurements, cells constructed using polyimide 2555 with the four coating parameters shown in Table 9 below.

Table 9: The coatings made to study the effect of polyimide coating parameters on the apparent dielectric response.

<table>
<thead>
<tr>
<th>Coating #</th>
<th>PAA Concentration (%)</th>
<th>Spin Speed (rpm)</th>
<th>Polyimide Thickness (Angstroms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3000</td>
<td>276 ± 2</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1500</td>
<td>460 ± 2</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>3000</td>
<td>482 ± 3</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>1500</td>
<td>762 ± 4</td>
</tr>
</tbody>
</table>

After measuring the empty cell impedance of these cells, they were filled with a number of different mixtures to make sure that the effect of increased apparent dielectric response was not unique to a particular system. The effect is not as apparent in pure liquid crystal mixtures; that is why the measurements for E7 and E31 are not reported.
Measurements of cells using a mixture containing 90% liquid crystal E7, 9% solvent N-Methyl Formamide (NMF), and 1% surfactant Didodecyl Ammonium Bromide (DDAB) are shown in Figure 2.9. An additional set of measurements for a cell filled with 88.19% liquid crystal E7, 8.81% solvent NMP, and 3% surfactant Didodecyl Ammonium Bromide (DDAB) are shown in the appendix.

![Graph showing apparent dielectric response](image)

**Figure 2.9:** The apparent dielectric response of a mixture of 90% liquid crystal E7, 9% solvent N-Methyl Formamide (NMF), and 1% surfactant Didodecyl Ammonium Bromide (DDAB) filled in a 10 micron thick cell coated with polyimide 2555 of varying concentrating and coating spin speed.

At first glance it may seem that the cells with 2% PAA coated at 3000rpm gives the biggest response and hence should be used for this study, but long-term studies and careful analysis of the data shows otherwise. Long-term studies of the apparent dielectric response of the cells show that the cells with the thinnest layer of polyimide (2% PAA solution spun at 3000 rpm) change over time (Figure 2.10). This could be due to a long-
term change of the alignment layer from one that induces a planar alignment to that that induces a homoetropic alignment. This can be seen by comparing the response of the aged thin planar layer (PI2555) cell to that of the same mixture in a cell constructed using the polyimide 7511 which induces a homoetropic alignment (Figure 2.10). The results show the aged thin polyimide layer cell response approaches that of the homeotropic (7511) cell. The change in relaxation time is significant since in general the relaxation frequency of a homeotropically-aligned cell is lower than that of a planar cell. Therefore, either the PI 2555 swells over time and changes its anchoring properties or the thin polyimide layers have a significant number of pinholes that over time allow the ITO to induce homeotropic alignment.

![Figure 2.10: The effect on the dielectric response of aging of a cell with a thin polyimide layer (symbols). As the cell ages the response approaches that of a cell constructed using polyimide 7511, a homeotropic inducing layer (line).](image-url)
Based on this result the next question could be framed as: “Which is the best cell to use – is it the one with the homeotropic layer since it gives you a bigger response?” To better answer this question the data to the circuit in Figure 2.11 below. It includes a resistor in series with a Havriliak-Negami (H-N) element in parallel with a constant phase element (CPE). The H-N element contains a will model the high frequency relaxation, while the CPE will be used to model the increase in both the real and imaginary responses that is especially apparent at lower frequencies. For a better dielectric response, the CPE response with exponent values less than \( n=1 \) (capacitive response) needs to be minimized, while the value of the exponent, \( n \), and the relaxation frequency needs to be maximized. A sample of the fit quality and the separate responses are shown in Figure 2.12.

Figure 2.11: The circuit used to fit the apparent dielectric constant measurements of the mixtures filled in cells with a 10 micron gap coated with polyimide 7511 and 2555.

The summary of the fits results are shown in Table 10. The fit results show that for the planar cells, the one with the thickest layer (4% PAA and spun at 1500rpm) has the response with the lowest portion coming from the CPE and also has the highest relaxation frequency. On the other hand the homeotropic cell has a very low relaxation frequency and a much larger contribution from the CPE.
Figure 2.12: The results of fitting to the apparent dielectric response an equivalent circuit consisting of a parallel arrangement of a H-N element (H) and a Constant Phase Element (Q) in series with a resistor. The fit result is the thick black line. The CPE and H-N responses obtained from the fit are plotted separately here to show their individual contributions to the overall response.
Table 10: Results of fitting a resistor in series to a HN element and constant phase element in parallel to the apparent dielectric measurements of cells coated with either PI 2555 (planar alignment) or PI7511 (homeotropic alignment). $H$ is the magnitude of the dielectric strength as defined by the Havriliak-Negami element, $\tau$ is the relaxation frequency of the relaxation mode, $\mu$ and $\phi$ are HN element coefficients, $A$ and $n$ are the dielectric response and the exponent of the constant phase element.

<table>
<thead>
<tr>
<th>Cell ID</th>
<th>PAA conc.</th>
<th>Spin Speed</th>
<th>H-N Element Parameters</th>
<th>CPE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$H$</td>
<td>$\tau$ (Hz)</td>
</tr>
<tr>
<td>Planar Polyimide 7511 Cell</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>182</td>
<td>2%</td>
<td>3000</td>
<td>1981</td>
<td>2.39E+03</td>
</tr>
<tr>
<td>176</td>
<td>2%</td>
<td>1500</td>
<td>1171</td>
<td>7.01E+03</td>
</tr>
<tr>
<td>194</td>
<td>4%</td>
<td>3000</td>
<td>292.5</td>
<td>1.29E+04</td>
</tr>
<tr>
<td>195</td>
<td>4%</td>
<td>1500</td>
<td>229</td>
<td>1.58E+04</td>
</tr>
<tr>
<td>Homeotropic Polyimide 7511 Cell</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>261</td>
<td>4%</td>
<td>1500</td>
<td>40900</td>
<td>179.35</td>
</tr>
</tbody>
</table>
2.3 Polyimide Thickness Measurements

As described earlier, our cell substrates have multiple coatings, including silicon dioxide and ITO layers. To measure the thickness of the polyimide layer on top of these other layers, a technique that allows one to separate out the non-alignment layers is necessary. Ellipsometry is an optical method that is well suited to precisely measure the thickness of polyimide film in situ with the silicon dioxide and ITO layers in place. It was used in the present study to characterize and measure these thin layers.

This section will follow the following plan. The next subsection will review the theory of ellipsometry. Since there is a voluminous literature on this topic only a very schematic view of this theory will be presented. This will be followed with a subsection discussing the experimental apparatus and the experimental procedure. The apparatus is a commercially available J.A. Woolam Variable Angle Spectrometric Ellipsometer (VASE®) and once more rather little detail on this instrument will be given. Finally, the experimental results and their interpretation will be presented and discussed.
2.3.1 Theory of Ellipsometry

Ellipsometry uses polarized light to characterize very thin films. Briefly, it measures the ratio of the two reflection coefficients $R_p$ and $R_s$, which are the reflection coefficients for light polarized parallel and perpendicular respectively to the plane of incidence (Figure 2.13). When the light is incident on a thick homogeneous slab of material, these reduce to the well-known Fresnel coefficients. When the light is incident on thin layers these terms are more complex and generally include a non-zero or $\pi$ phase shift. Using the standard complex number notation this can be expressed by stating that the reflection coefficients are given by a phase shift and a magnitude. Thus, $R_p$, the reflection coefficient for light polarized parallel to the plane of incidence is defined as:

$$R_p = \frac{E_{\text{reflected}}}{E_{\text{incident}}^{\parallel}}$$

where, $E_{\text{reflected}}^{\parallel}$ is the reflected electric field parallel to the plane of incidence and $E_{\text{incident}}^{\parallel}$ is the incident electric field parallel to the plane of incidence. Similarly, $R_s$ is the reflection coefficient for light polarized perpendicular to the plane of incidence,
\[ R_s = \frac{E_s^{\text{reflected}}}{E_s^{\text{incident}}} \]  \hspace{1cm} (2.7)

where, \( E_s^{\text{reflected}} \) is the reflected electric field perpendicular to the plane of incidence and \( E_s^{\text{incident}} \) is the incident electric field perpendicular to the plane of incidence.

**Figure 2.13:** The amplitudes of the electric field in the plane of incidence (\( E_p \)) and perpendicular to it (\( E_s \)).

The ratio of the reflection coefficients given by equations (2.6) and (2.7) give us the fundamental equation of ellipsometry\(^{76, 77}\)

\[ \frac{R_p}{R_s} = \tan(\psi) e^{i\Delta} \]  \hspace{1cm} (2.8)

Since \( R_p \) and \( R_s \) can be expressed as complex numbers, in general, this ratio is characterized by a magnitude given by \( \tan(\psi) \) and a phase difference \( \Delta \) between the p- and s- reflection coefficients. In this expression, \( i = \sqrt{-1} \). Ellipsometry measures this ratio of reflection coefficients as a function of incident angle, wavelength while other parameters of interest are held constant.

As an example, consider the situation when light is incident onto a thin film on a homogeneous substrate. Let \( d \) be the thickness of the film and \( n_1 \) be the (real, non-
absorbing) index of refraction of the film. The light is assumed to be incident from a material of index $n_0$. It is further assumed that the index of the substrate is $n_2$. Then for light of a given angle of incidence, $\phi_0$ and wavelength $\lambda$, one obtains two reflection coefficients given by:

$$ R^{p,s} = \frac{r_{01}^{p,s} + r_{12}^{p,s} \exp(-i2\beta)}{1 + r_{01}^{p,s}r_{12}^{p,s} \exp(-i2\beta)} \tag{2.9} $$

where $r_{01}^{p,s}$ is the Fresnel reflection coefficient for the $p$ ($s$) polarization for the beam at the incident medium (medium 0) to thin film (medium 1) interface, and $r_{12}^{p,s}$ is the Fresnel reflection coefficient for the $p$ ($s$) polarization for a beam incident onto the substrate (medium 2) from the thin film (medium 1), and $\beta$ is the phase thickness of the film.

$$ \beta = 2\pi \frac{d}{\lambda} \sqrt{n_1^2 - n_0^2 \sin^2 \phi_0} \tag{2.10} $$

When this type of analysis is applied to multiple thin films the result is more complex, but still susceptible to analytic solution.

In light of the above mathematics it is obvious that the thin film thickness and index of refraction need to be “backed out” of the data. When analyzing ellipsometric data to obtain film parameters such as thickness and index of refraction, one must realize that the results ($\psi$ and $\Delta$) obtained using ellipsometry are very precise, but interpreting them accurately in terms of film thicknesses, indices of refraction etc. requires careful and proper analysis of the results. In the absence of other data and physical constants
obtained from other independent sources and experiments it is important to check that the
parameters obtained from fits to ellipsometric data are physically possible and consistent
with known parameters. The fitting of the present ellipsometric data is done essentially
automatically by a non-linear least squares fitting routine. The parameters used to
determine the quality of the fit will be discussed in the next subsection.

The present experiments used a variable angle spectrometric ellipsometer that has
the ability to collect ellipsometric data at many angles of incidence as well as a wide
range of wavelengths from 190 to 1700 nm. This requires that one model the dispersion
of the optical parameters; however, due to the large amount of data that is collected one
can analyze multilayer films.

There are limitations to ellipsometry and the analysis of ellipsometric data. Ellipsometry works best on smooth surfaces when the wavelength of the light source is
neither much larger nor much smaller than the film thickness. When interpreting
ellipsometric data it is commonly assumed the film is ideal that is, it is smooth, that the
interfaces are abrupt and that there is no grading in the material\(^3\). In practice the non-
ideal and/or rough interface is accounted for after the data has been fit to a model that
assumes a homogeneous film with a smooth, flat interface. This is done by using
different models and seeing if one may obtain a better fit by taking into account that the
material is not ideal.

For example, one may model grading by dividing the film into a finite number of
layers of varying optical constants. This often allows one to obtain a better fit;\(^79\)

\(^3\) Here the grading phenomenon is when the optical characteristics vary with depth of the material
however, one must be certain that there is a physical basis for assuming a gradation in index and that the variation in index is reasonable. One can also model surface roughness by adding a layer of a mixture of voids and the material to approximate the roughness. Of course, in these cases other information may be needed. Film roughness is often modeled using an effective medium approximation. In this case the rough surface is replaced by a homogeneous layer of an effective index of refraction that is between the indices of the two adjoining media. The relationship between the effective medium’s indices and those of the two media generally are not linear. Commonly used models are associated with Maxwell-Garnett, Bruggeman and Lorentz-Lorenz and are discussed in a recent book by Choy.

2.3.2 Experimental Setup and Procedure

A J.A. Woolam Co., Inc. variable angle spectroscopic ellipsometer with an autoretarder (VASE® with Autoretarder™) was used to determine the ellipsometric parameters $\Delta(\lambda)$ and $\psi(\lambda)$ of the thin layers on glass substrates as a function of wavelength for a fixed (optimized) angles of incidence. The VASE® was connected to a PC that automated the data collection. The computer was responsible for controlling and tracking the polarizer and analyzer angles, the goniometers that controlled the light source and detector angles, the monochromator and collecting data from the detector. The computer was also used to analyze the data using the J.A. Woolam Co., Inc’s. optical
modeling program WVASE32®. Thus, once the sample was properly placed in the ellipsometer, the system is turn-key until the analysis begins.

Briefly, this ellipsometer operates as follows. This instrument has a polarizer that has a fixed orientation while the analyzer’s orientation is continuously varied. Ambient light is rejected by placing a monochromator just after the light source in the optical path; this makes the monochromatic probe beam much brighter than the ambient. The sample is mounted using a vacuum plate that can be aligned perpendicular to the probe beam. An alignment detector made of a four quadrant Si detector, is placed after the polarizer to assist with this alignment. Analysis of this configuration shows that when such a device is operated at a given wavelength and angle of incidence the output of the detector will be a sinusoidal wave with a DC offset:

\[
V(t) = DC + a \cos(2\omega t) + b \sin(2\omega t)
\]  

(2.11)

The analysis of the signal follows from a Jones matrix analysis of the optical system that gives an expression for the intensity of light on the detector:

\[
I \propto 1 + \frac{\tan^2 \psi - \tan^2 P}{\tan^2 \psi + \tan^2 P} \cos(2A(t)) + \frac{2\tan \psi \cos \Delta \tan P}{\tan^2 \psi + \tan^2 P} \sin(2A(t))
\]

(2.12)

where, \(P\) is the known polarizer azimuth angle and \(A(t)\) analyzer angle which is a harmonic function of time since the analyzer is continuously rotating. Equation (2.12) enables the computer to perform a Fourier analysis on the digitized signal voltage and calculate the values of \(\psi\) and \(\Delta\). This system works very well when the incoming light signal is almost circularly polarized, i.e. when the detector signal is almost constant. This
corresponds to the values of $a$ and $b$ in equation (2.11) being close to zero. Its weakness show up when $\Delta$ is near $0^0$ or $180^0$ (linearly polarized light). The loss of sensitivity of the analyzer is corrected by employing an auto retarder after the polarizer and before the sample that changes the retardation of the reflected light so that it is nearly circularly polarized.$^8$

Before each data collection run, a calibration was done to determine (through calculation) the absolute position of the polarizer and analyzer axes, and the relative position of the AC signal with respect to the DC signal. This calibration was performed by placing and aligning a 20 nm thick thermal oxide on Silicon film supplied with the instrument on the sample holder. The measurements from this sample calibrate the instrument at a wavelength of 500 nm and angle of incidence of $75^0$. After the calibration was complete, the calibration block was replaced by the sample to be studied that was again aligned using the alignment detector. For our experiments we left the alignment detector in because there was enough reflection from the sample to get good measurements.

Although it is possible to collect data at any number of desired angles, the data at the additional angles may not give any more information; this is especially true when the coatings are thinner than the probe beam wavelength or when there is a lot of refraction so that there is very little change in the path length inside the coating when the angle changes. Two or three angles should be sufficient for the program to analyze the data. For this reason, the ideal angles of incidence were determined first, these are angles where $\Delta$ is close to $90^0$ i.e. where the reflected light is circularly polarized, also called the
Pseudo-Brewster angle. The instrument manual suggests starting the data collection at incident angles between 65° and 75°, scanning over the wavelength range of the instrument and examining the values of $\Delta$. If $\Delta$ is close to 180°, then the angle of incidence needs to be increased, if it close to 0° the opposite is done. This is because for a particular wavelength, the value of delta changes from 180° to 0° as the angle of incidence is increased$^{82}$.

As discussed earlier, analysis is greatly facilitated by knowledge of some of layer parameters such as the number of layers and type of materials (dielectric or metal), the approximate thickness, and the process of coating (this may give us clues on grading and roughness) and known or approximately known (dispersive and complex) refractive index of each layer. These properties are necessary to decide the spectral range over which to collect the data. For example, if a material absorbs light over a certain wavelength range it may be necessary to take data in a different wavelength region. Fortunately, the indices of refraction for bulk samples of the materials used are available, and prediction of this behavior via the WVASE32®'s simulation mode is straightforward. For example, the material properties built in WVASE32® were used to predict the dispersion of the silicon dioxide layer$^{82,83}$.

As noted earlier, typically the cells used for liquid crystal displays have multiple layers as shown in Figure 2.14(c). Although VASE® is capable of determining thickness and optical constants of multiple layers; it was found that it was better to determine the optical properties of each layer separately because in our system the SiO$_2$ layer becomes difficult to distinguish once the other coatings are applied. Therefore in our experiments
we started with just a glass substrate and added the layers one at a time; the system was systematically made more complex. The first set of data was obtained on the system SiO$_2$ on glass. The next set of experiments added a layer of ITO on top of SiO$_2$ and so on. At each step the thickness and the optical parameters of the new layer are determined using ellipsometry and then fixed or used as a good starting point when a new layer is added.

