



Electrical properties of Magnesium Ion Conducting Biopolymer Electrolyte SPE Energy Storage

Research Project

Submitted to the department of Physic in partial fulfillment of
the requirement for the degree of B.A in physics

By :

Freshтта hassan rasul

Supervised by:

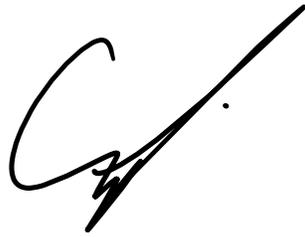
Asst. Prof. Dr. Mowfaq Jalil Ahmed

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Supervisor Certificate

This research project has been written under my supervision and has been submitted for the award of the degree of BSc. in (Physics).

Signature



Name: Asst. Prof. Dr. Mowfaq Jalil Ahmed

Date: 2024/04/12

I confirm that all requirements have been completed.

Signature:

Name: Asst. Prof. Dr. Asaad Hamed

Head of the Department of Physics

Date: / 4 / 2024

Dedication

My great parents, who never stop giving of themselves in countless ways.

My beloved and sisters.

To all my family and my friends who encourage and support me. All the people in my live who support me in academic life.

Acknowledgements

First and foremost, I must acknowledge my limitless thanks to Allah, the Ever-Magnificent; the Ever-Thankful, for His help and blessing. I owe a deep debt of gratitude to the physics department and Salahaddin University for giving us an opportunity to complete this work. I am very appreciative of my colleagues in the physics department. I am grateful to some people, who worked hard with me from the beginning till the completion of the present research particularly my supervisor Dr. Mowfaq Jalil Ahmed, has been always generous during all phases of the research. I would like to take this opportunity to say warm thanks to all my beloved friends, who have been so supportive along the way of doing my thesis. I also would like to express my wholehearted thanks to my family for the generous support they provided me throughout my entire life and particularly through the process of pursuing the thesis. Last but not least, deepest thanks go to all people who took part in making this thesis real.

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List of Abbreviations

<i>Abbreviation</i>	<i>Meaning</i>
<i>SPE</i>	solid polymer electrolyte
<i>CS</i>	chitosan
<i>POZ</i>	poly (2-ethyl-2-oxazoline)
<i>NH₄NO₃</i>	ammonium nitrate
<i>GL</i>	glycerol
<i>FTIR</i>	Fourier transform infrared
<i>ITP</i>	ion transport parameters
<i>n</i>	number of charge carriers
μ	ionic mobility
<i>D</i>	diffusion coefficient
<i>M_r</i>	real part of modulus
<i>M_i</i>	imaginary part of modulus
σ_{ac}	ac conductivity
<i>LE</i>	liquid electrolyte
<i>PEO</i>	poly (ethylene) oxide
σ_{dc}	dc conductivity
<i>PEG</i>	poly ethylene glycerol
<i>PPE</i>	plasticized polymer electrolyte
<i>R</i>	resistance
<i>C</i>	capacitance
ϵ_r	dielectric constant
ϵ_i	dielectric loss
<i>PVA</i>	poly vinyl alcohol
<i>GPE</i>	gel polymer electrolyte
<i>PVdF</i>	poly (vinyl denfluoride)
ϵ^*	dielectric permittivity
<i>Li⁺</i>	Lithium ion
<i>Mg⁺²</i>	Magnesium ion
<i>IS</i>	impedance spectroscopy
<i>tan δ</i>	loss tangent
<i>Z_r</i>	real part of impedance
<i>Z_i</i>	imaginary part of impedance
<i>Z[*]</i>	complex impedance
<i>EIS</i>	electrochemical impedance spectroscopy
<i>GL</i>	glycerol
<i>R</i>	resistance
<i>C</i>	capacitance
<i>D</i>	diffusion coefficient

Abstract

The study intended to investigate ion conduction and polarization effects in biopolymer-mix electrolyte systems. The dielectric characteristics of CSPVMGNT were examined to better understand energy storage and loss due to ion mobility. Polymer blends were delivered using chitosan (CS) and polyvinyl alcohol (PVA), with 50 wt. % magnesium nitrate ($Mg(NO_3)_2$) as a source of Mg^{+2} ions. The CS:PVA: $Mg(NO_3)_2$ system was reviewed with various glycerol plasticizer concentrations to enhance ion conductivity. The electrochemical properties of manufactured films were analyzed using several approaches to determine their viability as energy storage materials. Increased plasticizer content resulted in a significant improvement in dielectric constant. The presence of an asymmetric relaxation peak in $\tan\delta-M''$ spectra indicates non-Debye relaxation. The biopolymer mix electrolyte with a plasticizer level of 55 wt. % had the greatest DC conductivity, measuring $7.34 \times 10^{-5} Scm^{-1}$. results show promise for the potential application of the current plasticized magnesium ion-conducting biopolymer blend electrolyte in energy storage devices.

Chapter one

1.1 Introduction

Renewable energy sources include those that are obtained from naturally renewing sources such as the sun, wind, storms, oceans, seeds, algae, geothermal, and biodegradable polymer materials, and they have piqued the curiosity of many people due to the rising oil problem and environmental concerns. (Zhou, 2021), (Wang, 2020) Polymer electrolyte (PE) science is a broad field that includes polymer science, organic chemistry, electrochemistry, and inorganic chemistry. (Wang, 2009). A polymer electrolyte is an ion conducting membrane as well as separator with moderate to high ionic conductivity at ambient temperature. Polymers have recently been an important subject in material science, especially solid-state solutions, which are an example of ion conducting polymers (solid-state polymer electrolytes SPE). Researchers are interested in ion-conducting polymers as an example of solid electrolyte. Because of its application potential in electrochemical devices such rechargeable batteries, fuel cells, and supercapacitors. Lithium-ion batteries (LIB) and conventional liquid electrolytes (LES) have traditionally been the primary sources of power for different commercial electronic gadgets. However, flaws like as high flammability, chemical instability, and volatile liquid electrolytes can result in battery combustion and even explosion. (Jian, 2022).