![Schematic picture of the experimental protocol](image)

**Figure 2.14:** A schematic picture of the experimental protocol. Initial guesses for the film thicknesses are also shown the first time a layer is added. In figure (a) the thickness of SiO$_2$ layer is determined, with an initial guess of 25nm for its thickness. The ITO layer is added in figure (b). In this case, the thickness of the ITO film is determined while holding the SiO$_2$ thickness fixed at its value determined in part (a). Finally in figure (c) the polyimide layer is added and its properties determined. Here, the ITO and SiO$_2$ thickness are held constant or used as good staring points. Note that the underlying glass substrate is roughly 105 thicker than any film.

Data were obtained over a wavelength range from 300nm to 1700nm in 5nm steps in the reported experiments. The measurements were extended into the IR because of the optical effects of the ITO; this is discussed in greater detail later. Data were not collected in the 1340-1450nm range because the optical fiber supplied with the ellipsometer has an absorption in this range. The number of analyzer rotations per measurement was set at 50 to reduce noise. The initial incident angles chosen were 55°, 62.5° and 70°. In order to
ensure that there were no reflections from the back of the substrate, it was roughened using a sanding stone attached to a Dremmel® tool.

WVASE32® and the computer collected the data collection and provided plots of \( \psi \) and \( \Delta \) as a function of wavelength and angles of incidence. In order to obtain the desired parameters (thickness of the layer and index of refraction), the data were fitted to various models, and a model that best described the number and character of the layers was chosen. The data were first fit recursively by generating simulated data and then more accurately honed in using a nonlinear least squares fitting routine. Thus, once a model was built and good initial guesses for the thickness of various layers and optical properties were determined, data was generated using these parameters and compared with the experimental data. This process was repeated until a reasonable visual fit was obtained; then, a non-linear least squares fit was performed and the results checked for physical correctness and correlations between parameters. This two-step process was necessary because non-linear fitting schemes can be sensitive to poor starting points and from a given starting point may find a local rather than a global minimum. The criteria for the best fit are a) the fit has one of the smallest mean squared error (MSE) and b) the parameters used to determine the fit are not too strongly correlated. The MSE is a quantity that represents the quality of the match between experimental and modeled data, in WVASE32® it is calculated thus.
\[ MSE = \frac{1}{2N-M} \sum_{i=1}^{N} \left[ \left( \frac{\psi_i^{\text{model}} - \psi_i^{\text{experimental}}}{\sigma_{\psi,i}^{\text{experimental}}} \right)^2 + \left( \frac{\Delta_i^{\text{model}} - \Delta_i^{\text{experimental}}}{\sigma_{\Delta,i}^{\text{experimental}}} \right)^2 \right] \] (2.13)

where, \( N \) is the number of \((\psi, \Delta)\) pairs, \( M \) is the number of variable parameters in the model, \( \psi_i^{\text{model}} \) and \( \psi_i^{\text{experimental}} \) is the \( i^{th} \) \( \psi \) model and experimental data point respectively, \( \Delta_i^{\text{model}} \) and \( \Delta_i^{\text{experimental}} \) is the \( i^{th} \) \( \Delta \) model and experimental data point respectively, and \( \sigma_{\psi,i}^{\text{experimental}} \) and \( \sigma_{\Delta,i}^{\text{experimental}} \) is the standard deviation of the \( i^{th} \) \( \psi \) and \( \Delta \) data points respectively. For the correct fit, only one set of parameters should yield the obtained minimum. The correlation between the \( j^{th} \) and the \( k^{th} \) fit parameter is determined from the parameter correlation matrix obtained from the fit. This is the matrix that indicates how strongly a change in one parameter changes another. If the off diagonal elements of this matrix approach 1 or -1, it indicates a strong correlation between the parameters. Checking the obtained optical properties for physical correctness is another way of deciding on the correctness of the fit. For example, the real and imaginary parts of the index of refraction of a material are not independent. The Kramers-Kronig relation\(^9\) connects the real and imaginary parts of the index of refraction. Among other things, this relation means that the variation of the real index of refraction with frequency (dispersion) only occurs near frequencies of absorptions.

Initially the optical constants were varied independently at each measured wavelength by the program until the MSE was minimized. Since three incident angles were used and three parameters determined (thickness, real index of refraction and imaginary index of refraction) this was in fact possible. Consultations with a J.A.
Woolam, Inc., engineer\textsuperscript{88} indicated that it was better to parameterize the optical properties through an equation rather than doing a point-by-point fit. Such a parameterization involves choosing a continuous function dependent on several parameters, consistent with the Kramers-Kronig relationship, to describe the complex index of refraction. Fits using such a function reduce the total number of free parameters determined by the fit and reduce the effects of experimental noise. After a fit is complete, the parameters in the equation easily can be used to compare materials. This procedure does in fact provide less noisy information than comparing wavelength by wavelength point data.

The choice of model for the index of refraction depends on the material and to a certain extent the wavelength region chosen. The index of refraction of the glass and polyimide were parameterized by the Cauchy model given by\textsuperscript{76,89}:\n
$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$ \quad (2.14)\n
where, A, B, and C are real material dependent constants\textsuperscript{79,77}. The value of A is always positive and much larger than B or C. When this model is used in a fit, the strong correlation between the values of B and C needs to be monitored. Although it is possible for the values of either B or C to be negative, it is important to make sure that the result is physically reasonable, for example, making sure that the index does not increase with increasing wavelength. If both B and C are negative the results are always unphysical, so is the situation when B is negative when only A and B are used in the fit. Note that equation (2.14) only models the real part of the index of refraction. This assumes that the
extinction coefficient (k), or imaginary part of the index of refraction is zero over the experimental wavelength region. It also assumes that no wavelength of interest is larger than or terribly close to the wavelengths from which there is appreciable contribution to the Kramers-Kronig integral yielding the real part of the index. These assumptions are reasonable for all our materials except the transparent conductor ITO for which we will use another model described next.

A combination of the Lorentz (2.15) and Drude models were used to model the conducting ITO layer. These models assume that the index of refraction arises from a series of oscillators that model the free electrons in ITO. The Drude model is a Lorentz model (2.15) with zero center energy. The Drude model is especially useful in modeling the absorption of the free carriers near the Infrared region\textsuperscript{90, 91}. Here the dielectric constant is given by

\[
\bar{\varepsilon}(\nu) = \varepsilon(\infty) + \sum_k \frac{A_k}{E_k^2 - (\nu)^2 - iB_k \nu} \tag{2.15}
\]

where \(A_k\) is the amplitude of the \(k^{th}\) oscillator, \(E_k\) is the center energy of the \(k^{th}\) oscillator, \(B_k\) is the broadening of the \(k^{th}\) oscillator that leads to absorption, \(\nu\) is the photon energy, and \(\varepsilon(\infty)\) is the value of the real part of the dielectric constant at very large photon energies. The number and positions of the oscillators needed are determined by looking at the pseudo dielectric constant calculated from the experimental data.

Once a good fit has been obtained an even lower MSE value (lower \(\chi^2\)) was sometimes obtained by adding to the model surface roughness and grading. WVASE32® models roughness by adding an effective medium approximation (EMA) layer of the
material with 50% voids. There are three models employed for the EMA in WVASE32®: Linear, Maxwell-Garnett, and Bruggemann EMA. Grading is implemented by replacing the layer suspected of grading with multiple layers of the same material, each with optical properties that vary to mimic grading. For example, the absorption of the layers can gradually increase with each layer. In ITO films grading may be needed due to the method of deposition or post deposition annealing. It is important to realize that this is modeling and may not correspond to the actual physical situation. There needs to be good physical reasons for assuming grading or surface roughness.
2.3.3 Data and Analysis

2.3.3.1 The SiO₂ on Glass Layer

The samples used for these experiments were made from a single 35 cm square piece of ITO coated glass cut into appropriate sized samples. This was done to minimize variations that may occur in various sheets of glass. This glass was obtained Colorado Concepts Coating; it had a passivating SiO₂ layer on top of the glass and ITO of sheet resistance of 100Ω/□ on top of the SiO₂. To characterize the SiO₂ layer, the glass was placed in an acid bath to remove the ITO. The backside of the glass was then roughened as described above.

The ellipsometric data were collected from 300 to 1700 nm at light incident at 55°, 62.5° and 70° (Figure 2.15). The data collected were fitted by fixing the thickness of the substrate (1.1 mm) and using optical constants of silicon dioxide that were taken from literature⁹⁵, while the thickness of the SiO₂ film and the optical parameters of the Cauchy relationship for the glass substrate were fitting parameters. The thickness of the glass substrate had no effect on the thickness obtained for the SiO₂ layer. The best fit for the thickness of the SiO₂ film was 262 ± 2 Angstroms (Table 11). The fit using the fitted parameters and the Cauchy form for the index of refraction of glass obtained a lower MSE than was obtained using the built in file of optical constants for glass in WVASE32®. This is not surprising in light of the large number of glasses of slightly different index of refraction, and indicates the care needed in blindly accepting off the shelf values when performing ellipsometry.
Figure 2.15: Experimental and fit ellipsometric data of silicon dioxide on a glass substrate. Ellipsometric data were taken for light incident at 55°, 62.5°, and 70° (from the normal) for wavelengths between 300nm to 1700nm, with the autoretarder on. Data were not taken between 1340 to 1450nm because the optical fiber in the instrument absorbs in this wavelength range. The parameters used to model and fit the data are shown in the table below.
Table 11: Status and final values of parameters used to fit the ellipsometric data above. The optical properties for silicon dioxide were taken from literature, while the glass was fitted using Cauchy fit parameters. The final MSE of the fit was 1.533

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Parameter Status during Fit</th>
<th>Final Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon Dioxide</td>
<td>Varied</td>
<td>262 ± 2 Angstroms</td>
</tr>
<tr>
<td>Thickness</td>
<td>Fixed</td>
<td>Fixed</td>
</tr>
<tr>
<td>Glass Thickness</td>
<td>Fixed</td>
<td>1.1 mm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Glass Optical Constants (Cauchy)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Varied</td>
<td>1.5013 ± 0.0003</td>
</tr>
<tr>
<td>B</td>
<td>Varied</td>
<td>0.0083 ± 0.0002</td>
</tr>
<tr>
<td>C</td>
<td>Varied</td>
<td>-0.00043 ± 0.00003</td>
</tr>
</tbody>
</table>

2.3.3.2 The ITO Layer

The ellipsometric data for ITO layer was collected using the same settings for the wavelength range and incident angles used above. To determine the parameters relevant to the ITO layer from this data, the parameters that described the silicon dioxide and glass substrate obtained above were used and fixed in value. The ITO layer was modeled using a built in optical parametric file “ITO_L2” included with the software WVASE32®. The ITO_L2 file models the ITO layer using two oscillators, a Drude oscillator and a Lorentz oscillator with center energy 5.75eV. By reference to equation (2.15) it is clear that this ITO model has five parameters that need to be determined (two oscillator strengths, two energy dissipations, and the high frequency dielectric constant). In addition to these parameters, it was necessary to use a grading and a surface roughness layer to obtain a good fit.
Obtaining a better fit is not a physical basis for including surface roughness and layer gradation. When ITO is deposited it is amorphous, it has to be annealed in oxygen to make it conductive. Electron microscopy studies of ITO films on glass that are manufactured in the same manner as ours indicate that the surface is not smooth and flat. It is accurately portrayed as a random series of hills and mountains\textsuperscript{94}. The rapid crystallization of the amorphous ITO during annealing is thought to contribute to this\textsuperscript{96}. Thus, a model for surface roughness with voids is appropriate. Since ITO is a semiconductor made of both indium and tin, it commonly observed that the composition of the deposited layer is not uniform\textsuperscript{97, 98}. The surface of the film usually has a higher carrier density\textsuperscript{99} than the bottom due to creation of oxygen vacancies. This will show up a higher absorption in the IR for the top layer. Thus some grading of the index of refraction is also expected.

In WVASE32\textsuperscript{®} a model called “gradedsimple.mat” is available to model layers with a small amount of grading. This layer was added after an initial fit using ITO_L2 was completed. The parameters from the ITO_L2 layer were used as a starting point for the “gradedsimple.mat” layer (Table 12). The other starting parameters needed by this model are the number of layers that the ITO layer will be divided to model grading, the percentage variation of the index from the top to the bottom, and finally a number called the “exponent” that determines the shape of the grading profile\textsuperscript{4}. The surface roughness layer is modeled in the program as a layer of homogeneous material (defined through ITO_L2) half filled with voids, the thickness of this layer is the only fit parameter. Using

\textsuperscript{4} Note that a linear grade would have an exponent of one.
this model of with ten layers for grading and a 50% void layer on top it was possible calculate the thickness of the ITO.

During a fitting procedure it is essential to try and find a model that can describe the system and give the information needed with the least possible number of unknowns. With this in mind, it was found that eliminating some wavelength ranges enabled us to reduce parameters needed to fit the data. For example, eliminating data below 500nm reduces the ITO_L2 model to just one oscillator, the Drude oscillator. The data lost by doing this will not affect the fit of the polyimide layer, in fact including this wavelength range for the polyimide layer would have required additional and unnecessary parameters to account for some absorption of polyimide in the UV range.

Using the “gradedsimple.mat”, surface roughness layers the fit found the thickness of the graded layer to be 130 ± 3 Angstroms with a rough surface layer of thickness 114 ± 6 Angstroms. The quality of the fit, as quantified by the MSE was not as good as that obtained for the SiO₂ layer, but quite acceptable. A plot of the optical constants for the bottom and top layers of the ITO obtained from the fit is shown in Figure 2.17. Note that the top layer has a slightly higher absorption in the IR region, suggesting a higher carrier density at the surface. In the same figure the optical properties found from the ITO_L2 layer that were used as an input for the graded layer are shown.
Figure 2.16: Experimental and fit ellipsometric data obtained from a layer of ITO on a glass substrate passivated by silicon dioxide. Ellipsometric data were taken for light incident at 55°, 62.5°, and 70° from 300nm to 1700nm, with the autoretarder on. Data were not taken between 1340 to 1450nm because the optical fiber in the instrument absorbs in this wavelength range. The parameters used to model and fit the data are shown in the next table.
Table 12: Status, initial and final values of parameters used to fit the ellipsometric from the ITO layer on top of silicon dioxide passivated glass. The final MSE of the fit was 3.708. Note that the values of ITO_L2 were used as parameters for the graded layer.

<table>
<thead>
<tr>
<th>Parameter Description</th>
<th>Initial Value</th>
<th>Parameter Status during Fit</th>
<th>Final Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Roughness</td>
<td>100 Angstroms</td>
<td>Varied</td>
<td>114 ± 6 Angstroms</td>
</tr>
<tr>
<td>Thickness of Graded ITO layer</td>
<td>200 Angstroms</td>
<td>Varied</td>
<td>130 ± 3 Angstroms</td>
</tr>
<tr>
<td># of grade layers</td>
<td>10 Fixed</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Variation (graded layer)</td>
<td>10% Varied</td>
<td></td>
<td>85 ± 1 %</td>
</tr>
<tr>
<td>Exponent (graded layer)</td>
<td>1 Fixed</td>
<td></td>
<td>1.0 ± 0.2</td>
</tr>
</tbody>
</table>

**ITO_L2 Parameters**

<table>
<thead>
<tr>
<th>Parameter Description</th>
<th>Initial Value</th>
<th>Parameter Status during Fit</th>
<th>Final Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Freq. Dielectric Constant ε(∞)</td>
<td>4 Varied</td>
<td></td>
<td>3.68 ± 0.06</td>
</tr>
<tr>
<td>Amplitude of Osc#1 (A₁)</td>
<td>2.5 Varied</td>
<td></td>
<td>3.28 ± 0.05</td>
</tr>
<tr>
<td>Broadening of Osc#1 (Br₁)</td>
<td>0.2 Varied</td>
<td></td>
<td>0.0982 ± 0.0006</td>
</tr>
<tr>
<td>Amplitude of Osc#2 (A₂)</td>
<td>NOT USED NOT USED</td>
<td></td>
<td>N/A</td>
</tr>
<tr>
<td>Broadening of Osc#2 (Br₂)</td>
<td>NOT USED NOT USED</td>
<td></td>
<td>N/A</td>
</tr>
</tbody>
</table>
Figure 2.17: A plot of the optical constants of the ITO layer obtained from the parametric fit to the experimental data shown in Figure 2.16. The optical properties from the ITO_L2 layer (shown in solid and broken black lines) were used as an input for the graded layer whose top and bottom are shown here. Solid symbols correspond to the real index of refraction, while the extinction coefficients are indicated by the open symbols. Note the higher absorption at longer wavelengths in the top layer of the graded ITO layer. Data were not taken between 1340 to 1450nm because the optical fiber in the instrument absorbs in this wavelength range.
2.3.3.3 The Polyimide Layer on ITO Glass

The above analysis was performed on several samples, and the properties of the SiO$_2$ and ITO layers characteristics were reproducibly obtained from analysis of the data. These well characterized substrates were then coated with a solution of polyamic acid (Pyralin® PI2555) (PAA) solution that was thermally polymerized to form the polyimide films. The acid solution was spun coated at different spin speeds and several solution concentrations. The relationship between concentration of PAA in the solution and film thickness is known$^{100}$. The coating and concentration parameters of the samples studies are shown in Table 13. The stock PAA was diluted to these concentrations using NMP (N-Methyl-2-Pyrrolidone) and then following the manufacturer’s directions these films were pre-baked on a hot plate for 90 seconds at 90$^\circ$C then baked in an oven at 275$^\circ$C for an hour.

Table 13: The coating and concentration parameters used to coat the polyimide films

<table>
<thead>
<tr>
<th>Coating #</th>
<th>PAA Concentration (%)</th>
<th>Spin Speed (rpm)</th>
<th>Polyimide Thickness (Angstroms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3000</td>
<td>276 ± 2</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1500</td>
<td>460 ± 2</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>3000</td>
<td>482 ± 3</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>1500</td>
<td>762 ± 4</td>
</tr>
</tbody>
</table>
These ellipsometric data were collected for these substrates coated with polyimide using the same setting described above. In order to fit the ellipsometric data, the properties of the glass and silicon dioxide layers were held at the values found above, while the ITO and Polyimide layer properties were varied. The polyimide layer was modeled using the Cauchy equation (2.14).

Obtaining the best fit to the data that gave both a reasonable MSE and results that were consistent for all four coatings involved changing the model more than once. For example, the ITO parameters found above could no longer be used; they just served as a good starting point. First, the surface roughness layer had to be replaced because the voids were now probably filled with polyimide, therefore this layer was replaced with an intermix layer that modeled a transition layer from ITO to polyimide. This intermix layer had to be eventually removed because the fit kept on returning zero for the thickness of this layer. It was also found that replacing the graded layer with a uniform layer improved the fit, because it was difficult for the program to obtain the grading parameters without them being over-determined. Fixing the grading parameters to those found in the earlier studies gave poor fits to the data. The other major improvement in the fits came from excluding data below 500nm. As explained earlier, exclusion of this data allowed for reducing the number of terms needed to fit the data. By avoiding this region, the need for the Lorentz oscillator to model the ITO was eliminated and so was the term to model absorption from the polyimide layer. Adding these terms would have not given any more information to determine the thickness of the films. Finally, reducing the number of terms in the Cauchy equation to the first two leading terms gave more consistent results.
Therefore the final model consists of the glass and silicon dioxide layers whose parameters were determined earlier, the ITO layer modeled using the Drude model, and a polyimide layer modeled using the two leading terms (A and B) of the Cauchy equation for dispersion.

The ellipsometric data for the 2% solids solution coated at 3000rpm the ellipsometric data is shown in Figure 2.18 while the graphs of the optical constant are shown in Figure 2.19 with the fit results in Table 14, in the same order that coated at 1500rpm is shown in Figure 2.20, Figure 2.21 and Table 15, for the 4% solids solution coated at 3000rpm it is shown in Figure 2.22, Figure 2.23 and Table 16 and finally the 4% solids solution coated at 1500rpm it is shown in Figure 2.24, Figure 2.25 and Table 17.
Figure 2.18: Experimental and fit ellipsometric data obtained from a layer of polyimide spun coated on ITO glass. The solution used to produce the film contained 2% polyamic acid. The solution was spun coated at 3000rpm before being thermally cured. Ellipsometric data were taken for light incident at 55°, 62.5°, and 70° from 300nm to 1700nm, with the autoretarder on. Data were not taken between 1340 to 1450nm because the optical fiber in the instrument absorbs in this wavelength range. The parameters used to model and fit the data are shown in the table below.
Table 14: Status, initial and final values of parameters used to fit the ellipsometric data of a polyimide film on ITO glass coated from a 2% solids solution at 3000rpm. The final MSE of the fit was 2.261.

<table>
<thead>
<tr>
<th>Parameter Status during Fit</th>
<th>Initial Value</th>
<th>Final Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness of Polyimide Layer</td>
<td>Varied</td>
<td>276 ± 2 Angstroms</td>
</tr>
<tr>
<td>Thickness of ITO Layer</td>
<td>Varied</td>
<td>197 ± 2 Angstroms</td>
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</table>

**Cauchy (Polyimide) Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial Value</th>
<th>Status</th>
<th>Final Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Varied</td>
<td>1.628 ± 0.002</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Varied</td>
<td>0.0527 ± 0.0006</td>
<td></td>
</tr>
</tbody>
</table>

**ITO Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial Value</th>
<th>Status</th>
<th>Final Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Freq. Dielectric Constant $\varepsilon(\infty)$</td>
<td>4</td>
<td>Varied</td>
<td>4.17 ± 0.01</td>
</tr>
<tr>
<td>Amplitude of Osc#1 ($A_1$)</td>
<td>2.5</td>
<td>Varied</td>
<td>2.24 ± 0.01</td>
</tr>
<tr>
<td>Broadening of Osc#1 ($B_{r1}$)</td>
<td>0.2</td>
<td>Varied</td>
<td>0.0956 ± 0.0008</td>
</tr>
</tbody>
</table>
Figure 2.19: A plot of the optical constants of the ITO and Polyimide layer obtained from the parametric fit to the experimental data for a 2% polyamic acid solution spun coated at 3000rpm before being thermally cured. The real index of refraction are solid symbols or lines, while the extinction coefficients are the open symbols or broken lines. Data were not taken between 1340 to 1450nm because the optical fiber in the instrument absorbs in this wavelength range.
Figure 2.20: Experimental and fit ellipsometric data obtained from a layer of polyimide spun coated on ITO glass. The solution used to produce the film contained 2% polyamic acid. The solution was spun coated at 1500rpm before being thermally cured. Ellipsometric data were taken for light incident at 55°, 62.5°, and 70° from 300nm to 1700nm, with the autoretarder on. Data were not taken between 1340 to 1450nm because the optical fiber in the instrument absorbs in this wavelength range. The parameters used to model and fit the data are shown in the table below.
Table 15: Status, initial and final values of parameters used to fit the ellipsometric data of a polyimide film on ITO glass coated from a 2% solids solution at 1500rpm. The final MSE of the fit was 2.828.

<table>
<thead>
<tr>
<th>Parameter Status during Fit</th>
<th>Initial Value</th>
<th>Final Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness of Polyimide Layer</td>
<td>Varied</td>
<td>460 ± 2 Angstroms</td>
</tr>
<tr>
<td>Thickness of ITO Layer</td>
<td>Varied</td>
<td>210 ± 2 Angstroms</td>
</tr>
</tbody>
</table>

Cauchy (Polyimide) Parameters

<table>
<thead>
<tr>
<th>Parameter Status during Fit</th>
<th>Initial Value</th>
<th>Final Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Varied</td>
<td>1.625 ± 0.001</td>
</tr>
<tr>
<td>B</td>
<td>Varied</td>
<td>0.0502 ± 0.0006</td>
</tr>
</tbody>
</table>

ITO Parameters

<table>
<thead>
<tr>
<th>Parameter Status during Fit</th>
<th>Initial Value</th>
<th>Final Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Freq. Dielectric Constant $\varepsilon(\infty)$</td>
<td>Varied</td>
<td>4.09 ± 0.01</td>
</tr>
<tr>
<td>Amplitude of Osc#1 $(A_1)$</td>
<td>Varied</td>
<td>2.337 ± 0.008</td>
</tr>
<tr>
<td>Broadening of Osc#1 $(B_{r1})$</td>
<td>Varied</td>
<td>0.09998 ± 0.0008</td>
</tr>
</tbody>
</table>
Figure 2.21: A plot of the optical constants of the ITO and Polyimide layer obtained from the parametric fit to the experimental data for a 2% polyamic acid solution spun coated at 1500rpm before being thermally cured. The real index of refraction is the solid symbols or lines, while the extinction coefficients are the open symbols or broken lines. Data were not taken between 1340 to 1450nm because the optical fiber in the instrument absorbs in this wavelength range.
Figure 2.22: Experimental and fit ellipsometric data obtained from a layer of polyimide spun coated on ITO glass. The solution used to produce the film contained 4% polyamic acid. The solution was spun coated at 3000rpm before being thermally cured. Ellipsometric data were taken for light incident at 55°, 62.5°, and 70° from 300nm to 1700nm, with the autoretarder on. Data were not taken between 1340 to 1450nm because the optical fiber in the instrument absorbs in this wavelength range. The parameters used to model and fit the data are shown in the table below.
Table 16: Status, initial and final values of parameters used to fit the ellipsometric data of a polyimide film on ITO glass coated from a 4% solids solution at 3000rpm. The final MSE of the fit was 3.047.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial Value</th>
<th>Parameter Status during Fit</th>
<th>Final Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness of Polyimide Layer</td>
<td>Varied</td>
<td>482 ± 3 Angstroms</td>
<td></td>
</tr>
<tr>
<td>Thickness of ITO Layer</td>
<td>Varied</td>
<td>206 ± 2 Angstroms</td>
<td></td>
</tr>
</tbody>
</table>

**Cauchy (Polyimide) Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial Value</th>
<th>Parameter Status during Fit</th>
<th>Final Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Varied</td>
<td>1.623 ± 0.001</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Varied</td>
<td>0.0502 ± 0.0007</td>
<td></td>
</tr>
</tbody>
</table>

**ITO Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial Value</th>
<th>Parameter Status during Fit</th>
<th>Final Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Freq. Dielectric Constant $\varepsilon(\infty)$</td>
<td>4</td>
<td>Varied</td>
<td>4.14 ± 0.02</td>
</tr>
<tr>
<td>Amplitude of Osc#1 ($A_1$)</td>
<td>2.5</td>
<td>Varied</td>
<td>2.26 ± 0.01</td>
</tr>
<tr>
<td>Broadening of Osc#1 ($B_r_1$)</td>
<td>0.2</td>
<td>Varied</td>
<td>0.09642 ± 0.0009</td>
</tr>
</tbody>
</table>
Figure 2.23: A plot of the optical constants of the ITO and Polyimide layer obtained from the parametric fit to the experimental data for a 4% polyamic acid solution spun coated at 3000rpm before being thermally cured. The real index of refraction is the solid symbols or lines, while the extinction coefficients are the open symbols or broken lines. Data were not taken between 1340 to 1450nm because the optical fiber in the instrument absorbs in this wavelength range.
Figure 2.24: Experimental and fit ellipsometric data obtained from a layer of polyimide spun coated on ITO glass. The solution used to produce the film contained 4% polyamic acid. The solution was spun coated at 1500rpm before being thermally cured. Ellipsometric data were taken for light incident at 52.5°, 60°, and 67.5° from 300nm to 1700nm, with the autoretarder on. Data were not taken between 1340 to 1450nm because the optical fiber in the instrument absorbs in this wavelength range. The parameters used to model and fit the data are shown in the table below.
Table 17: Status, initial and final values of parameters used to fit the ellipsometric data of a polyimide film on ITO glass coated from a 4% solids solution at 1500rpm. The final MSE of the fit was 3.751.

<table>
<thead>
<tr>
<th>Parameter Status during Fit</th>
<th>Initial Value</th>
<th>Final Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness of Polyimide Layer</td>
<td>Varied</td>
<td>762 ± 4 Angstroms</td>
</tr>
<tr>
<td>Thickness of ITO Layer</td>
<td>Varied</td>
<td>205 ± 2 Angstroms</td>
</tr>
</tbody>
</table>

**Cauchy (Polyimide) Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Status</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Varied</td>
<td>1.635 ± 0.001</td>
</tr>
<tr>
<td>B</td>
<td>Varied</td>
<td>0.0414 ± 0.0009</td>
</tr>
</tbody>
</table>

**ITO Parameters**

<table>
<thead>
<tr>
<th>Parameter Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Freq. Dielectric Constant ( \varepsilon(\infty) )</td>
<td>4</td>
</tr>
<tr>
<td>Amplitude of Osc#1 ( A_1 )</td>
<td>2.5</td>
</tr>
<tr>
<td>Broadening of Osc#1 ( B_1 )</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Figure 2.25: A plot of the optical constants of the ITO and Polyimide layer obtained from the parametric fit to the experimental data for a 4% polyamic acid solution spun coated at 1500rpm before being thermally cured. The real index of refraction is the solid symbols or lines, while the extinction coefficients are the open symbols or broken lines. Data were not taken between 1340 to 1450nm because the optical fiber in the instrument absorbs in this wavelength range.
2.3.4 Summary of Results

The thickness of the SiO$_2$ layer was not varied, because variation did not improve the fit. Moreover the layer is index matched to the glass, thus any analysis after other layers are added is difficult. Therefore for all our analyses the thickness and optical constants of the SiO$_2$ layer, were fixed as found earlier above.

The ITO layer had to be fitted for all the experiments. The typical values for $\varepsilon(\infty)$, the value of the real part of the dielectric constant was $4.13 \pm 0.01$, the amplitude and broadening of the Drude model were $2.27 \pm 0.02$ and $0.0973 \pm 0.0008$ respectively. The typical thickness of the ITO layer was $205 \pm 2$ Angstroms. This thickness is typical for the resistivity of the ITO ($100 \, \Omega/\square$).

The thickness of the polyimide films were found to depend on the concentration of the solution and the spin speed. The thickness of the film made from a solution of 2% solids spun at 3000rpm was $276 \pm 2$ Angstroms, while a film made from the same solution but spun at 1500rpm was $460 \pm 2$ Angstroms. For film made of a 4% solids solution spun at 3000rpm the thickness was $482 \pm 3$ Angstroms, while the film spun at a slower 1500rpm was $762 \pm 4$ Angstroms. These results are summarized in Table 18 below. The results show that the thickness of the final cured film depends on the spin speed and solution concentration.
Table 18: Summary of the results from the ellipsometric measurements taken from polyimide films coated on ITO glass used to make sample holders for the dielectric mixtures. The results show that the thickness of the final cured films depend on the spin speed and solution concentration.

<table>
<thead>
<tr>
<th>Polyimide Conc.</th>
<th>2%</th>
<th>4%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin Speed</td>
<td>3000rpm</td>
<td>1500rpm</td>
</tr>
<tr>
<td>MSE</td>
<td>2.261</td>
<td>2.828</td>
</tr>
<tr>
<td>Polyimide Layer Thickness (Angstroms)</td>
<td>276 ± 2</td>
<td>460 ± 2</td>
</tr>
</tbody>
</table>

**Polyimide Cauchy Parameters**

| A                | 1.628± 0.002 | 1.625± 0.001 | 1.623± 0.001 | 1.635± 0.001 |
| B                | 0.0527± 0.0006 | 0.0502 ± 0.0006 | 0.0503± 0.0007 | 0.0414± 0.0009 |
2.4 Discussion and Summary

In order to obtain meaningful dielectric responses of the materials being studied, there are properties of the sample holder (the cell) that need to be well characterized. These include the response of the empty cell, the resistance of the electrode (ITO) and the presence type and thickness of the alignment layer. In this chapter it has been shown that the sample holder cannot be assumed to be an ideal capacitor as it has frequency dependence due to the resistance of the electrodes. The alignment layer is also critical, if the alignment layer is too thin, nonexistent or homeotropic, the response of the sample is masked by electrode polarization and conductivity. With these findings the cell chosen for standard measurements was the cell coated with 4% polyimide 2555 spun at 3000rpm (482 angstroms thick). Although it would have been preferable to use the thicker film spun at 1500rpm (761 angstroms thick), the higher spin speed was chosen due to yield issues.
CHAPTER 3

The Individual Components

This chapter covers the dielectric measurements and analysis of the components used to make the binary and ternary mixtures studied. There are essentially three components in the systems studied; a liquid crystal, a surfactant and an organic solvent. The purpose and choice of these components will be discussed in a later section. The measurements of these individual components are reported as a reference to be compared to the results obtained in the multi-component systems.

From the previous chapter it is clear that we needed to standardize our sample holder. Therefore, the cells were constructed with the same ITO glass and etched to form an electrode area of 1 cm$^2$ spaced at 10 microns. For cells that promoted a planar alignment, a 4% solution of Dupont’s PI2555 was spun coated at 3000rpm and imidized at 275°C for an hour and then rubbed with a velvet cloth. For the cells promoting homeotropic alignment, the same procedure was followed using Nissan’s 7511 as the precursor and no rubbing was performed.
3.1 Liquid Crystals

The measurements for the liquid crystals E7 and E31 were presented earlier in the previous chapter. A few commercially available ferroelectric liquid crystals (FLC’s) were also measured. These were filled into cells whose inner surfaces were coated with PI255® and rubbed and assembled for planar alignment. The cells were then heated to a temperature above the isotropic-nematic transition and cooled at 0.2 degrees per minute using an Instek hot stage. Cooling slowly from the isotropic promoted a good bookshelf structure\textsuperscript{101,102}, where the smectic C$^*$ director is perpendicular to the substrate (Figure 3.1).

\[
\begin{align*}
\vec{c} & \quad \vec{p} \\
\theta & \quad \phi \Delta
\end{align*}
\]

Figure 3.1: The definitions of the various angles and vectors used to describe the orientation of a ferroelectric liquid crystal. $\vec{P}$ is the vector representing $\vec{c} \times \vec{k}$, which is the spontaneous polarization of the ferroelectric liquid crystal molecule. $\theta$ is the tilt angle, $\phi$ is the azimuthal angle, $\Delta \phi$ is the change in the azimuthal angle when an electric field is applied.
In this alignment the contribution from the spontaneous polarization to the dielectric response is enhanced. As an example, the dielectric response of the ferroelectric crystal FELIX® 017-100 before and after this alignment procedure is shown in Figure 3.2. Note that this mode has a low relaxation frequency of less than a 1000 Hertz\(^{103}\). This contribution is known as the Goldstone mode\(^{104,105}\) which involves the variation of the azimuthal angle \(\phi\) when an electric field is applied parallel to the \(\mathbf{c}\) vector

\[
\Delta \varepsilon_{\text{Goldstone}} = \frac{1}{8\pi \varepsilon_0 K} \left( \frac{pP}{\theta} \right)^2
\]

where, \(\Delta \varepsilon_{\text{Goldstone}}\) is the contribution to the dielectric response from the Goldstone mode, \(\varepsilon_0\) is the permittivity of free space (8.854*10\(^{-12}\)F/m), \(K \sim 10^{-11}\) is the elastic constant associated with the deformation of the helical structure, \(p\) is the helical pitch, \(P\) is the spontaneous polarization described earlier and \(\theta\) is the tilt angle.