The study attempted to examine at the behavior of ion conduction and polarization effects in biopolymer mix electrolyte systems. The dielectric properties of the CSPVMGNT were investigated to understand the energy storage and the energy loss from the mobility of ions.

1.2 Literature review

Wright (1975), a polymer scientist from Sheffield, invented conductive SPEs. (Wright, 1975) Poly(ethylene) oxide (PEO) has been utilized to dissolve inorganic salts and conduct ions at ambient temperature circumstances since its discovery by Wright and colleagues in 1975. (Hamdan, 2014). SPEs are regarded as really multifunctional materials because of their versatility as an ion transportation medium in critical applications such as energy storage and electrochemical displays. (Wright, 1998). SPEs are being developed to replace standard LEs. LEs are incompatible for use for a variety of reasons, including poor electrochemical stability, leakage, and environmental effect. SPE is offered as a solution to these issues in this work due to its compatibility with electrodes, ease of processing, low weight, and coast ability. (Hafiza, 2014). Because they are solvent-free, SPEs are recognized for their excellent safety performance. SPEs with strong elastic relaxation qualities under stress are simple to operate with and process (Ibrahim, 2014). Scientists are now looking for a novel polymer host that has improved conductivity and mechanical characteristics while being cost-effective and ecologically safe. . In comparison to gel and LE, SPE has several advantages, including no leakage and simple manufacture. However, because of its low conductivity value, it is challenging for researchers to develop high-quality polymer electrolytes with good ionic conductivity. (Hafiza, 2014). These problems can be solved in a variety of ways, such as by combining two polymers, adding nano-sized fillers to the polymer matrix, plasticizing it with a liquid additive, etc. (Hirankumar, 2018). Polymers are classified into two types: synthetic and natural. The removal of waste and the depletion of nonrenewable fossil fuels have driven the development of ecologically acceptable alternative energy sources. Because plastic rubbish does not degrade when it is abandoned, it continues to damage the environment. As a result, there has been a

drive to develop biodegradable polymers to replace those that are not. Furthermore, synthetic-based polymers are petroleum-derived, have a high material cost, and are nonbiodegradable in nature. To reduce the need for petroleum-based polymers, researchers have attempted to create natural biopolymers. (Rani, 2015). An ion-pairing effect appears to be associated to a decrease in conductivity and polarization, according to the literature. Due to the low dielectric permittivity of host polymers, a variety of methods have been suggested to improve DC conductivity (DC), including plasticization, salt doping, polymer grafting, polymer blending, and salt doping (Aziz, Hamsan, 2020). Plasticization, which increases salt dissociation, is an important stage that raises conductivity. (Asnawi, 2020). In addition to plasticization, utilizing two polymers as the host material for ionic conduction may enhance the conductivity of a polymer electrolyte (Rani, 2015). When two polymers are joined, extra complexation sites are formed, which increases ion movement, exchange, and conductivity. The electrical conductivity of natural CS films is very low. The hydrogen atoms in the CS monomer are strongly linked and cannot be mobilized by an electric field. Polymer blends based on POZ:CS electrolyte systems impregnated with varied NH_4NO_3 compositions electrolyte systems were created by solution casting in the presence of 1% acetic acid solvent (Rani, 2015).

POZ has been suggested as a possible biological candidate in several research investigations (Aziz, woo, 2020). Understanding how ions conduct through polymers is essential to create more efficient polymer electrolytes for electrochemical devices (Navaratnam, 2015). Plasticization is another approach to improve the conductivity of an electrolyte. Adding a little quantity of liquid to a polymer matrix can plasticize the polymer chain and accelerate the rate of salt dissociation. A high dielectric constant plasticizer may dissolve more salt and create more free mobile ions (Shukur, 2013). The plasticization process affects salt

dissociation through offering more conducting paths for mobile ions to travel, increasing the ionic conductivity of the polymer electrolyte (Asnawi, 2020). Furthermore, plasticizer has the ability to increase the amorphous nature of SPE, leading to an increase in the segmental motion of the polymer chain, which supports more ion mobility due to a lower energy barrier and is expected to increase ionic conductivity (Hafiza,Isa,M.I.N , 2020). Because of the polymers' strong connections, several researchers moved their emphasis to polymer mixing, one of the most effective ways for improving the electrical and mechanical properties of electrolytes systems (Rani, 2015). Researchers are interested in polymer blending because of the simplicity of the preparation and the ability to control the physical properties of the films (Shukur, Ithnin, Kadir, 2014). One aspect that influences the conductivity of polymer mixtures is their miscibility. Blends that do not have phase separation will have greater conductivities than blends that do. Magnesium nitrate salt ($Mg(NO_3)_2$) (Aziz, Ahmed 2023) was used in this study because Magnesium salts are known to be effective polymer matrix proton donors. CS is a popular polysaccharide in blending systems with other polymers. As a natural polymer, CS is used as a host polymer since it is non-toxic and biodegradable (Navaratnam, 2015). This natural biopolymer's availability, cheap cost, biocompatibility, biodegradability, and simplicity of chemical modification are all benefits. CS can be used in various applications, such as water treatment, pharmaceutical products, agriculture, and membrane formation. Biodegradable polymers, such as CS, can create solid electrolytes that are environmentally safe and have good processing capabilities for producing thin films, allowing for more creative battery system designs, such as multiple cell battery systems (Sudaryanto,2015). When two polymers are joined, additional complexation sites are formed, which increases ion movement, exchange, and conductivity. The electrical conductivity of natural CS films is quite low. The hydrogen atoms in the CS monomer are firmly linked and