Figure 3.2: The dielectric responses of the ferroelectric liquid crystal FELIX 017-100. The liquid crystal was aligned by cooling from the isotropic temperature at a rate of 0.2°C / min. The response before alignment is shown using open triangles while the aligned data is shown using solid triangles.
The parameters of FELIX® 017-100 and the other FLC’s studied are shown in Table 19. From this information and using equation (3.1) it was possible to calculate the expected contribution from the Goldstone mode for these materials.

**Table 19: The expected Goldstone mode contribution of the ferroelectric liquid crystals studied calculated from the properties provided in the suppliers specification sheet.**

<table>
<thead>
<tr>
<th>Liquid Crystal</th>
<th>Spontaneous Polarization nC/cm²</th>
<th>pitch</th>
<th>Tilt Angle</th>
<th>Expected ( \Delta \varepsilon ) Goldstone</th>
</tr>
</thead>
<tbody>
<tr>
<td>FELIX 016-100</td>
<td>-10.5</td>
<td>29</td>
<td>27.15</td>
<td>1.86E+4</td>
</tr>
<tr>
<td>FELIX 017-100</td>
<td>47</td>
<td>18</td>
<td>27.55</td>
<td>1.39E+5</td>
</tr>
<tr>
<td>CS 2005</td>
<td>-72.7</td>
<td>14</td>
<td>43</td>
<td>8.27E+4</td>
</tr>
<tr>
<td>MLC4851-100</td>
<td>13.8</td>
<td>25.2</td>
<td>55</td>
<td>5.90E+3</td>
</tr>
</tbody>
</table>

Figure 3.3 shows the response of the other ferroelectric liquid crystals after alignment, from this response a table was constructed showing the Goldstone relaxation frequency and the values of the apparent dielectric response at frequencies well below the relaxation (Table 20). The values of the dielectric response are much lower than those expected, this is due to the very low external field applied (0.01/micron) which was probably not sufficient to unwind the helix. The polarizing optical microscope pictures of the cells before and after alignment are shown in Figure 3.4 and Figure 3.5.
Figure 3.3: The apparent dielectric responses of a select few ferroelectric liquid crystals. The liquid crystals were aligned by cooling from the isotropic temperature at a rate of 0.2°C / min. The real responses are shown on the left while the imaginary response is on the right. With the exception of FELIX 16, the Goldstone mode is approximately 1 kHz.

Table 20: The Goldstone mode relaxation frequency and the dielectric responses determined from the dielectric measurements of the FLC’s above. The expected contribution from the Goldstone mode to the dielectric response is also reported.
Figure 3.4: Polarizing optical microscope photographs before aligning FELIX-016 (a), FELIX 017(c), after alignment of the same (b) and (d).
Figure 3.5: Polarizing optical microscope photographs before aligning CS2005 (a) and MLC4851(c), and after alignment of the same (b) and (d).
3.2 Solvents

Two water soluble solvents were used in the mixtures. These solvents on their own have high dielectric constants that arise from their large dipole moments. N-Methylformamide was obtained from Aldrich (catalog no. 473936) and was used without further purification (Figure 3.6a). It has a high static dielectric constant of about 182.4, a dipole moment of about 3.8D\(^{106}\) and a boiling point of 198°C. The other solvent was N-Methyl-2-pyrrolidone (Figure 3.6b) used without further purification from Aldrich (catalog number M6762). It has a dipole moment of 4.09D\(^{107}\) and a boiling point of 202°C. Its dielectric constant, which is ranges from 340 to 200 at -40°C and 25°C respectively has been the subject of very extensive study\(^{108,109,110}\).

![Molecular structures](a)(b)

Figure 3.6: (a) The molecular structure of the solvent N-Methylformamide, and (b) the molecular structure of the solvent N-Methyl-2-pyrrolidone (NMP)

The measurements of the dielectric constants of these solvents filled in the ITO glass cells are shown in Figure 3.7. These solvents are too lossy as pure solvents to be used in dielectric capacitors. However, there may be small amounts of water in these solvents that contribute significantly to their loss. Nevertheless, the data were fitted to the same circuit used in the previous chapter, but is shown here again for reference in Figure 3.8.
Recall that the impedance of the constant phase element is $Z_{\text{CPE}} = Q(j\omega)^{-n}$, which helps us model surface roughness of the electrode, conductivity and electrode polarization. Therefore from the fit, whose results are shown in Table 21, NMF has a much larger portion of its apparent dielectric response originating from the Constant Phase Element (CPE). Note that the value of $n$ in NMF is approaching that of a Warburg element ($n=0.5$) which models infinite diffusion.

![Graph](image.png)

Figure 3.7: The apparent dielectric response of the organic solvents used as components in the mixtures studied. The solvents are NMP (1-Methyl-2-pyrrolidione) and NMF (N-Methylformamide). The real response as a function of frequency is shown on the right while the imaginary is shown on the left.
Figure 3.8: The equivalent circuit used to model the dielectric response of the solvents NMP and NMF. The circuit contains a resistor in series with a capacitor and constant phase element in parallel.

Table 21: The results of fitting a circuit made of a resistor in series with a capacitor and constant phase element in parallel. The capacitance of the capacitor is reported as a dielectric constant.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>R (Ohms)</th>
<th>CPE</th>
<th>ε</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Q</td>
<td>n</td>
</tr>
<tr>
<td>NMF</td>
<td>36.82</td>
<td>1071</td>
<td>0.56</td>
</tr>
<tr>
<td>NMP</td>
<td>53.41</td>
<td>313.5</td>
<td>0.66</td>
</tr>
</tbody>
</table>
3.3 Surfactants

Several classes of surfactants were studied including ionic and nonionic surfactants, Fluorinated surfactants, and tri-block polymeric surfactants. The list of surfactants screened is shown in Table 22. A short description of the surfactants follows.

Table 22: List and types of surfactants screened

<table>
<thead>
<tr>
<th>ID</th>
<th>Chemical Name</th>
<th>Type of Surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Poly(dimethyl Siloxane-b-ethylene oxide)</td>
<td>Polymeric block</td>
</tr>
<tr>
<td>S2</td>
<td>Poly(diallyl dimethyl ammonium chloride)</td>
<td>Polymeric Cationic</td>
</tr>
<tr>
<td>S3</td>
<td>Dioctyl Sulfo succinate Sodium Salt</td>
<td>Anionic</td>
</tr>
<tr>
<td>S4</td>
<td>Dodecyl benzene sulphonic acid</td>
<td>Anionic</td>
</tr>
<tr>
<td>S5</td>
<td>Sodium dodecylbenzenesulfonate</td>
<td>Anionic</td>
</tr>
<tr>
<td>S6</td>
<td>Perfluoroundecanoic acid</td>
<td>Fluorinated</td>
</tr>
<tr>
<td>S7</td>
<td>Didodecyl dimethylammonium bromide</td>
<td>Cationic</td>
</tr>
<tr>
<td>S8</td>
<td>Novek FC4430</td>
<td>Fluorinated</td>
</tr>
<tr>
<td>S9</td>
<td>Novek FC4432</td>
<td>Fluorinated</td>
</tr>
<tr>
<td>EPE0-EPE4</td>
<td>Poly(ethylene glycol-b-poly(propylene glycol)-b-poly(ethylene glycol)</td>
<td>Polymeric Triblock</td>
</tr>
<tr>
<td>PEP0-PEP1</td>
<td>Poly(propylene glycol-b-poly(ethylene glycol)-b-poly(propylene glycol)</td>
<td>Polymeric Triblock</td>
</tr>
</tbody>
</table>
Polymer based surfactants

S1, Poly(dimethylsiloxane-b-ethylene oxide) CAS number 68937-54-2, is a diblock copolymer surfactant that has a hydrophobic block due to the siloxane block and a hydrophilic block due to ethylene oxide as shown in Figure 3.9a. The ratio of the hydrophobic to the hydrophilic part is 80:20.

S2, Poly (diallyl dimethyl ammonium chloride) CAS number 26062-79-3 is a water soluble cationic polymer that has an affinity to negatively charged species (Figure 3.9b).

S7, Didodecylidimethylammonium bromide CAS number 3282-73-3 is a non-polymeric version of S2 (cationic surfactant) (Figure 3.9c).

Anionic Surfactants

S3, Dioctyl Sulfosuccinate Sodium Salt CAS number 577117 is a negatively charged ionic surfactant used to make reverse (oil in water) micelles \(^{111}\).

S4, Dodecylbenzenesulfonic acid CAS number 27176-87-0.

S5, Sodium dodecylbenzenesulfonate CAS number 25155300 also form oil in water micelles \(^{112,113}\). They are used extensively as cleaners, for example, in oily environments such as on an oil rig \(^{114}\). The chemical structures of these compounds are shown in Figure 9a-c.

Fluorinated ionic surfactants

S6, Perfluoroundecanoic acid CAS number 2058-94-8, is an ionic fluorinated ionic surfactant.

S8, Novek FC4430 and

S9, Novek FC4432 are proprietary 3M® fluorinated polymeric surfactants.
Figure 3.9: Some surfactants studied:

(a) S1, Poly(dimethylsiloxane-b-ethylene oxide) CAS number 68937-54-2. The m-block is hydrophilic, while the n-group is hydrophobic.

(b) S2, Poly(diallyl dimethyl ammonium chloride) CAS number 26062-79-3

(c) S7, Didodecyldimethylammonium bromide CAS number 3282-73-3.
Figure 3.10: Anionic Surfactants used:

(a) S3, Dioctyl Sulfosuccinate Sodium Salt CAS number 577117

(b) S4, Dodecyl benzene sulfonic acid 27176-87-0

(c) S5, Sodium dodecylbenzenesulfonate CAS number 25155300
3.3.1 Polymeric Triblock Surfactants

**EPE**, Poly(ethylene glycol)-b-poly(propylene glycol)-b-poly(ethylene glycol), is a triblock polymeric surfactant with a hydrophobic center block flanked by two hydrophilic blocks (Figure 3.11). The polyethylene glycol block [PEG] is hydrophilic, while the polypropylene glycol [PPG] is the hydrophobic part. Its cousin **PEP** (Figure 3.12), poly(propylene glycol)-b-poly(ethylene glycol)-b-poly(propylene glycol) has the hydrophilic part at the center of the block. A series of these surfactants with increasing proportion of polyethylene glycol were studied. In the **EPE** triblock surfactant series, the available compositions contained the following proportion of PEG 10% (**EPE0**, Aldrich 435430), 30% (**EPE1**, Aldrich 435465), 40% (**EPE2**, Aldrich 435449), 50% (**EPE3**, Aldrich 435414) and 80% (**EPE4**, Aldrich 412325). For the **PEP** series the proportions of PEG available were 10% (**PEP0**, Aldrich 435503) and 50% (**PEP1**, Aldrich 435473).

The changing proportions of PEG affects a property of these surfactants called the Hydrophilic-Lipophilic Balance (HLB). The HLB is used to classify a surfactant according to the proportion of the hydrophilic part. Although not an exact measure, it is based on a calculation of the ratio of the molecular weight of the hydrophobic portion to the total molecular weight of the surfactant.\[^{115,116}\] A lower ratio corresponds to a mostly hydrophilic molecule while a higher ratio corresponds to a hydrophobic molecule. This value can help determine the type of emulsion the surfactant can form as shown in Figure
3.13. Mixtures of surfactants can yield a surfactant with an intermediate HLB according to

\[ HLB_{mixture} = \phi HLB_A + (1 - \phi) HLB_B \]  

(3.2)

Where \( \phi \) is the volume fraction of surfactant A and \( HLB_A \) and \( HLB_B \) are the HLB values of surfactant A and B respectively. A mixture of surfactants with high and low HLB values seem to give more stable emulsions. The HLB, the percentage of PEG and molecular weights of the EPE and PEP series studied are shown in Table 23. From the table it seems that EPE0, EPE1 and PEP0 would be good water in oil emulsifiers.
Figure 3.11: (a) The structure of EPE poly(ethylene glycol)-b-poly(propylene glycol)-b- poly(ethylene glycol) family (b) The proportion of x, y, and z in EPE0, EPE1, EPE2, EPE3, and EPE4.
Figure 3.12: (a) The structure of PEP poly(propylene glycol)-b-poly(ethylene glycol)-b-poly(propylene glycol) family (b) The proportion of x, y, and z in PEP0 and PEP.
Figure 3.13: The HLB scale. The lower the number the more likely it is to form water in oil emulsions (from ref.117).

Table 23: The HLB, average molecular weight, and the PEG% composition in a the EPE and PEP copolymer series. Mn is the number average molecular weight of the polymer.

<table>
<thead>
<tr>
<th></th>
<th>EPE0</th>
<th>EPE1</th>
<th>EPE2</th>
<th>EPE3</th>
<th>EPE4</th>
<th>PEP0</th>
<th>PEP1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>2800</td>
<td>5800</td>
<td>2900</td>
<td>1900</td>
<td>8400</td>
<td>3300</td>
<td>2000</td>
</tr>
<tr>
<td>PEG %</td>
<td>10</td>
<td>30</td>
<td>40</td>
<td>50</td>
<td>80</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>HLB</td>
<td>1-7</td>
<td>7-9</td>
<td>12-18</td>
<td>18-23</td>
<td>&gt;24</td>
<td>2-7</td>
<td>12-18</td>
</tr>
</tbody>
</table>
These surfactants were filled into cells spaced at 7 microns with an electrode area of 1cm\(^2\) coated with 4% solids solution of PI2555 spun coated at 3000rpm. The results of the dielectric measurements are shown in Figure 3.14. The measurements show that the surfactants have almost the same response except that the low frequency relaxation frequency moves to higher frequencies with increasing HLB values (Table 24). It was difficult to obtain good results for the low frequency measurements for EPE4 because it was very viscous and thus difficult to fill into the cell.

![Figure 3.14: The apparent dielectric response of the polymeric triblock surfactant series of EPE and PEP. These were filled in a cells with 7 micron spacing with an electrode area of 1cm\(^2\) coated with 4% solids PI2555 solution spun coated at 1500rpm. The real response is shown on the left while the imaginary is on the right.](image-url)
Table 24: The low frequency relaxation frequency of the EPE and PEP surfactant series obtained from the data above. Note the increase in relaxation frequency as the HLB and PEG% in the surfactant increases.

<table>
<thead>
<tr>
<th></th>
<th>EPE0</th>
<th>EPE1</th>
<th>EPE2</th>
<th>EPE3</th>
<th>EPE4</th>
<th>PEP0</th>
<th>PEP1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>2800</td>
<td>5800</td>
<td>2900</td>
<td>1900</td>
<td>8400</td>
<td>3300</td>
<td>2000</td>
</tr>
<tr>
<td>PEG %</td>
<td>10</td>
<td>30</td>
<td>40</td>
<td>50</td>
<td>80</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>HLB</td>
<td>1-7</td>
<td>7-9</td>
<td>12-18</td>
<td>18-23</td>
<td>&gt;24</td>
<td>2-7</td>
<td>12-18</td>
</tr>
<tr>
<td>Relaxation Frequency (Hz)</td>
<td>27.7</td>
<td>219</td>
<td>106</td>
<td>287</td>
<td>-</td>
<td>7</td>
<td>155</td>
</tr>
</tbody>
</table>

3.4 Summary

The individual components may have high dielectric constants, but make poor dielectrics for energy storage purposes due to their high losses. In addition the liquid crystal components are highly susceptible to applied fields, with their dielectric responses and losses increasing with applied field. Nevertheless, these individual components will be used as components to make binary and heterogeneous systems. When these components are correctly placed in a heterogeneous or binary system they have the potential to provide a high dielectric constant with low loss over a broad frequency range.
CHAPTER 4

Binary Mixtures

The focus of this chapter is the effect on the dielectric response of binary mixtures containing any two of the following: liquid crystals, ionic additives, surfactants, and organic solvents. The purpose of this work was to broadly determine whether any appreciable enhancement to the dielectric response could be obtained by the employing additives to the individual components. For this purpose many series of experiments were performed. Generally, these experiments indicated that binary mixtures are too lossy for use in real devices. For this reason only a few series of binary mixtures will be discussed in detail. These include a series of binary mixtures made by mixing the polymeric block surfactant S1 with MLC4851, and mixtures containing the cationic surfactant Didodecyldimethylammonium bromide (DDAB), S7 and nematic liquid crystal E31.

A further goal of this study was to determine the factors that could lead to the diminution of the desired dielectric response; that is large real dielectric constant and small imaginary dielectric constant at low frequencies. Therefore, the effect of increasing concentrations of Calcium Fluoride (CaF₂) in the Ferroelectric liquid crystal MLC4851 and in the block polymeric surfactant S1, Poly (dimethyl Siloxane-b-ethylene oxide) on
the dielectric response was explored. One area of particular interest was the effect of this ionic additive on low frequency dielectric losses.

4.1 The Effect of Ionic Dopants on the Dielectric Response

4.1.1 In Liquid Crystals

In the previous chapter, the apparent dielectric response of the ferroelectric liquid crystal MLC4851 was presented. Here the effect on the dielectric response of adding increasing amounts of Calcium Fluoride to MLC4851 is presented. The weight percentages of CaF$_2$ added to the liquid crystal were 1, 3, 7, 18 and 35 percent. These mixtures were filled into the standard cell for dielectric measurements. These cells just like those of the pure ferroelectric liquid crystals were aligned by cooling them from the isotropic temperature at a rate of 0.2°C per minute.

The dielectric response of these mixtures and that of plain MLC4851 are presented in Figure 4.2. From these measurements, increasing the salt concentration lowers the Goldstone frequency and has an effect of increasing both the real and imaginary response at lower frequencies. The data was obtained prior to acquiring the SI1296 dielectric interface, hence the noisy data at lower frequencies. Suspecting increased conductivity and electrode polarization with increasing salt concentration, a constant phase element in series with a resistor was used to fit the data in the 1Hz to 1kHz frequency range. A simple resistance in series with a capacitor would not be
sufficient to fit the data as both the real and imaginary responses are increasing with lower frequency. Recall that the impedance of the constant phase element is:

$$Z_{\text{CPE}} = Q(j\omega)^{-n}$$  \hspace{1cm} (4.1)

For a perfect capacitor the value of $n$ in the CPE should be 1, as electrode polarization (evident with increasing values of both the real and imaginary responses at lower frequencies) the values of $Q$ increases while the exponent, $n$ should decrease. The parameters obtained from these fits, shown in Figure 4.1 below, indicate an initial increase in magnitude of the constant phase element, while the exponent decreases. The subsequent trend reversal is probably due to saturation of the ferroelectric liquid crystal that may have caused only some of the Calcium Fluoride to be filled in the cells. Polarizing optical microscope pictures of the filled cells are shown in Figure 4.3. These indicate that the samples have ferroelectric liquid crystal features, even at high Calcium Fluoride doping. This indicates that the salt composition in these mixtures may not be the same as the amount added i.e. phase separation occurred.

![Figure 4.1: The value of Q and n the magnitude and exponent respectively of the constant phase element as a function of concentration of Calcium Fluoride in MLC4851.](image)
Figure 4.2: The apparent dielectric response of binary mixtures containing increasing concentrations of Calcium Fluoride in ferroelectric liquid crystal MLC4851. The top graphs (a) show the whole frequency range, while the bottom graphs (b) show the response over the lowest three decades of frequency.
Figure 4.3: Polarizing optical microscopy pictures of cells filled with ferroelectric liquid crystal MLC4851 and (a) 0% (b) 1% (c) 3% (d) 7% (e) 18% and (f) 35% Calcium Fluoride.
4.1.2 In Surfactants

The dielectric response obtained by adding Calcium Fluoride to the polymeric block surfactant S1 Poly (dimethyl Siloxane-b-ethylene oxide) on the dielectric response is shown in Figure 4.5. The lower frequency response shows a relaxation around 5Hz. These mixtures lack the response at around 100Hz from the Goldstone mode of the ferroelectric liquid crystal. The same circuit elements used to fit the ferroelectric liquid crystal-CaF$_2$ system was used to fit the data at lower frequencies. The parameters obtained from these fits are shown in Figure 4.4. The magnitude of the constant phase element, Q, is over ten times larger than that in the MLC4851-CaF$_2$ mixture, but the value of the exponent, n, stays close to 0.9 suggesting that the low frequency response contribution is mostly due to electrode polarization.

![Figure 4.4: The value of Q and n magnitude and exponent respectively of the constant phase element as a function of the concentration of Calcium Fluoride in the polymeric block surfactant, S1.](image-url)
Figure 4.5: The apparent dielectric response of binary mixtures containing increasing concentrations of Calcium Fluoride in the block polymeric surfactant S1. The top graphs (a) show the whole measured frequency range, while the bottom graphs (b) shows the response over the lower two decades of frequency.
4.2 The Effects of Surfactant Additives on the Dielectric Response of Liquid Crystals

Addition of surfactants that spontaneously form vesicles with the ionic impurities inside, to liquid crystals may lead to enhanced the dielectric properties of the mixture. In this section, the results of adding surfactants to liquid crystals are presented. In the first study, increasing concentrations of the polymeric block surfactant S1 Poly (dimethyl Siloxane-b-ethylene oxide) were added to the ferroelectric liquid crystal MLC4851. The results of the dielectric measurements after the cells were cooled from isotropic temperature at a rate of 0.2°C/minute are shown in Figure 4.6, while the results of fitting a constant phase element in series with a resistor to the low frequency data are shown in Figure 4.7. Again the fitting parameters indicate an increase of electrode polarization. The value of the exponent n approaches that of a capacitor (n=1) because the capacitor causing the electrode polarization starts to relax at higher frequencies, that can be seen as a peak forming in the imaginary response as the surfactant concentration increases. The polarizing optical microscopy pictures of the 2% and 80% surfactant concentrations are shown in Figure 4.8.
Figure 4.6: The apparent dielectric response of binary mixtures containing the surfactant S1 in the ferroelectric liquid crystal MLC4851. The top graphs (a) show the whole measured frequency range, while the bottom graphs (b) shows the response over the lowest three decades of frequency.
Figure 4.7: The value of Q and n the magnitude and exponent respectively of the constant phase element as the concentration of the polymeric block surfactant, S1 is increased in the ferroelectric liquid crystal MLC4851.
Figure 4.8: Polarizing optical microscopy pictures of cells filled with (a) 2% and (b) 80% S1 in MLC4851.
Other surfactants were also added to the ferroelectric liquid crystal MLC485. These include 3% each of S3 Dioctyl Sulfsuccinate Sodium Salt, S4 Dodecyl Benzene Sulphonic Acid, and S5 Sodium Dodecylbenzenesulfonate. As in the previous mixtures, no desirable effects to the dielectric response were observed. While the real dielectric constant increased so did the imaginary dielectric constant resulting in a very lossy low frequency dielectric.

### 4.2.1 DDAB (S7) in E31

An increase in the real dielectric constant and relatively little change in loss was observed upon the addition of the cationic surfactant S7 Didodecyldimethylammonium Bromide (DDAB) to the nematic liquid crystal E31 (Figure 4.10). In these mixtures addition of just 1% S7 caused the relaxation frequency of the mixture to move from 3.26 Hz to 4kHz, with a corresponding increase in the real dielectric constant from 6.2 to 132, while reducing losses in this frequency region.

At first glance, increasing the amount of surfactant in 1% increments seems to give modest increases in both the relaxation frequency and real part of the response, but on analysis of the data by fitting to the data the circuit shown in Figure 4.9, below indicates otherwise. The circuit is made of a resistor in series with a capacitor, a constant phase element and the Havriliak-Negami (H-N) element in parallel.
Figure 4.9: The circuit used to model the apparent dielectric response measurements of mixtures of the liquid crystal E31 with increasing amounts of S7 Didodecyldimethylammonium Bromide (DDAB). H-N is the Havriliak-Negami element, Q is the constant phase element and C a capacitor.

The circuit elements are supposed to model the following, the resistance models the ITO resistance, the constant phase element (Q) represents the “lossy” part of the capacitor or contributions from electrode polarization, the capacitor represents the capacitance originating from the liquid crystal that dominates the response after the contribution from the heterogeneous system modeled by the H-N element becomes small. The results of the fits to the data are shown in Table 25. From the data not only is the relaxation frequency increasing (Figure 4.11(a)), the contribution of the electrode polarization is decreasing and the value of $n$ is approaching that of a capacitor as the concentration of DDAB is increased (Figure 4.11(b)).
Figure 4.10: The effect to the dielectric response of adding to the nematic liquid crystal E31, the cationic surfactant S7 (DDAB). Note the dramatic increase in the relaxation frequency as the surfactant is added. The top graphs (a) show the whole measured frequency range, while the bottom graph (b) shows the region of interest where the relaxation frequency increases slightly with increasing surfactant concentration above 1%.
Table 25 : The results of the fitting the circuit above to the apparent dielectric response measurements of mixtures of the liquid crystal E31 with increasing amounts of S7 Didodecyldimethylammonium Bromide (DDAB). The values of C are reported as dielectric constant.

<table>
<thead>
<tr>
<th>DDAB%</th>
<th>R (Ohms)</th>
<th>H-N</th>
<th>CPE</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H</td>
<td>Rel. Freq. (Hz)</td>
<td>mu</td>
</tr>
<tr>
<td>0</td>
<td>45.60</td>
<td>122.8</td>
<td>3.14E+01</td>
<td>0.98</td>
</tr>
<tr>
<td>1</td>
<td>45.79</td>
<td>126.7</td>
<td>4.60E+03</td>
<td>0.98</td>
</tr>
<tr>
<td>2</td>
<td>42.96</td>
<td>127.6</td>
<td>7.91E+03</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>43</td>
<td>128.6</td>
<td>8.08E+03</td>
<td>0.99</td>
</tr>
<tr>
<td>4</td>
<td>34.47</td>
<td>125.5</td>
<td>1.10E+04</td>
<td>0.99</td>
</tr>
</tbody>
</table>
Figure 4.11: The results of the fit to the apparent dielectric response measurements of mixtures of the liquid crystal E31 with increasing amounts of S7 Didodecyldimethylammonium Bromide (DDAB). The result (a) shows the increase in the relaxation frequency as the concentration of DDAB is increased, while (b) shows the magnitude (Q) and exponent (n) of the constant phase element.
4.3 Summary

In this chapter the dielectric effects of the ionic additive Calcium Fluoride to either liquid crystal or surfactant were discussed. In summary, its addition had a detrimental effect on the dielectric response. The ions appeared to increase the electrode polarization and hence both the real and imaginary responses making a very lossy dielectric.

Addition of surfactants to liquid crystals also had the same dielectric effect with the exception of the cationic surfactant S7 Didodecyldimethylammonium Bromide (DDAB) dispersed in the nematic liquid crystal E31. In these systems addition of S7 caused the relaxation frequency of the mixture to move to higher frequencies, with a corresponding increase in the real dielectric constant, and some decrease in losses in this region. This is shown again in Figure 4.12, as a plot of loss tangent angle as a function of frequency for neat liquid crystal E31 and the same doped with increasing amounts of S7. The loss tangent is the angle in the complex plane that the response makes with the imaginary plane, and it is calculated as:

\[
\delta = \tan^{-1} \frac{\varepsilon'}{\varepsilon}
\]  

(4.2)

where \(\delta\) is the loss tangent angle, \(\varepsilon'\) is the imaginary and \(\varepsilon\) is the real dielectric response respectively. A perfect capacitor would have a value of \(\delta\) close to zero. Therefore in this system surfactant addition lowered the loss tangent at lower frequency but the increase of
the dissipation factor of the mixtures at lower frequencies (<10Hz) is a concern that can probably be mitigated by heterogeneous systems.

Figure 4.12: The loss tangent of E31 and the same doped with increasing amounts of S7 as a function of frequency. A lower the loss tangent corresponds to a better dielectric.
CHAPTER 5

Heterogeneous Systems

In the previous chapter, two components were mixed with the goal of enhancing the dielectric properties over that of the individual components. The origin of this enhancement of the dielectric properties is beyond that of the simple sum of the individual components, which would limit the dielectric response to at most the response of the better dielectric. The desired response originates from surface phenomena such as interfacial polarization. This phenomenon needs to take place in the bulk of the dielectric as any effect at the electrode leads to electrode polarization.

In the binary system of the nematic liquid crystal E31 doped with a small amount of surfactant S7 Didodecyldimethylammonium Bromide (DDAB), the dielectric response increased beyond that of the individual components, but low frequency losses and contributions from electrode polarization were large. This behavior is generally due to the presence of free ionic impurities. The addition of a third component may have the desired effect of sequestering these ions, and lowering both the conductivity and electrode polarization. The combination of high dielectric constant oil-like liquid crystal as the host with surfactants and solvents as dopants may create type of system needed to create a high dielectric constant, low loss and high breakdown voltage dielectric shown in
Addition of ionic dopants into the water phase will enhance the interfacial polarization and hence the dielectric response.

Initial studies of these systems involved adding to the ferroelectric liquid crystal MLC4851, surfactants and a small amount of Calcium Fluoride.

(Figure 5.1). The response will be higher than the contributions from the individual components, due to contributions from interfacial polarization. Interfacial polarization will occur at the water-surfactant – oil interfaces and can be enhanced by increasing the conductivity of the water like part.
5.1 Ternary Systems containing Ferroelectric Liquid Crystals and Calcium Fluoride

To take advantage of their already high dielectric constant the initial studies were done using ferroelectric liquid crystals. These mixtures were prepared by adding to the ferroelectric liquid crystals MLC4851, one of several surfactants and Calcium Fluoride. These mixtures were heated to the clearing point and occasionally shaken to assist the mixing. After this, the mixture was placed in an ultrasonic bath at room temperature for fifteen minutes to prompt formation of heterogeneous systems presumably containing vesicles of small radii. The mixture was then filled into the standard glass cells and sealed. The cell was then cooled at 0.2°C per minute to help align the ferroelectric liquid crystal phase. The effect on the dielectric response of aligning the mixture depends on the mixture; sometimes it is small and in some cases the spectra dramatically changes. For example, in the ferroelectric liquid crystal mixture containing 1% Calcium Fluoride and 3% of the surfactant S3 (Dioctyl Sulfosuccinate Sodium Salt) the effect is small (Figure 5.2a), while in a mixture with another surfactant S6 (Perfluoroundecanoic Acid) (Figure 5.2b), the effect is rather large. Polarizing optical microscope pictures of the cells before and after alignment are shown in Figure 5.3. Even when other surfactants were tried, the real and imaginary components of the dielectric coefficient differ by at most a factor of ten as shown in Figure 5.4. In summary, adding Calcium Fluoride and any other surfactant to MLC4851 showed no favorable results in the dielectric response of the mixture.
Figure 5.2: The effect of aligning ferroelectric liquid crystal MLC4851 mixtures containing 1% Calcium Fluoride and (a) 3% S3 Dioctyl Sulphosuccinate Sodium Salt and (b) 3% S6 Perfluoroundecanoic acid. Note that the effect of alignment is larger for the S3 surfactant mixture.
Figure 5.3: Polarizing optical microscopy pictures of cells before and after alignment of ferroelectric liquid crystal MLC4851 mixtures containing 1% Calcium Fluoride and (a & b) 3% S3 Dioctyl Sulfo succinate Sodium Salt and (c & d) 3% S6 Perfluoroundecanoic acid. The cells after alignment are shown on the right.
Figure 5.4: The effect on the dielectric response of adding 1% Calcium Fluoride and 3% of a surfactant: S1, S2, S3, S4, S5, S6 or S8 to the ferroelectric liquid crystal MLC4851. The response of the neat MLC4851 has a better response at lower frequencies as those of the multi-component mixtures.
5.2 Ternary Systems containing Nematic Liquid Crystals

Further exploration of heterogeneous systems was accomplished by replacing the ferroelectric liquid crystal with nematic liquid crystals. The high cost, limited availability and the need to align ferroelectric liquid crystals were all factors used in making this decision. However, it was though that once a promising formula was found, the nematic would have been replaced with a ferroelectric liquid crystal. It was surprising that the addition of just 1% surfactant S7 (Didodecyldimethylammonium Bromide) to the nematic liquid crystal E31 had a very favorable effect to the dielectric response when compared to a ferroelectric liquid crystal doped with the same. Therefore, the research went in this direction.

The addition of a third component, the solvent N-Methylformamide (NMF), to this system resulted in an additional increase in the dielectric response and relaxation frequency (Figure 5.6). The dielectric response of the solvent NMF is also shown for reference. Note the very poor dielectric response of NMF at lower frequencies where both the real and imaginary responses are both increasing almost simultaneously in the fashion of a Warburg element. To better compare the responses, the results were fitted to the same circuit used to model the binary mixtures; a resistor in series with a capacitor, constant phase element and Havriliak-Negami (H-N) element in parallel (Figure 5.5). The results of this fit are shown in Table 26.

The results show that the solvent NMF’s response at lower frequencies (<10⁴Hz) is mostly made of a Warburg element with $n$ approaching 0.5. Also note that the ternary
mixture has a higher relaxation frequency \((2.73 \times 10^4 \text{Hz})\) than the binary mixture \((4.6 \times 10^3 \text{Hz})\), and also has a larger contribution from the H-N element. Although the contribution from the lossy portion of the capacitor (CPE) is greater in the ternary mixture (41% of the total apparent response in the ternary system as opposed to 17% in the binary system) the value of \(n\) in the constant phase element is smaller.

Figure 5.5 : The circuit used to model the dielectric responses of NMF and the ternary and binary mixtures. H-N is the Havriliak-Negami element, Q is the constant phase element and C a capacitor.
Figure 5.6: The apparent dielectric response of a binary mixture made of 1% S7 and 99% E31 and that of a ternary mixture of 1% S7, 90% E31 and 9% NMF. The response of neat NMF is also shown.