cannot be mobilized by an electric field. Polymer blend electrolyte systems were developed by solution casting in the presence of 1% acetic acid solvent on the basis of POZ:CS electrolyte systems impregnated with varied $(\text{Mg}(\text{NO}_3)_2)$ compositions (Rani, 2015). POZ has been identified as a possible biological candidate in several research investigations (Aziz, Woo, 2020). Understanding how ions conduct through polymers is essential for developing more efficient polymer electrolytes for electrochemical devices (Navaratnam, 2015). Plasticization is another approach for improving the conductivity of an electrolyte. A small quantity of liquid added to the polymer matrix can plasticize the polymer chain and increase the rate of salt dissociation. A high dielectric constant plasticizer may dissolve more salt and create more free mobile ions (Shukur, 2013). The plasticization process affects salt dissociation by providing more conducting paths for mobile ions to travel, increasing the ionic conductivity of the polymer electrolyte. Furthermore, plasticizer has the ability to increase the amorphous nature of SPE, which promotes an increase in the segmental motion of the polymer chain, which encourages more ion mobility due to a lower energy barrier and is expected to increase ionic conductivity (Hafiza, Isa, M.I.N , 2020). Plasticized SPE is often inflexible due to the strong interactions of the polymers. The attraction forces between polymer chains can be lowered by adding plasticizer to improve their flexibility. Plasticizers are frequently composed of polymers with low molecular weight or nonvolatile organic solvents. Polyethylene glycol (PEG-200, PEG-400, PEG-600), and dimethylformamide are examples of acceptable plasticizers. (DMF), ethylene carbonate (EC), propylene carbonate (PC), etc. (Hirankumar, 2018). GL is a colorless, odorless liquid that is produced as an inevitable by-product of the transesterification of vegetable oils used to manufacture biodiesel. It can also be generated from less toxic materials such as microalgae or cellulose. It is frequently used in drugs due to its inexpensive cost, low toxicity, and unique physicochemical properties, such as water solubility and

hygroscopicity (Sadiq,Aziz, 2022). At room temperature, GL is a non-toxic chemical with a high boiling point (290 °C) and a low melting point (18 °C), preventing evaporation and solidification. According to its chemical formula (C₃H₈O₃), GL has a multi-hydroxyl group structure, which suggests it has more accessible electron lone pairs for ionic conduction. The high dielectric constant (GL) of glycerol (42.5) increases salt dissociation and decreases interactions between polymers. Polymer electrolytes frequently exhibit crystalline and amorphous phases. Considering the fact that ion conduction occurs mostly in the amorphous phase. Ion relaxation and charge transport processes are among the most studied concerns in SPE, a branch of condensed matter physics (Aziz, 2010). FTIR has previously been used to determine the complexation of polymers with salt. FTIR spectroscopy and electrochemical impedance spectroscopy (EIS) have been demonstrated to be efficient approaches for examining the polymer host's interactions with charge carriers and establishing the charge carriers' transport characteristics (Asnawi,Aziz, 2021). Sharma et al. (Kamboj, 2021) have investigated the polymer-ion interaction using FTIR. It was demonstrated that anion peak deconvolution is a new approach for distinguishing between regions associated with single free ions and regions associated with pairs of ions.

Chapter two

Methodology

2.1 Solution Casting Method

The solution casting method, also known as the direct casting method, is one of the most commonly used to prepare polymeric films for food, pharmaceuticals, and biomedical applications (Figure 2.1). This method is straightforward and has been used for a long time to develop film-based polymeric systems. Hence, many authors regard this method as the conventional solution casting method. The method involves the dissolution of the polymers in suitable solvents. The polymeric solutions, which may contain various additives, such as plasticizers.

The blends of chitosan can also be used to develop films. Blends are prepared by mixing two or more polymers to tailor the physical properties of the resultant films over the films made with pristine polymer(s). The polymeric blends may either form a homogenous matrix or a phase-separated matrix system. It has been reported that blends of chitosan with different polymers (natural or synthetic) can improve the physical, mechanical, thermal, optical, and barrier properties [Haghighi, 2020]. The natural polymers used for this purpose are classified as polysaccharides and proteins [Haghighi, 2020]. The derivatives of these polymers have also been employed. The examples of polysaccharide-based natural polymers include pectin, starches from different sources (e.g., cassava starch, purple yam starch, and potato starch), bacterial cellulose, carboxymethyl cellulose, and gum Arabic. Protein-based natural polymers include collagen, gelatin, fish myofibrillar protein, soy protein isolate, and zein [Haghighi, 2020].