Table 26: The results of fitting a circuit, containing a resistor in series with a capacitor, constant phase element (CPE) and a Havriliak – Negami (H-N) element in parallel to model the data above. The capacitances are reported as dielectric constants. Note that the solvent NMF is mostly a Warburg element at lower frequencies (the exponent \( n \) of the CPE is around 0.5). Portion of the CPE is defined as \( Q/(H+Q) \times 100\% \)

<table>
<thead>
<tr>
<th>Mixture</th>
<th>R (Ohms)</th>
<th>H-N</th>
<th>CPE</th>
<th>( \varepsilon )</th>
<th>Portion of CPE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMF</td>
<td>31.04</td>
<td>47.98</td>
<td>7.25E+05</td>
<td>0.68</td>
<td>1</td>
</tr>
<tr>
<td>Binary Mixture</td>
<td>45.79</td>
<td>126.7</td>
<td>4.60E+03</td>
<td>0.99</td>
<td>1</td>
</tr>
<tr>
<td>Ternary Mixture</td>
<td>11.42</td>
<td>168</td>
<td>2.73E+04</td>
<td>0.96</td>
<td>1</td>
</tr>
</tbody>
</table>
Further studies of this system included systematically increasing the concentration of the solvent and surfactant. The concentration the solvent was increased from 9% to 29% and 69% while holding the concentration of surfactant S7 Didodecyldimethylammonium Bromide at 1%. Increasing the concentration of NMF did not improve the dielectric response of the mixture as shown in the measurements (Figure 5.7) and fits to the data (Table 27). The data were fit to the same circuit shown in Figure 5.5. The result of increasing the NMF concentration from 9% to 29% is an increase in the loss, as shown in the increased imaginary component of the dielectric response and the increase in Q, the magnitude of the constant phase element. Increasing the concentration of NMF to 69% seems to change the type of heterogeneous system, where the Liquid Crystal is surrounded by NMF as shown in the microphotographs in Figure 5.8. This probably results in the additional relaxation at around 3Hz.

In the binary system, increased surfactant concentration seemed to lower the losses at lower frequencies; therefore the concentration of S7 was increased while holding the ratio of NMF to liquid crystal constant. The ratios studied were the same as those used for the NMF concentration ramp; that is 1:10, 1:2.4 and 1:0.44. Unfortunately, the results of this exercise were not fruitful. For reference, the dielectric spectra of these mixtures are shown in the appendix.
Figure 5.7: The effect of increasing the amount of NMF in a mixture containing 1% surfactant and nematic liquid crystal E31. In addition to the surfactant, cell 105.d contains 9% NMF and 90% E31, cell 107.d contains 29% NMF and 70% E31, while cell 111.d contains 69% NMF and 30% E31.

Table 27: The results of fitting a circuit, containing a resistor in series with a capacitor, constant phase element (CPE) and a Havriliak – Negami (H-N) element in parallel to model the data above. The capacitances are reported as dielectric constants. Note the low frequency relaxation at 3.13Hz for the 69% NMF mixture.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>R (Ohms)</th>
<th>H-N</th>
<th>CPE</th>
<th>ε</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H (ε)</td>
<td>Rel. Freq. (Hz)</td>
<td>mu</td>
</tr>
<tr>
<td>9% NMF</td>
<td>11.42</td>
<td>168</td>
<td>2.73E+04</td>
<td>0.96</td>
</tr>
<tr>
<td>29% NMF</td>
<td>34.93</td>
<td>173.3</td>
<td>9.27E+04</td>
<td>0.72</td>
</tr>
<tr>
<td>69% NMF</td>
<td>41.01</td>
<td>109.7</td>
<td>3.13</td>
<td>0.82</td>
</tr>
</tbody>
</table>
Figure 5.8: Polarizing optical microscopy photographs of cells filled with (a) 9% NMF, 90% E31 and 1% surfactant S7 and (b) 69% NMF, 30% E31 and 1% surfactant S7.
5.2.1 Replacing NMF with NMP

The results described in the previous section make it clear that increasing the concentration of the solvent N-Methylformamide (NMF) increased the losses. Increasing the concentration of the surfactant did not mitigate the problem. Therefore the solvent was replaced with N-Methyl-2-Pyrrolidone (NMP) whose dielectric response (discussed in Chapter 3) showed a lower portion of its apparent dielectric response originating from diffusion and other loss mechanisms as modeled by a constant phase element. The results of fitting a resistor in series with a constant phase element in parallel with a capacitor (Figure 5.5) to the apparent dielectric response of NMF and NMP are shown again for reference in Table 28.

Table 28: The results of fitting to the dielectric response of NMF and NMP, a circuit made of a resistor in series with a capacitor and constant phase element in parallel. The capacitance of the capacitor is reported as a dielectric constant.

<table>
<thead>
<tr>
<th>Component</th>
<th>R (Ohms)</th>
<th>CPE</th>
<th>ε</th>
<th>Portion of CPE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Q</td>
<td>n</td>
<td></td>
</tr>
<tr>
<td>NMF</td>
<td>36.82</td>
<td>1071</td>
<td>0.56</td>
<td>46.27</td>
</tr>
<tr>
<td>NMP</td>
<td>53.41</td>
<td>313.5</td>
<td>0.66</td>
<td>158.6</td>
</tr>
</tbody>
</table>

A few mixtures were made to compare the apparent dielectric responses obtained by replacing NMF with NMP. The first sets of mixtures were made of 1% surfactant S7, 90% liquid crystal E7 and 9% of either solvent NMF or NMP. The dielectric responses are shown in Figure 5.9, while the results of the fit to the data using the circuit shown in Figure 5.5 is shown in Table 29. The fits show that although NMF containing mixture
has the higher response, the NMP mixture has a much smaller portion of its apparent
dielectric response originating from loss mechanism as modeled by the Constant Phase
Element (CPE).

![Graph showing dielectric response comparison between NMF and NMP mixtures](image)

Figure 5.9: Comparing the apparent dielectric responses of mixtures containing 1% surfactant S7,
90% liquid crystal E7 and 9% of either solvent NMP or NMF.

Table 29: The fit to the data above to a circuit comprising of a resistor in series with parallel
combination of a capacitor, H-N element and constant phase element. The capacitance is reported as
the dielectric response. The portion of the apparent dielectric response contribution from low
frequency responses is shown in the last column.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>R (Ohms)</th>
<th>H-N</th>
<th>CPE</th>
<th>Fraction of low freq. response (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMF (196)</td>
<td>41</td>
<td>324</td>
<td>6900</td>
<td>1.00</td>
</tr>
<tr>
<td>NMP (194)</td>
<td>22</td>
<td>237</td>
<td>3470</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Increasing the concentration of the surfactant to 2% while holding the ratio of liquid crystal to solvent concentration constant at 10:1 results in the response shown in Figure 5.10 below. Fitting these responses to the circuit in Figure 5.5 shows that (Table 30) for the NMP mixtures, increasing the surfactant concentration increases the capacitive (non-loss) portion of the response as modeled by the H-N element and the capacitor. Again, although the apparent dielectric response measurements of the NMF mixtures seem to be much higher than those of NMP, a much larger portion (~50%) of the NMF response is from loss mechanisms.

![Figure 5.10](image_url)

**Figure 5.10**: Measurements showing the effect of increasing the surfactant S7 concentration in mixtures containing a 1:10 ratio of solvent to liquid crystal E7. The mixtures with the solvent NMP are shown with symbols, while those with NMF are shown with lines.
Table 30: The fit to the measurements showing the effect of increasing the surfactant S7 concentration in mixtures containing a 1:10 ratio of solvent to liquid crystal E7 to a circuit comprising of a resistor in series with parallel combination of a capacitor, constant phase element and H-N element. The capacitance is reported as the dielectric constant. The portion of the apparent dielectric response contribution from the CPE is shown in the last column.

<table>
<thead>
<tr>
<th>Mixture (sample)</th>
<th>R (Ohms)</th>
<th>H-N</th>
<th>CPE</th>
<th>ε</th>
<th>Portion of CPE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H (ε)</td>
<td>Rel. Freq. (Hz)</td>
<td>mu</td>
<td>psi</td>
</tr>
<tr>
<td><strong>NMF MIXTURES</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% Surf (194)</td>
<td>41</td>
<td>324</td>
<td>6900</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>2% Surf (248)</td>
<td>14.57</td>
<td>355.2</td>
<td>1.00E+04</td>
<td>0.92</td>
<td>1.00</td>
</tr>
<tr>
<td><strong>NMP MIXTURES</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% Surf (196)</td>
<td>22</td>
<td>237</td>
<td>3470</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>2% Surf (244)</td>
<td>30.83</td>
<td>282.7</td>
<td>1.13E+04</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Other mixture compositions were also studied, and included increasing the concentration of the solvents, while holding the amount of surfactant at 2%. The dielectric responses of these mixtures are shown in Figure 5.11, while the results of fitting the circuit shown in Figure 5.5 to the responses are shown in Table 31. Note that for the 20 and 60% NMP concentrations there is a relaxation at 0.02 Hz and 0.88 Hz respectively which was modeled by the H-N element, in these cases the CPE element was not used in the fit. Therefore in the analysis of the data (Figure 5.12), in addition to including the CPE in determining the portions of the response originating from loss.
mechanisms the response from the low frequency relaxations (H-N element) was also included. This was done because the low frequency response was assumed to be of ionic origin. Later work confirmed this assumption.

Again, the NMP mixtures had a smaller portion of the response originating from loss mechanisms. With the exception of the NMP mixtures at concentrations>20%, higher solvent concentration results in a larger portion of the response originating from the CPE (Figure 5.12a). The capacitive response (Figure 5.12b) initially decreases then increases with increasing solvent concentration. In these mixtures the NMP mixtures have a larger capacitive dielectric response.

In summary, these experiments show that in order to reduce the contribution from loss mechanisms as modeled by the constant phase element and low frequency relaxation responses the solvent N-Methylformamide (NMF) needs to be replaced with N-Methyl-2-Pyrrolidone (NMP).
Figure 5.11: Comparing the apparent dielectric responses of ternary mixtures containing the nematic liquid crystal E7, 2% surfactant S7 and increasing concentrations of either solvent NMP or NMF. The mixtures with NMP are shown with symbols, while the mixtures with NMF are shown with lines.
Table 31: The fit to the data above showing the effect of increasing the solvent concentration, to a circuit comprising of a resistor in series with parallel combination of a capacitor, constant phase element and H-N element. The capacitance is reported as the dielectric constant. The portion of the apparent dielectric response contribution from the CPE or low frequency responses is shown in the last column.

<table>
<thead>
<tr>
<th>Solvent Conc. (%)</th>
<th>R (Ohms)</th>
<th>H-N</th>
<th>CPE</th>
<th>Portion of CPE or low freq. response (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H (ε)</td>
<td>Rel. Freq. (Hz)</td>
<td>Q</td>
</tr>
<tr>
<td>NMF Mixtures</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.9% NMF</td>
<td>14.57</td>
<td>355.2</td>
<td>1.13E+04</td>
<td>0.92</td>
</tr>
<tr>
<td>20% NMF</td>
<td>20.62</td>
<td>264</td>
<td>1.31E+04</td>
<td>1.00</td>
</tr>
<tr>
<td>60% NMF</td>
<td>27.31</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NMP Mixtures</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.9% NMP</td>
<td>30.83</td>
<td>282.7</td>
<td>1.00E+04</td>
<td>1.00</td>
</tr>
<tr>
<td>20% NMP</td>
<td>40.95</td>
<td>201</td>
<td>0.02</td>
<td>0.7716</td>
</tr>
<tr>
<td>60% NMP</td>
<td>27.94</td>
<td>143</td>
<td>0.88</td>
<td>0.71</td>
</tr>
</tbody>
</table>
Figure 5.12: The effect of increasing the solvent concentration on the apparent dielectric response.

(a) With higher solvent concentration a higher portion of the response originates from loss mechanisms except for the NMP mixture which starts decreasing after 20%.

(b) The capacitive dielectric response after eliminating loss mechanisms (CPE contribution and low frequency relaxations) initially lowers then increases with increasing solvent concentration. Note that the NMP mixtures have a lower contribution from loss mechanisms than the NMF mixtures.
5.2.2 Other Surfactants

In addition to replacing the solvent NMF with NMP, mixtures with other surfactants were also explored. To compare the effect on the dielectric response of the surfactants in ternary mixtures, 1% of the surfactants were added to 90% liquid crystal E7 and 9% NMP. All the surfactants described in the single component section were used in this exploration with the exception of the NOVEK® surfactants. The triblock surfactant studies in ternary systems will be reported in a separate section.

The results of the dielectric measurements are shown in Figure 5.13. Note that they all have two relaxation frequencies; it is the position of the lower frequency relaxation that is of interest, the higher this relaxation frequency the better. The response after the initial relaxation originates from the response of pure liquid crystal E7. This response has a real dielectric coefficient between 7 and 12. These values are in agreement with the range of E7’s dielectric response that ranges from 5.31 to 21.

To simplify the analysis, the data were fitted to the circuit shown in Figure 5.5, the results of which are shown in Table 32. In comparing the mixtures, the best dielectric would the one with highest contribution to the dielectric response from pure capacitance and has the highest relaxation frequency in that order. The response from pure capacitance was calculated by eliminating from the total response the contribution from loss mechanisms and electrode polarization. These include the response of the low frequency relaxation (<100Hz) and the constant phase element. If the contribution from the constant phase element with a value of the exponent \( n \) was closer to that of an ideal capacitor (\( n=1 \)), then its contribution was not eliminated. Therefore, for example, the
mixture containing the surfactant S2 has a response that relaxes at 22Hz and has a contribution from the constant phase element (\(n=0.01\)) that makes up 97% of the total response; this makes it a poor dielectric.

Using these rules of thumb, Figure 5.14(a) shows the portion of the total dielectric response of mixtures made using various surfactants originating from either capacitance or loss. The relaxation frequency of these mixtures is also reported. Figure 5.14(b), reports the dielectric response of the capacitor portion of these mixtures. Of these mixtures the best dielectrics would be the mixtures containing S1 (poly(dimethyl Siloxane-b-ethlene oxide)) and S6 (Perfluroundecanoic acid), because they have the highest portion of their responses from a capacitor. Of the two mixtures, the S6 mixture has the higher relaxation frequency making it the better dielectric.

Although the S3 (Sodium Dioctyl Sulfo succinate), S5 (Sodium dodecylbenzenesulfonate) and S7 (Didodecyldimethylammonium Bromide) mixtures have higher relaxation frequencies, the loss portion of these mixtures needs to be minimized. This could be done by increasing the surfactant concentration as shown with the S7 mixtures above.
Figure 5.13: Comparing the apparent dielectric responses of ternary mixtures of containing 1% surfactant, 90% liquid crystal E7 and 9% solvent NMP. The response for the mixture containing the surfactant S7 is shown here reference.
Table 32: The fit to the data above showing the effect of substituting various surfactants in a mixture containing 1% surfactant, 90% liquid crystal E7 and 9% solvent NMP, to a circuit comprising of a resistor in series with parallel combination of a capacitor, constant phase element and H-N element. The capacitance is reported as the dielectric constant. The portion of the apparent dielectric response contribution from the CPE or low frequency responses is shown in the last column.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>R (Ohms)</th>
<th>H-N (ε)</th>
<th>Rel. Freq. (Hz)</th>
<th>Mu</th>
<th>psi</th>
<th>Q</th>
<th>n</th>
<th>ε</th>
<th>Portion of CPE or low freq. response (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s1</td>
<td>24.01</td>
<td>184.6</td>
<td>163</td>
<td>0.99</td>
<td>1</td>
<td>12.9</td>
<td>0.57</td>
<td>12</td>
<td>6%</td>
</tr>
<tr>
<td>s2</td>
<td>24.72</td>
<td>226.9</td>
<td>22</td>
<td>0.96</td>
<td>1</td>
<td>5</td>
<td>0.01</td>
<td>7.2</td>
<td>97%</td>
</tr>
<tr>
<td>s3</td>
<td>25.40</td>
<td>178.6</td>
<td>4519</td>
<td>0.99</td>
<td>1</td>
<td>35.33</td>
<td>0.65</td>
<td>11.72</td>
<td>16%</td>
</tr>
<tr>
<td>s5</td>
<td>24.76</td>
<td>180</td>
<td>4190</td>
<td>0.99</td>
<td>1</td>
<td>37.74</td>
<td>0.64</td>
<td>11.97</td>
<td>16%</td>
</tr>
<tr>
<td>s6</td>
<td>23.29</td>
<td>180</td>
<td>1496</td>
<td>0.99</td>
<td>1</td>
<td>11.3</td>
<td>0.50</td>
<td>12</td>
<td>6%</td>
</tr>
<tr>
<td>s7</td>
<td>22</td>
<td>237</td>
<td>3470</td>
<td>1</td>
<td>1</td>
<td>67.32</td>
<td>0.8</td>
<td>7</td>
<td>22%</td>
</tr>
</tbody>
</table>
Figure 5.14: Graphs showing (a) the portion of the total apparent dielectric response of mixtures made using various surfactants originating from either capacitance or loss. The relaxation frequency of these mixtures is reported using the right-hand scale. (b) The capacitive response of the mixtures at frequencies well below the relaxation frequency.
5.2.3 Triblock Polymeric Surfactants

In addition to the surfactants discussed above, the triblock polymeric surfactants made of blocks of hydrophilic poly(ethylene glycol) and hydrophobic poly(propylene glycol) were also studied. These surfactants are separated into two classes depending on the position of the hydrophilic block. The first class PEP describes the polymer in which the poly(ethylene glycol) block is positioned in the center and flanked by two hydrophobic poly(propylene glycol) blocks. The second class EPE occurs when the poly(ethylene glycol) block flanks a central hydrophobic poly(propylene glycol) block. Diblock versions of these molecules were not available for testing. The molecular weights and structures of the surfactants used were presented earlier.

It is still not clear if the two classes of surfactants produce differing systems when introduced into a mixture of liquid crystal E7 and the solvent NMP. For example, at low solvent concentrations would the PEP class of surfactants encapsulate the solvent as shown in Figure 5.15(a) and would the EPE class do the same as shown in Figure 5.15(b)? Although this is not known, mixtures were made with these surfactants and the dielectric responses were measured.
Figure 5.15: Possible solvent encapsulation in a liquid crystal host when, (a) the PEP class of surfactants is introduced, and (b) the EPE class of surfactants is introduced. The hydrophilic blocks are represented solid blocks while the hydrophobic blocks are shaded.
Due to availability, the initial studies of these classes of surfactants were with, **EPE1**, **EPE2** and **PEP1**. The properties of these surfactants were presented earlier, but are shown again in Table 33, below. Note that **EPE2** and **PEP1** have the same range of HLB value (12-18) while **EPE1** has HLB value of around 7, therefore **EPE1** may form the water in oil (NMP in E7) system we need.

**Table 33: Summary of properties of the initial set of Polymeric Triblock Surfactants**

<table>
<thead>
<tr>
<th></th>
<th>EPE1</th>
<th>EPE2</th>
<th>PEP1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>5800</td>
<td>2900</td>
<td>2000</td>
</tr>
<tr>
<td>PEG %</td>
<td>30</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>HLB</td>
<td>7-9</td>
<td>12-18</td>
<td>12-18</td>
</tr>
</tbody>
</table>

The initial mixtures made were of the same composition used to compare the surfactants earlier: 1% surfactant, 90% liquid crystal E7 and 9% solvent NMP. The results of the dielectric measurements and the results of fitting these data to the same circuit are shown in Figure 5.16 and Table 34 respectively. The results from using the copolymer surfactant **S1** in the mixture is also shown. At first glance it may seem that the surfactant **S1** has the best response as it has the smallest portion of the response originating from the constant phase element (Figure 5.17a), but on further analysis of the exponent of the constant phase element, $n$, the Triblock Polymeric Surfactants are superior (Figure 5.17b). The triblock polymeric surfactants have a values closest to that of a capacitor ($n=1$), while the mixture with surfactant S1 has a value closer to a Warburg diffusion element ($n=0.5$). Note that although the HLB values of **PEP1** and **EPE2** were similar, they produced differing dielectrics when used in the mixtures with **EPE2**.
showing better dielectric properties. EPE1 with a HLB of 7 produced a mixture with a response similar to EPE2 but with a higher capacitance.

Figure 5.16: The apparent dielectric response of mixtures containing 1% either Triblock Polymeric Surfactants EPE1, EPE2 or PEP1 in 90% E7 and 9% NMP. The response of the mixture containing surfactant S1 is shown for reference.
Table 34: The fit to the data above showing the effect of using copolymer surfactants in a mixture containing 1% surfactant, 90% liquid crystal E7 and 9% solvent NMP, to a circuit comprising of a resistor in series with parallel combination of a capacitor, constant phase element and H-N element. The capacitance is reported as the dielectric constant. The portion of the apparent dielectric response contribution from the CPE is shown in the last column. Portion CPE = $Q/(H+Q+\varepsilon)$.

<table>
<thead>
<tr>
<th>Mix.</th>
<th>HLB</th>
<th>R (Ohms)</th>
<th>H-N</th>
<th>CPE</th>
<th>$\varepsilon$</th>
<th>Portion of CPE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>H ($\varepsilon$)</td>
<td>Rel. Freq. (Hz)</td>
<td>mu</td>
<td>psi</td>
</tr>
<tr>
<td>EPE1</td>
<td>7-9</td>
<td>25</td>
<td>217</td>
<td>90</td>
<td>0.93</td>
<td>1</td>
</tr>
<tr>
<td>EPE2</td>
<td>12-18</td>
<td>28</td>
<td>208</td>
<td>115</td>
<td>0.95</td>
<td>1</td>
</tr>
<tr>
<td>PEP1</td>
<td>12-18</td>
<td>26.38</td>
<td>190</td>
<td>117</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>s1</td>
<td></td>
<td>24.01</td>
<td>184.6</td>
<td>163</td>
<td>0.99</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 5.17: Graphs showing (a) the portion of the total apparent dielectric response of mixtures made using copolymer surfactants in a mixture containing 1% surfactant, 90% liquid crystal E7 and 9% solvent NMP originating from either capacitance or loss. The relaxation frequency of these mixtures is reported using the right hand scale. (b) The capacitive response (open boxes flanking the diagonally filled box) and the value of the exponent (diagonal lines), $n$, of the constant phase element of these mixtures.
5.2.3.1 Effects of Increased Surfactant Concentration

These experiments were performed with the goal of reducing the contribution from the constant phase element and other loss mechanisms by increasing the concentration of surfactant while holding the ratio of liquid crystal to solvent constant at (10:1). The results of the dielectric measurements of these mixtures containing EPE1, EPE2 and PEP1 are shown in Figure 5.18, Figure 5.19 and Figure 5.20 respectively, while the results of fitting these data to the circuit shown in Figure 5.5 are shown in Table 35, Table 36 and Table 37 respectively. A summary of these results showing the capacitive portion of the response and the value of the exponent of the constant phase element are shown in (Figure 5.21a) and (Figure 5.21b) respectively. From these results, the mixture that maximizes both the parameters is the better dielectric. With the exception of the 1% surfactant concentration, the performances of these surfactants can be ranked in the following order PEP1, EPE2 and EPE1, with the 2% PEP1 being the best dielectric.
Figure 5.18: The apparent dielectric response of mixtures containing increasing concentration of triblock polymeric surfactant EPE1 in a solvent that is at 10:1 ratio of E7 to NMP.

Table 35: The fit to the data above showing the effect of increasing the amount of surfactant EPE1 in solvent that is at 10:1 ratio of E7 to NMP, to a circuit comprising of a resistor in series with parallel combination of a capacitor, constant phase element and H-N element. The capacitance is reported as the dielectric constant. The portion of the apparent dielectric response contribution from the CPE is shown in the last column.

<table>
<thead>
<tr>
<th>Surf. Conc. (%)</th>
<th>R (Ohms)</th>
<th>H-N</th>
<th>CPE</th>
<th></th>
<th></th>
<th></th>
<th>Portion of CPE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H (ε)</td>
<td>Rel. Freq. (Hz)</td>
<td>μ</td>
<td>psi</td>
<td>Q</td>
<td>n</td>
</tr>
<tr>
<td>1%</td>
<td>24.76</td>
<td>217</td>
<td>90.74</td>
<td>0.93</td>
<td>1</td>
<td>31.39</td>
<td>0.86</td>
</tr>
<tr>
<td>2%</td>
<td>24.51</td>
<td>207</td>
<td>120.48</td>
<td>0.89</td>
<td>1</td>
<td>58.95</td>
<td>0.82</td>
</tr>
<tr>
<td>3%</td>
<td>22.48</td>
<td>209</td>
<td>260.91</td>
<td>0.98</td>
<td>1</td>
<td>63.69</td>
<td>0.84</td>
</tr>
</tbody>
</table>
Figure 5.19: The apparent dielectric response of mixtures containing increasing concentration of triblock polymeric surfactant EPE2 in a solvent that is at 10:1 ratio of E7 to NMP.

Table 36: The fit to the data above showing the effect of increasing the amount of surfactant EPE2 in a solvent that is at a 10:1 ratio of E7 to NMP, to a circuit comprising of a resistor in series with parallel combination of a capacitor, constant phase element and H-N element. The capacitance is reported as the dielectric constant. The portion of the apparent dielectric response contribution from the CPE is shown in the last column.
Figure 5.20: The apparent dielectric response of mixtures containing increasing concentration of triblock polymeric surfactant PEP1 in a solvent that is at 10:1 ratio of E7 to NMP.

Table 37: The fit to the data above showing the effect of increasing the amount of surfactant PEP1 in a solvent that is at a 10:1 ratio of E7 to NMP, to a circuit comprising of a resistor in series with parallel combination of a capacitor, constant phase element and H-N element. The capacitance is reported as the dielectric constant. The portion of the apparent dielectric response contribution from the CPE is shown in the last column.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>R (Ohms)</th>
<th>H-N</th>
<th>CPE</th>
<th>ε</th>
<th>Portion of CPE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H (ε)</td>
<td>Rel. Freq. (Hz)</td>
<td>mu</td>
<td>psi</td>
</tr>
<tr>
<td>1%</td>
<td>26.38</td>
<td>190</td>
<td>117.46</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2%</td>
<td>29.64</td>
<td>204</td>
<td>135.22</td>
<td>0.97</td>
<td>1</td>
</tr>
<tr>
<td>3%</td>
<td>30.13</td>
<td>242</td>
<td>93.84</td>
<td>0.97</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 5.21: The effect of increasing the concentrations of either EPE1, EPE2 or PEP1 in a solvent that is at a 10:1 ratio of E7 to NMP (a) the capacitive portion and (b) the value of the exponent of the constant phase element, $n$. The best mixture would be the one which maximizes both the capacitive component and $n$. 
5.2.3.2 Effects of Increased NMP Concentration

Increasing the amount of solvent (NMP) in these systems produced rather interesting results. In the earlier mixtures, the effects of increasing the solvent concentration were to increase the losses and modestly increase in the capacitive component. The dielectric measurements of mixtures made with increasing amounts of NMP in mixtures containing 2% PEP1 and liquid crystal E7 are shown in Figure 5.22, while the results of fitting the data are shown in Table 38. The same circuit, figure 5.5 was sufficient to model the data, except for the 60% NMP concentration where the low frequency response at 0.3Hz had to be modeled using the H-N element. Therefore, as before the contribution from the H-N element at this concentration (60% NMP) was considered to be a loss mechanism, while the CPE element \( n=1 \) was used to model one of the capacitive portions.

Note that with increasing NMP concentration both the relaxation frequency (Figure 5.23a) and the capacitive response (Figure 5.23b) increases. This increase does come at a cost, the portion originating from pure capacitance and the exponent of the constant phase element decrease, especially for the 50% NMP concentration.

The same general trends were observed for the mixtures made using EPE1 and EPE2 surfactants. The dielectric responses for the mixtures made with 2% EPE1 in mixtures with increasing concentrations of NMP in liquid crystal E7 are shown in Figure 5.24, while the results of fitting the data are shown in Table 39 and the analysis in Figure 5.25.
Figure 5.22: The apparent dielectric response of mixtures containing increasing concentrations of NMP in mixtures containing 2% PEP1 and liquid crystal E7.
Table 38: The fit to the data above showing the effect of increasing the amount of NMP in a mixtures containing 2% PEP1 and liquid crystal E7, to a circuit comprising of a resistor in series with parallel combination of a capacitor, constant phase element and H-N element. The capacitance is reported as the dielectric constant. The portion of the apparent dielectric response contribution from loss mechanisms is shown in the last column.

<table>
<thead>
<tr>
<th>NMP Conc.</th>
<th>R (Ohms)</th>
<th>H-N</th>
<th>CPE</th>
<th>Portion of CPE or low freq. response (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H (ε)</td>
<td>Rel. Freq. (Hz)</td>
<td>mu</td>
</tr>
<tr>
<td>8.9%</td>
<td>29.64</td>
<td>204</td>
<td>135</td>
<td>1</td>
</tr>
<tr>
<td>20%</td>
<td>25.04</td>
<td>203.9</td>
<td>596.53</td>
<td>1</td>
</tr>
<tr>
<td>30%</td>
<td>24.06</td>
<td>210</td>
<td>1,754.93</td>
<td>1</td>
</tr>
<tr>
<td>40%</td>
<td>27.34</td>
<td>259</td>
<td>2,578.24</td>
<td>1</td>
</tr>
<tr>
<td>50%</td>
<td>27.34</td>
<td>256</td>
<td>4,019.06</td>
<td>1</td>
</tr>
<tr>
<td>60%</td>
<td>4.23</td>
<td>117.9</td>
<td>0.03</td>
<td>0.7</td>
</tr>
</tbody>
</table>
Figure 5.23: Graphs showing (a) the portion of the total apparent dielectric response of mixtures made from increasing concentrations of NMP in 2% PEP1 in liquid crystal E7 originating from either capacitance or loss. The relaxation frequency of these mixtures is also reported on the right axis. (b) The capacitive response (open box flanking by diagonal box) and the value of the exponent, \( n \), of the constant phase element of these mixtures (box with diagonal).
Figure 5.24: The apparent dielectric response of mixtures containing increasing concentrations of NMP in mixtures containing 2% EPE1 and liquid crystal E7.
Table 39: The fit to the data above showing the effect of increasing the amount of NMP in a mixtures containing 2% EPEI and liquid crystal E7, to a circuit comprising of a resistor in series with parallel combination of a capacitor, constant phase element and H-N element. The capacitance is reported as the dielectric constant. The portion of the apparent dielectric response contribution from loss mechanisms is shown in the last column.

<table>
<thead>
<tr>
<th>NMP Conc. (Ohms)</th>
<th>R (Ohms)</th>
<th>H-N</th>
<th>CPE</th>
<th></th>
<th>Portion of CPE or low freq. response (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.9%</td>
<td>24.51</td>
<td>207</td>
<td>120.48</td>
<td>0.89</td>
<td>1</td>
</tr>
<tr>
<td>20%</td>
<td>24.90</td>
<td>214</td>
<td>1,189.50</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>60%</td>
<td>23.39</td>
<td>172</td>
<td>0.04</td>
<td>0.55</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 5.25: Graphs showing (a) the portion of the total apparent dielectric response of mixtures made from increasing concentrations of NMP in 2% EPE1 in liquid crystal E7 originating from either capacitance or loss. The relaxation frequency of these mixtures is also reported on the right axis. (b) The capacitive response (open box flanking diagonal box) and the value of the exponent, \( n \), (box with diagonals) of the constant phase element of these mixtures.
5.2.3.3 Mixing Surfactants

Earlier in Chapter 3 it was stated that an intermediate HLB could be obtained by mixing surfactants of differing HLB values, and the resulting value would be:

\[
HLB_{\text{mixture}} = \phi HLB_A + (1-\phi) HLB_B
\]  

(5.1)

With this in mind, mixtures were prepared; their concentrations are summarized in Table 40. Note that theoretically both these mixtures should have the same HLB although they contain differing components. These surfactant mixtures were used to make mixtures containing 2% of the surfactant mixture, 8.91% NMP and 89% E7. The dielectric response of these mixtures were compared to those made from the neat surfactants, that is mixtures containing 2% of either PEP1, EPE1 or EPE2 and 8.91% NMP and 89% E7 (Figure 5.26). The effect of mixing the surfactants is to make a poorer dielectric although the mixtures HLB were intermediate. In the next section a better way of controlling the HLB will be explored.

Table 40: Surfactant mixtures made to obtain an intermediate HLB.

<table>
<thead>
<tr>
<th></th>
<th>PEP1 (%)</th>
<th>PEP1 (HLB)</th>
<th>EPE1 (%)</th>
<th>EPE1 (HLB)</th>
<th>EPE2 (%)</th>
<th>EPE2 (HLB)</th>
<th>$HLB_{\text{mixture}}$</th>
</tr>
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<tbody>
<tr>
<td>Mix #1</td>
<td>50</td>
<td>20.5±2.5</td>
<td>50</td>
<td>8±1</td>
<td>0</td>
<td>20.5±2.5</td>
<td>14.25±1.75</td>
</tr>
<tr>
<td>Mix #2</td>
<td>0</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td></td>
<td></td>
<td>14.25±1.75</td>
</tr>
</tbody>
</table>
Figure 5.26: The effect of mixing surfactants of differing HLB values on the dielectric response. The effect of mixing surfactants (open symbols) on the dielectric response is to make a lossier dielectric.
5.2.3.4 The effect of increased PEG

The effect of increasing the percentage of the polyethylene glycol (PEG) block in the triblock surfactant was also explored. With increased PEG concentration the HLB values increases, a table of these values is shown in Table 41. The apparent dielectric response and the fit results of the two mixture concentrations reported here to explore any trends, are for a mixture of 1% surfactant, 9% NMP and 90% liquid crystal E7 (Figure 5.27 and Table 41) and another of 2% surfactant, 20% NMP and 78% E7 (Figure 5.28 and Table 42).

Although they were no clear trends such as those related to the relaxation frequency, for both the compositions the capacitive response generally decreases with increased PEG portion for the EPE class of surfactants while the capacitive response increases for the PEP class of surfactants (Figure 5.29). This means that with increasing HLB in the EPE system the capacitive portion of the response decreases while in the PEP system it is opposite.
Figure 5.27: The effect of increasing the portion of the polyethylene glycol block in the copolymer on the apparent dielectric response of a mixture made of 1% surfactant, 9% NMP and 90% E7. Both the EPE and PEP class of surfactants were used.
Table 41: The fit to the data above showing the effect of increasing the portion of the polyethylene glycol block in the copolymer on the apparent dielectric response of a mixture made of 1% surfactant, 9% NMP and 90% E7, to a circuit comprising of a resistor in series with parallel combination of a capacitor, constant phase element and H-N element. The capacitance is reported as the dielectric constant. The portion of the apparent dielectric response contribution from loss mechanisms is shown in the last column.