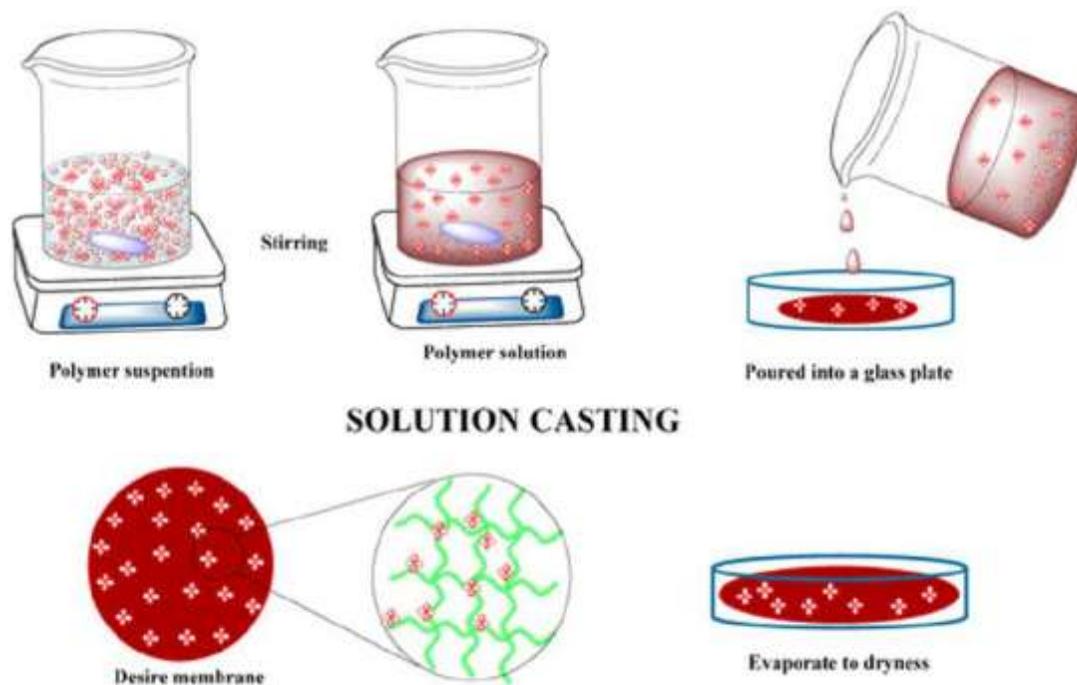


Figure (2.1) General steps in the solution casting method [Ilyas, etal 2022).

Some of the synthetic polymers employed in conjunction with chitosan include poly (vinyl alcohol), poly (ϵ -caprolactone), and ethylene-vinyl alcohol. These polymers are mixed with chitosan solution and homogenized before the degassing stage, and this is then used for the film casting.

The functionality of the chitosan films (pristine or blend) can further be improved by adding additives. Various additives, such as essential oils and nanoparticles, are being added to enhance the mechanical and barrier properties. These components are added to the chitosan solution or chitosan blends and are subsequently homogenized to form stable emulsions or dispersions.

2.2 Sample Preparation

Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$), polyvinyl alcohol (PVA), and chitosan (CS) are required to create the CS:PVA: $\text{Mg}(\text{NO}_3)_2$ matrix of hosts. Magnesium nitrate provides Mg-ions to the mixture. The solvent acetic acid (CH_3COOH) and double-distilled water were needed as agents for polymeric materials in the solution-cast method.

The present samples have been prepared previously using the solution casting method (Aziz,2023).

To prepare the biopolymer mix host matrix, 1g of CS was disseminated in 60 mL of 1% acetic acid solution using a magnetic stirrer for several hours at room temperature. Meanwhile, 1g of PVA was completely dissolved in 60mL of double-distilled water after constant stirring at 80^0c for many hours.

After the PVA solution had cooled to room temperature, the two polymer solutions were constantly mixed to form a homogeneous viscous solution. Following that, 50 wt.% $\text{Mg}(\text{NO}_3)_2$ salt was added to the CS: PVA blended solutions while stirring to ensure a homogeneous mixture. Following that, glycerol concentrations ranging from 11 to 55 wt.% were gradually added to each solution in increments of 11 wt. percent. Each prepared solution was then placed in a clean, labeled Petri dish, and the solvent was allowed to evaporate at room temperature to produce the film gradually. Finally, the electrolyte systems with glycerol incorporation of 11, 22, 33, 44, and 55 wt.% were coded as CSPVMGNT1, CSPVMGNT2, CSPVMGNT3, CSPVMGNT4, and CSPVMGNT5, respectively.

2.3 Fabrication of the EDLC device

An EDLC is made by blending 6.25% carbon black (CB) and 81.25 % activated carbon (AC) in a planetary ball mill for 20 minutes at 500 rpm. The resulting powder mixture (AC: CB) is then dissolved in 15 mL of N-methy-2-pyrrolidone (NMP) with a 12.5% polyvinylidene fluoride (PVdF) binder until the solution becomes thick and black. Next, use the doctor blading technique to apply the black solution on the 0.25 mm thick metal foil. The coated aluminum foils are then quickly dried in an oven at 60°C. After drying the electrodes, a disk with a geometric area of 2.01 cm^2 is created. Figure (2,2) depicts an EDLC assembly with the AC electrode, highest conductive electrolyte, and AC electrode positioned in that sequence. This design included the cell within a CR2032 coin, which was then put in a Teflon housing as shown in figure (2.2).

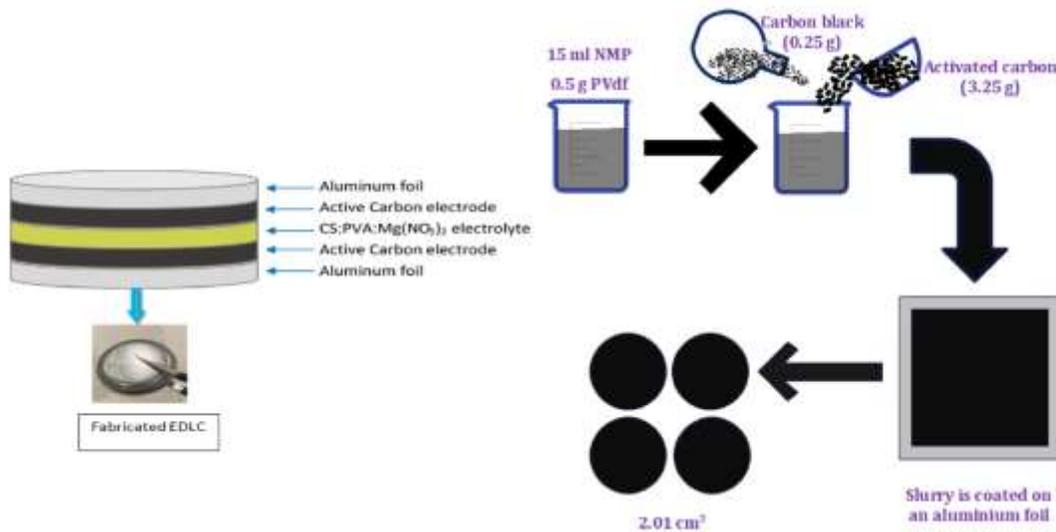


Figure (2.2) Schematic of the EDLC arrangement and electrode formation.

2.4 Impedance Related Function

Impedance spectroscopy, or IS, is an effective method for determining many of the electrical characteristics of materials and their interactions with electrically

conducting electrodes. It may be used to study the dynamics of bound or mobile charge in the bulk or interfacial areas of many kinds of solid or liquid materials, including ionic, semiconducting, mixed electronic-ionic, and even insulators (dielectrics). Several additional measured or calculated impedance variables frequently play an essential role in IS. Other similar functions used in IS include complex admittance ($Y(\omega)$), complex permittivity $\varepsilon(\omega)$, and complex electric modulus $M(\omega)$. The four fundamental impedance response values can be indicated by the generic phrase immittance, whereas the two quantities are commonly characterized as the complex dielectric constant or dielectric permittivity.

$$\varepsilon^* = (j\omega C_0 Z^*)^{-1} = \varepsilon_r - j\varepsilon_i \quad \dots (2.1)$$

$$M^* = j\omega C_0 Z^* = M_r - jM_i \quad \dots (2.2)$$

The dielectric parameters such as dielectric constant (ε_r), dielectric loss (ε_i), loss tangent ($\tan\delta$), complex electric modulus (M_r and M_i) and σ_{ac} was derived from the impedance-related functions as follows (Nofal, 2022) :

$$\varepsilon_r = \frac{Z_i}{\omega C_0 (Z_r^2 + Z_i^2)} \quad \dots(2.3)$$

$$\varepsilon_i = \frac{Z_r}{\omega C_0 (Z_r^2 + Z_i^2)} \quad \dots (2.4)$$

$$\tan \delta = \frac{\varepsilon_i}{\varepsilon_r} \quad \dots(2.5)$$

$$M_r = \frac{\varepsilon_r}{(\varepsilon_r^2 - \varepsilon_i^2)} \quad \dots(2.7)$$

$$M_i = \frac{\varepsilon_i}{(\varepsilon_r^2 - \varepsilon_i^2)} \quad \dots(2.8)$$

$$\sigma_{ac} = \omega \varepsilon_0 \varepsilon_i = \left[\frac{Z_r}{(Z_r^2 + Z_i^2)} \right] \left(\frac{t}{A} \right) \quad \dots (2.9)$$

here, C_0 is vacuum capacitance of the cell and is equal to $\frac{\varepsilon_0 A}{d}$, where ε_0 is the

permittivity of free space 8.85×10^{-12} F/m, A and d are the area and the thickness of the sample, respectively and $\omega = 2\pi f$, where f is frequency of the power source, z_r is the real part of impedance, z_i is the imaginary part of impedance, and $\tan \delta$ is loss tangent.

Chapter Three

Results and discussion

3.1 Dielectric Constants

The dielectric constant determined the polarity of the polymers and the energy stored in each cycle, whereas the dielectric loss characterized the energy lost owing to ion mobility (Liu,2020).

The study examined a material's dielectric characteristics under various situations, including ambient temperature and different frequencies.

Figures 2 and 3 show the measured values of the dielectric constant and dielectric loss. At low frequencies, large dielectric properties were observed, indicating that the electrodes were being polarized due to space-charge effects. The polarization area's size was critical for predicting mobility and effective ion concentration, both of which are important elements in the creation of high capacitance EDLC devices (Machappa,2009).

The results also revealed that at low frequencies, the dielectric constant and dielectric loss values were larger, owing to interfacial polarization. This phenomenon was caused by a rise in charge carrier concentration at the interface, rather than by the electrolyte's bulk properties. At higher frequencies, the dielectric constant and dielectric loss values dropped nonlinearly before reaching a steady state. The dielectric constant and dielectric loss measurements were predicted to plateau at lower frequencies and then show power law dispersion at higher frequencies. This was consistent with Klein et al.'s theoretical study of electrode polarization. The present electrolyte system's ϵ' and ϵ'' spectra clearly demonstrate these characteristics.

Figures 3.1 and 3.2 indicate a rise in ϵ' and ϵ'' values as a fraction of the plasticizer content in the system, owing to an increase in charge carrier concentration (Bhajantri,2021). The present plasticized CS-PVA-Mg (NO₃)₂ biopolymer blend electrolyte systems, notably the CSPVMGNT5 sample, show a significant rise in the ϵ' due to the sample's strong ionic conductivity in the low frequency region. On the other hand, a higher dielectric constant of SPE corresponds to a better ability of the matrix to dissolve salts (Wang,2016). The relaxation behavior of the CSPVMGNT biopolymer blend electrolyte systems was determined by examining the loss tangent ($\tan \delta$).