<table>
<thead>
<tr>
<th>Surf Name</th>
<th>PEG %</th>
<th>HLB</th>
<th>R (Ohm s)</th>
<th>H-N</th>
<th>CPE</th>
<th>ε</th>
<th>CPE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.28: The effect of increasing the portion of the polyethylene glycol block in the copolymer on the apparent dielectric response of a mixture made of 2% surfactant, 20% NMP and 78% E7. Both the EPE and PEP class of surfactants were used.
Table 42: The fit to the data above showing the effect of increasing the portion of the polyethylene glycol block in the copolymer on the apparent dielectric response of a mixture made of 2% surfactant, 20% NMP and 78% E7, to a circuit comprising of a resistor in series with parallel combination of a capacitor, constant phase element and H-N element. The capacitance is reported as the dielectric constant. The portion of the apparent dielectric response contribution from loss mechanisms is shown in the last column.

<table>
<thead>
<tr>
<th>Surf Name</th>
<th>PEG %</th>
<th>HLB</th>
<th>R (Ohm s)</th>
<th>H-N</th>
<th>CPE</th>
<th>ε</th>
<th>CPE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H (ε)</td>
<td>Rel. Freq. (Hz)</td>
<td>μ</td>
<td>psi</td>
</tr>
<tr>
<td>EPE Mixtures</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPE0</td>
<td>10</td>
<td>1-7</td>
<td>26.49</td>
<td>268</td>
<td>330.20</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>EPE1</td>
<td>30</td>
<td>7-9</td>
<td>24.90</td>
<td>214</td>
<td>1,189</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>EPE3</td>
<td>50</td>
<td>18-23</td>
<td>20.79</td>
<td>169</td>
<td>497.36</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>EPE4</td>
<td>80</td>
<td>&gt;24</td>
<td>21.05</td>
<td>166.9</td>
<td>363.53</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PEP Mixtures</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEP0</td>
<td>10</td>
<td>2-7</td>
<td>22</td>
<td>164.7</td>
<td>597.43</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PEP1</td>
<td>50</td>
<td>12-18</td>
<td>20</td>
<td>203.9</td>
<td>596.53</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 5.29: The effect of increasing the portion of the PEG block on the magnitude of the capacitive response of mixtures containing (a) 1% surfactant, 9% NMP and 90% E7 and (b) 2% surfactant, 20% NMP and 78% E7. In both these mixture compositions (a) and (b) the capacitive response decreases for the EPE class with increasing PEG %, while it increases for the PEP class of surfactants.
5.2.4 Polymer Binders

With the goal of trying to reduce ionic mobility and possibly create new interface some mixtures were mixed either the mesogenic monomer RM82 or TEGDA and a small amount of photoinitiator Irgacure 651 so that they could be gelled. Surprisingly the effect of polymerization on the dielectric response of both the RM82 and TEDGA systems was negligible. As examples, the results of the dielectric response measurements for two different mixtures polymerized with either 5% TEDGA or RM82 are shown in (Figure 5.30a) and (Figure 5.30b) respectively. This may be because the polymer simply encapsulated the mixtures by polymerization induced phase separation, without changing the mixture.
Figure 5.30: The effect on the apparent dielectric response of polymerizing using (a) 5% TEDGA and (b) 5% RM82 of two different mixtures one with 2% PEP1, 58% E7 and 40% NMP and the other 3% S7, 88.19% E7 and 8.81% NMP. The responses of the materials without polymer are shown as lines while those polymerized are symbols.
5.3 Summary

The goal of the research described in this chapter was to reduce the losses and maximize the capacitive portion of a mixture by making heterogeneous systems using liquid crystals. Results show that the losses that were observed in the individual components and binary systems were reduced by using a third component. It was found that simply having an oil-like host, a water-like component and a surfactant did not provide a good dielectric. Some non intuitive findings were observed. Replacing the ferroelectric liquid crystal with nematic liquid crystal and replacing the solvent NMF with NMP provided a better dielectric. This is surprising as the FLC’s have a higher dielectric response than nematics at lower frequencies, and the conductivity of NMF is higher than NMP. Predictions from Maxwell-Wagner’s theory would have preferred the FLC and NMF combination.

The right choice of surfactant was also important. For example, when the mixtures made using Triblock polymeric surfactants are compared with those prepared using the surfactant S7, the improvement is dramatic (Figure 5.31 and Table 43). Not only is the capacitive portion of the response increased in the PEP1 mixtures, the loss portions of the PEP1 mixtures are closer to capacitive responses (i.e. the value of the exponent $n$ of the CPE are close to 1).

The trends observed in one system did not necessarily transfer to another system. For example, in the mixture with the surfactant S7, increasing the concentration of
solvent while holding the S7 concentration constant only increased the losses, while in the polymeric Triblock surfactant system; this increases the relaxation frequency and also the portion of the capacitive response.

The effect on the dielectric response of using triblock polymeric surfactants in mixtures with increasing hydrophilic portion (PEG) depended on the class of surfactant. For the EPE class where the hydrophobic group is flanked by hydrophilic groups the effect of increased PEG portion is to increase losses, while for the PEP class where the hydrophilic block is flanked by two hydrophobic blocks it is opposite.

A quick attempt at reducing ionic mobility and increasing interfacial surfaces using polymers found that the resulting composites dielectric response were not different from the original mixtures.

![Figure 5.31: Comparing the capacitive portions of mixtures made using either 2% of surfactant S7 or PEP1 in mixtures containing increasing concentrations of NMP in liquid crystal E7.](image-url)
Table 43: Comparing the fits to the data of mixtures made using either 2% of surfactant S7 or PEP1 in mixtures containing increasing concentrations of NMP in liquid crystal E7

<table>
<thead>
<tr>
<th>NMP Conc.</th>
<th>R (Ohms)</th>
<th>H-N</th>
<th>CPE</th>
<th>ε</th>
<th>Portion of CPE or low freq. response (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H (ε)</td>
<td>Rel. Freq. (Hz)</td>
<td>mu</td>
<td>psi</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEP1 Mixtures</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.9%</td>
<td>29.64</td>
<td>204</td>
<td>135</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>20%</td>
<td>25.04</td>
<td>203.9</td>
<td>596.53</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>60%</td>
<td>4.23</td>
<td>117.9</td>
<td>0.03</td>
<td>0.7</td>
<td>0.94</td>
</tr>
<tr>
<td>S7 Mixtures</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.9%</td>
<td>30.83</td>
<td>282.7</td>
<td>10000</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>20%</td>
<td>40.95</td>
<td>201</td>
<td>0.02</td>
<td>0.7716</td>
<td>0.5</td>
</tr>
<tr>
<td>60%</td>
<td>27.94</td>
<td>143</td>
<td>0.88</td>
<td>0.71</td>
<td>0.91</td>
</tr>
</tbody>
</table>
CHAPTER 6

Conclusions

In this dissertation, the possibility of using liquid crystals and mixtures containing liquid crystals as dielectrics were explored using impedance spectroscopy. A measurement methodology that would allow for the correct characterization and comparison of these high dielectric constant heterogeneous systems was developed. The mixtures developed had much better dielectric properties than the individual components. These mixtures developed had a high dielectric response and low losses. For example, the dielectric constant of the best mixture made using low molecular weigh surfactants had a capacitive dielectric constant of 282.7 while the best mixture made using triblock polymeric surfactant had a capacitive dielectric response of 217. These mixtures were developed so that these contributions would originate from low loss Maxwell-Wagner polarization. The very simple process of making these high dielectric constant, low loss mixtures make them very attractive candidates for dielectrics.

Impedance spectroscopy allowed for the measurement both the real and imaginary dielectric constants of the materials over a broad frequency range (1mHz to 1MHz). This enabled a better understanding of the dielectric properties of the mixtures there are many well understood models that could be fitted to the data.
The choice of the model that corresponded to the most probable situation in the material required the knowledge of the properties of the sample holder (the cell) that could have an effect on the measured dielectric response. It was found that the cells have a frequency dependent dielectric response that was related to the surface resistance of the ITO. Hence measurements of the empty cell prior to filling were required. The thickness of the polyimide alignment coating controlled by the Polyamic Acid (PAA) solution concentration and coating spin speed was measured using Variable Angle Spectroscopic Ellipsometry. The thickness and chemical composition of this layer was important. Layers that promoted an alignment of liquid crystal perpendicular to the electrode showed higher electrode polarization. Very thin coatings of PI2555, a polyimide that promote parallel alignment of liquid crystal to the electrode, showed responses similar to those of homeotropic promoting layers. These findings helped separate features that were due cell parameters and those originating from the mixture. Although, electrode polarization is an intrinsic part of the mixture, it is separated from the mixture response because it varies from cell to cell. This contribution was one of the parameters that needed to be minimized.

Knowledge of the most probable structure of the sample was at best a good guess based on the materials used. In this dissertation, in addition to exploring liquid crystals, the materials were chosen to create the best possible structure that would enhance the contribution to the dielectric response from the Maxwell-Wagner effect. The origin of this effect is collection of charges at the interface of materials with different conductivities and / or dielectric constants. This effect was best modeled by the
Havriliak-Negami model, which models the frequency dependence of the dielectric response which changes from a low frequency high value to a high frequency low value at the frequency where the contribution from the Maxwell-Wagner approaches zero.

In the case of Liquid Crystals, although they did exhibit high dielectric response – higher than most polymers, they make poor dielectrics for energy storage purposes due to their high losses.

Dispersing certain solvents and surfactants into liquid crystals had an effect of increasing the contribution from the Maxwell-Wagner effect, including increasing the magnitude, relaxation frequency and decreasing losses. For example, adding just 1% of surfactant S7 to liquid crystal E31 caused the relaxation frequency to move from 3.26 Hz to 4000Hz, with a corresponding increase in the real dielectric constant from 6.2 to 132, while reducing losses in this frequency region.

Losses could be reduced even more by the addition of a third component, the solvent NMP. There were some general trends that were observed in some systems, including a decrease in losses and an increase in the dielectric response on addition of surfactant and the increase in relaxation time as more solvent was added. Mixtures made using nematic liquid crystal E7, the solvent NMP and triblock polymeric surfactants created the mixtures with the lowest losses. Extensive work was done with this systems including studying the effects of block placement and proportion. In the end it was the mixture containing the EPE class of surfactants that was most promising.

Further work that should be done with these systems is to further explore effects of increased addition of surfactant. The use of Fluorinated liquid crystals that have a
lower conductivity would further enhance these dielectrics by lowering the losses due to DC conductivity. To further improve and ruggedize these systems the structures formed would have to be gelled so that they would withstand high temperature and voltages. This could be achieved by the use of polymerizable block surfactants. Although some preliminary work was done to try and identify the structure of these systems using fluorescence microscopy, more work has to be done to better understand the physical structure and the location of the components of the systems.
APPENDIX

Setup of the Schlumberger® 1260 and Solartron® 1296

The same procedures and settings outlined below were used for all measurements.

SETUP: (steps 1 and 2 should need to be done only once)

1a) The GPIB address has to be set on the rear of the SI 1260, this is done by using dip switches. (If you are using the Solartron® 1296 dielectric interface you need to set its GPIB address in a similar fashion making sure that its address does not conflict with the SI 1260.)

1b) The “F1”, “F2” and “TALK ONLY” switches must be set to “OFF”.

1c) Connect the SI 1260 and the SI 1296 with a GPIB cable, and the three BNC cable provided. The BNC cables connect the generator output, V1 and V2 BNC terminals on the SI 1296 to the corresponding BNC terminals on the SI 1260.

1d) To connect to the PC the National Instruments high speed USB to GPIB converter was used. Before connecting to the PC install the program NI 488.2, this is the driver for the National Instruments GPIB card.

2) Launch the SMaRT program and follow the following steps to connect to the SI 1260 (and SI 1296 if connected)
2a) Follow the menu Tools>>Hardware Settings>>Interface to obtain the following dialog box to select the equipment you are using. (Fig 1) Select “None (1260 stand alone mode)” if you are not using the SI 1296, select SI 1296 otherwise. Here you will need to enter the SI 1296 GPIB address if used.

Fig 1: Dialog box obtained from Tools>>Hardware Settings>>Interface. It is used to select model number of equipment used.

2b) Set the GPIB address and card number of the Gain/Phase analyzer by clicking on the FRA tab. (Fig 2)

Fig 2: Hardware settings for the GPIB address of the SI 1260. If you are unsure of the address you chose click on “Search GPIB” and take down the even numbered address, this will be the GPIB address of the SI 1260.
When this is complete the PC should be able to communicate with the SI 1260.

3) The SI 1260 now needs to know the voltage, frequency range, and integration time to be applied to the cell, in SMaRT this is called an “experiment”.

3a) Follow File>>New>>Experiment to get to the experiment editor (Fig 3). The editor launches with a default program, you can individually edit each line by clicking on that line. For example, you can set the AC voltage applied to the cell by clicking on the “set AC level” line. This will bring up a dialog box that lets you choose a ramp or a fixed voltage, we used a fixed voltage of 500mV A.C. and zero volts D.C. We used a logarithmic sweep taking ten points per decade over the frequency range 1MHz to 1 mHz.

3b) To measure the impedance we set the integration time to ten cycles, with the current and voltage range set to “Auto”. Note that we decided to use whole cycles to comply with the filtering capabilities of the analyzer discussed earlier. Although setting the current input to “auto” made the measurements longer, it was easier than estimating the current for each sample that we measured.

3c) When all these parameters are set the “experiment” needs to be saved.

3d) The data collection begins by simply clicking the icon labeled with a traffic light.
Fig 3: The experiment editor dialog box obtained from File>>New>>Experiment. Note that it opens with a default program.
Testing the Instruments

Periodically it is recommended that the SI 1260 be checked using the following phase and amplitude test recommended by the manufacturer were performed:

a) Use the front panel keys and program a 1 volt amplitude and sweep frequency from 1MHz to 1Hz and to display V1/V2.

b) Connect channels 1 and 2 via a 'T' connector using BNC cables.

c) Run the program.

d) V1/V2 displayed will be dispalyed. The result shown should be 1 throughout the sweep, with a phase value of zero degrees.

e) The experiment should then be repeated displaying only the V1 value, the voltage displayed should be approximately 1 (although this may vary slightly at high frequency).

f) This can then be repeated displaying V2 to check that similar results are obtained.

g) The generator output can be checked via connection to an oscilloscope.
Program Used to Obtain the Apparent Dielectric Response

Fig 4: The front panel of the LabView® program used to obtain the apparent dielectric response from the empty cell impedance. The program takes in the empty and filled cell impedances as inputs and outputs the apparent dielectric response shown here in the graph window.

```
Bottom=CemptyRE**2+CemptyIM**2;

CapRE=((CmeasRE * CemptyRE )+ (CmeasIM * CemptyIM))/Bottom;

CapIm=((CmeasIM * CemptyRE)-(CmeasRE*CemptyIM))/Bottom;
```

Fig 5: The portion of the Labview program used to calculate the apparent dielectric response from the empty and filled cell impedance.
The Effect of Polyimide Thickness on the Dielectric Response

Fig 6: The apparent dielectric response of a mixture of 88.19% liquid crystal E7, 8.81% solvent N-Methyl Formamide (NMF), and 3% surfactant Didodecyl Ammonium Bromide (DDAB) filled in a 10 micron thick cell coated with polyimide 2555 of varying concentrating and coating spin speed.
Table 44: Results of fitting a resistor in series to a HN element and Constant phase element in parallel to the apparent dielectric measurements above. H is the magnitude of the dielectric strength as defined by the Havriliak-Negami element, tau is the relaxation frequency of the relaxation mode, mu and psi are HN element coefficients, Q and n are the dielectric response and the exponent of the constant phase element respectively and R is resistance of the Capacitor.

<table>
<thead>
<tr>
<th>Cell ID</th>
<th>Imide conc.</th>
<th>Spin Speed</th>
<th>H</th>
<th>tau (sec)</th>
<th>mu</th>
<th>psi</th>
<th>Q</th>
<th>n</th>
<th>R</th>
<th>% of Q in Apparent dielectric Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>191</td>
<td>2%</td>
<td>3000</td>
<td>842.10</td>
<td>5.06E-05</td>
<td>0.9641</td>
<td>1</td>
<td>170.9</td>
<td>0.7366</td>
<td>n/a</td>
<td>17%</td>
</tr>
<tr>
<td>200</td>
<td>2%</td>
<td>1500</td>
<td>554.6</td>
<td>2.19E-05</td>
<td>0.9956</td>
<td>1</td>
<td>160</td>
<td>0.8174</td>
<td>396.05</td>
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</tr>
<tr>
<td>222</td>
<td>4%</td>
<td>3000</td>
<td>232</td>
<td>1.53E-05</td>
<td>1</td>
<td>0.7084</td>
<td>43.7</td>
<td>0.7095</td>
<td>225.76</td>
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</tr>
<tr>
<td>219</td>
<td>4%</td>
<td>1500</td>
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<td>1.08E-05</td>
<td>1</td>
<td>0.9028</td>
<td>54.49</td>
<td>0.7819</td>
<td>n/a</td>
<td>26%</td>
</tr>
</tbody>
</table>
The Effects of Increasing the Surfactant Concentration on Dielectric Response

S7 + NMF + E31 mixtures

Fig 7: The effect of increasing the amount of surfactant in mixtures containing 1:10 mixture of the solvent NMF to Liquid Crystal E31.
Fig 8: The effect of increasing the amount of surfactant in mixtures containing 1:2.4 mixture of the solvent NMF to Liquid Crystal E31.

Fig 9: The effect of increasing the amount of surfactant in mixtures containing 1:0.44 mixture of the solvent NMF to Liquid Crystal E31.
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