Figure 3.3 illustrates how the tangent loss ($\tan \delta$) of CSPVMGNT films varies with frequency and temperature. The $\tan \delta$ increased with frequency and peaked at a given frequency before continuously falling after that. This is due to the active (ohmic) component rising quicker than the reactive (capacitive) component at low frequencies. At higher frequencies, the ohmic component loses its frequency dependency, but the capacitive component increases according to frequency.

This pattern of change has already been seen in numerous SPE systems. The system exhibits a wide single peak at the mid-frequency of $\tan \delta$, indicating a non-Debye type dielectric relaxation process (Tripathi,2020). The relaxation time of all plasticized SPEs was calculated using the peak location of $\tan \delta$, which listed in table (3.1).

Table 3.1 The relaxation time of all plasticized SPEs samples

Sample code	relaxation time (s)
CSPVMGNT1	1.32×10^{-3}
CSPVMGNT2	7.58×10^{-4}
CSPVMGNT3	6.06×10^{-5}
CSPVMGNT4	9.23×10^{-6}
CSPVMGNT4	$1.63 \times 10^{-6}s$

As a consequence, the appearance of $\tan \delta$ peaks and the resulting shift in their position with increasing plasticizer concentration support the dielectric relaxation phenomena. SPE films are polarized when an external electric field is applied via microscopic rearrangements of ions, electrons, atoms, and molecules to line up with the external field.

According to previous research, when polymers are mixed together to produce a SPE matrix, the amorphous phase expands and more salts dissolve. This resulted in increased chain length and polymer segmental mobility. Increased polymer chain segmental mobility has been demonstrated to minimize relaxation time, hence accelerating up the ion transport process. When glycerol plasticizer is introduced, the ϵ' rises, and the relaxation peak in the $\tan \delta$ plot changes to higher frequencies, which indicates a shorter relaxation period. Because of a rise in segmental motion within the system, which produces an increase in the mobility of the ions, the ion conductivity rises.

3.2 Electric Modulus Analysis

The Electric Modulus Formalism is a useful tool for understanding the conductivity relaxation processes that occur in ion-conducting fluids. The complex electric modulus (M^*), the inverse of complex electric permittivity, may be used to investigate how ion relaxation impacts polymer electrical characteristics ($M^* = 1/\epsilon^*$). This technique has the benefit of reducing the electrode polarization effects caused by charge formation in the interfacial area (Chérif, 202-).

Figures 3.4 and 3.5 show the real (M') and imaginary (M'') graphs of the electric modulus vs frequency. It is obvious that M' and M'' increase as the frequency scans toward relatively high values, reducing electrode polarization processes at low

frequencies. The fact that M' approaches maximum saturation when the dielectric constant drops at a certain frequency is highly intriguing.

In particular, the more stronger relaxation peak, which appears to vary with glycerol content, occurs in the middle-frequency region of M'' . As the glycerol concentration increases, the loss maxima decrease monotonically. As frequency increases, the peak frequency signifies a transition from long-range to short-range mobility, while the peak value in M'' reflects the components' real dielectric spin relaxation process. This demonstrates that when plasticizer concentration rises, relaxing time decreases.

3.3 Conductivity Analysis

The effect of applied frequency on AC conductivity (σ_{ac}) for all plasticized CS: PVA:Mg(NO₃) Figure 3.6 shows two biopolymer mix electrolyte samples at room temperature. The high salt concentration samples may be divided into three sectors: low, intermediate, and high-frequency areas (CSPVMGNT3, CSPVMGNT4, and CSPVMGNT5).

The conventional electrode polarization effect is visible at low frequencies. The low-frequency dispersion zone is defined as a parabolic region that corresponds to bulk DC conductivity and is correctly connected to compound concentration. A significant finding is that when salt content increases, the relaxation process switches, resulting in the production of AC conductivity in the high-frequency region. Ions are more likely to travel to a more advantageous location before returning to their original place at higher frequencies.

This increased probability explains why higher frequencies have more conductivity, which indicates dispersion. Charge carrier confinement across the sample causes the AC conductivity phenomenon. According to Jonscher's universal power law (Papathanassiou,2006), the large dispersion zone of AC conductivity at high frequency is determined by frequency as a power law with a near to one exponent.

The AC conductivity data in Fig. 7 and table 3.2 were used to estimate the DC conductivity value of each plasticized biopolymer electrolyte.

Table 3.2 AC conductivity of samples at ambient temperature

Sample code	$\sigma_{ac} (S\text{cm}^{-1})$
CSPVMGNT1	9.17×10^9
CSPVMGNT2	1.69×10^7
CSPVMGNT3	2.98×10^6
CSPVMGNT4	1.57×10^5
CSPVMGNT4	7.34×10^5

The DC conductivity clearly rises with increased plasticizer content, while the relaxation time decreases (Fig.4). In other words, the variation in DC conductivity contradicts the interpretation in relaxation time. As more plasticizer is used, the amorphous region grows, resulting in weak and loose molecular packing. As a result, with high glycerol concentration, the polymer chain is simpler to align, resulting in a shorter relaxation time.

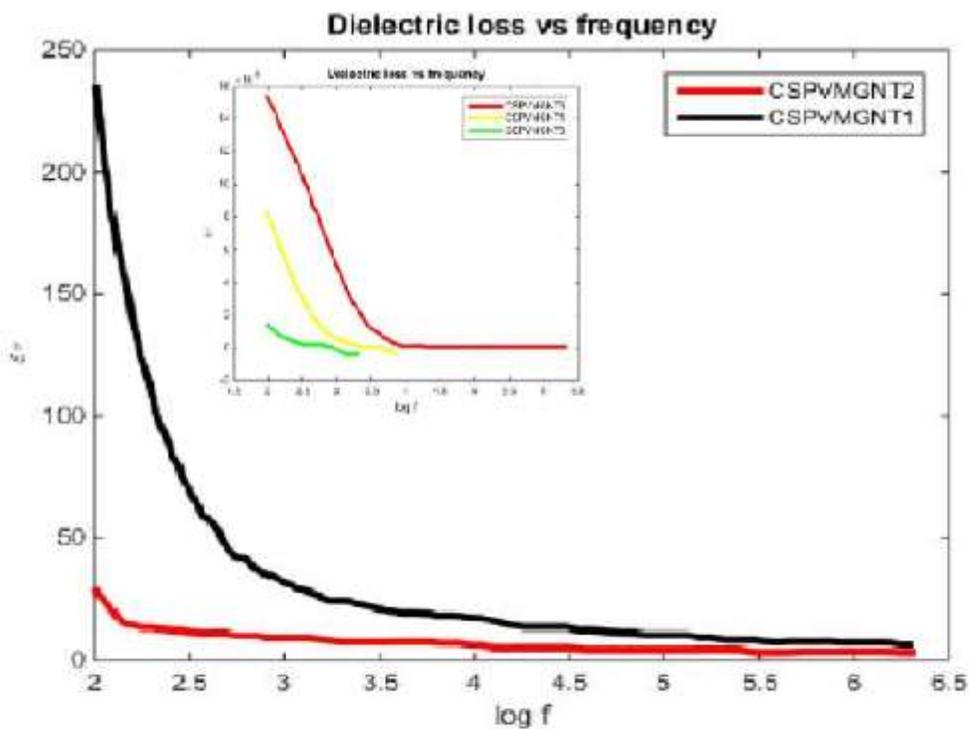


Fig. 3.1. The change of dielectric constant with respect to frequency for biopolymer blend electrolyte systems of CSPVMGNT at room temperature.

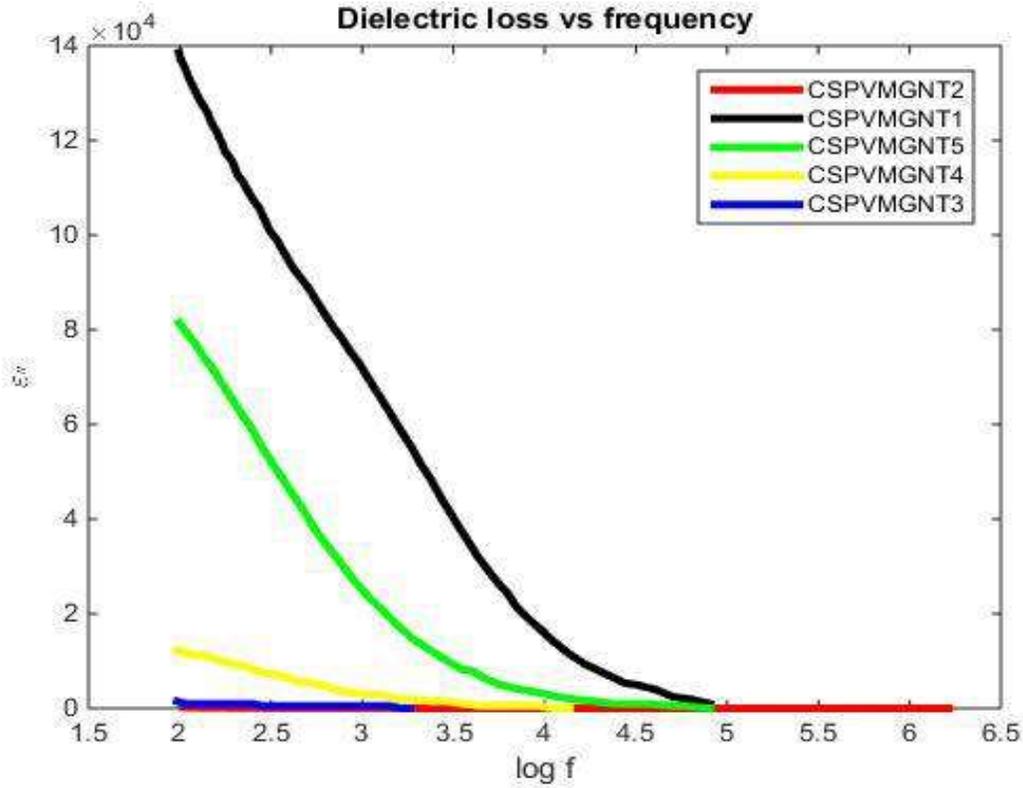


Fig.3.2. The change of dielectric loss with respect to frequency for biopolymer blend electrolyte systems of CSPVMGNT at room temperature.

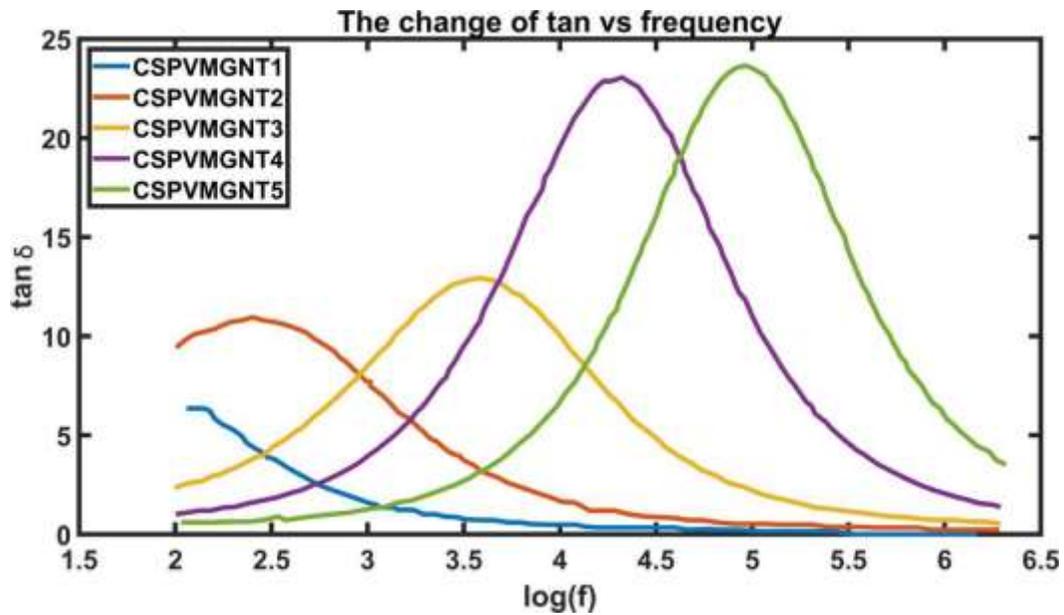


Fig. 3.3. The change of ($\tan \delta$) with respect to frequency for biopolymer blend electrolyte systems of CSPVMGNT at room temperature.

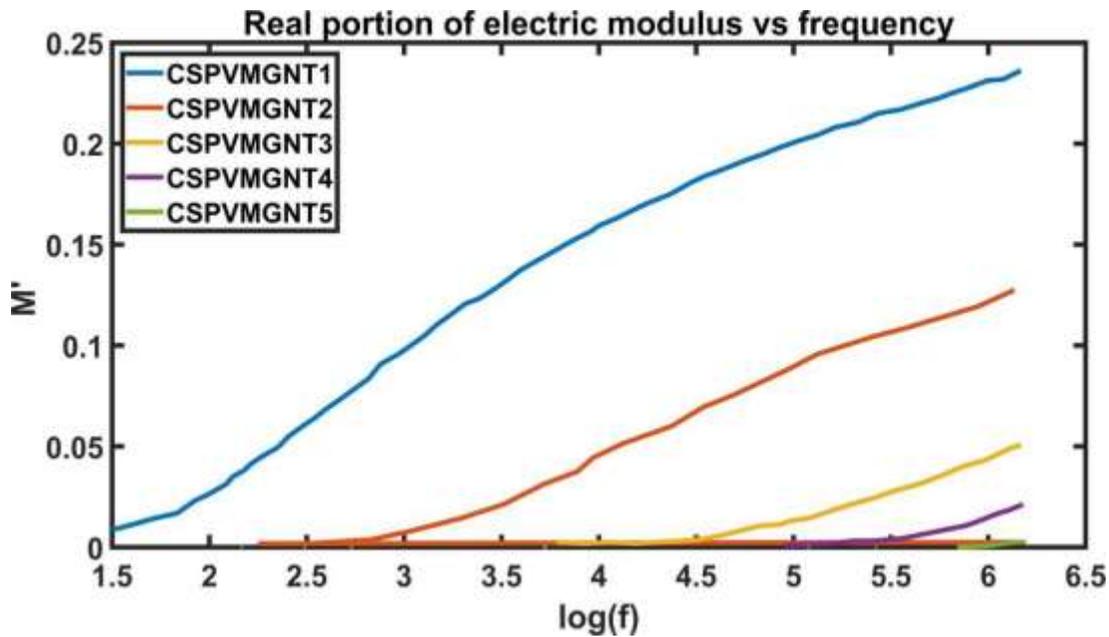


Fig. 3.4. Real portion of electric modulus (M') with respect to frequency for plasticized CS:PVA:Mg(NO₃)₂ biopolymer blend electrolyte systems at ambient temperature

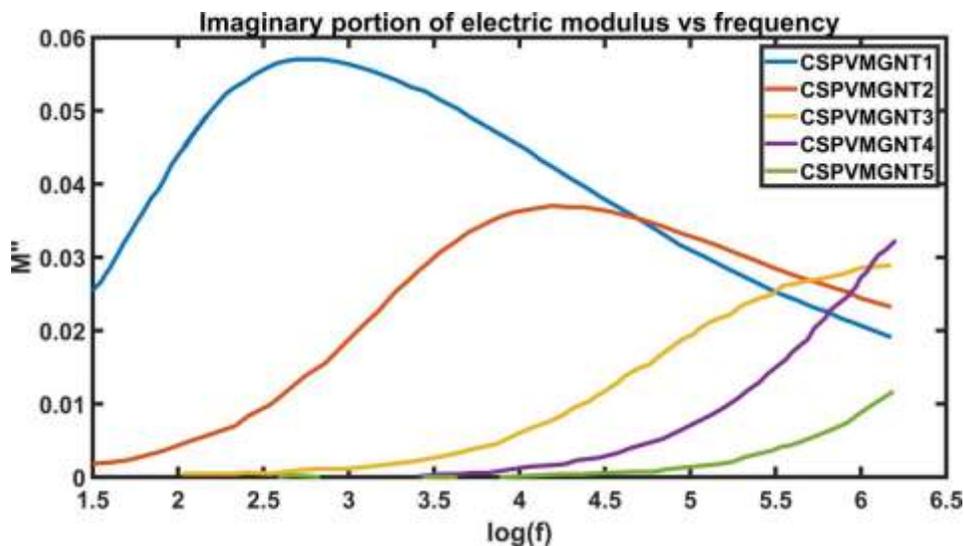
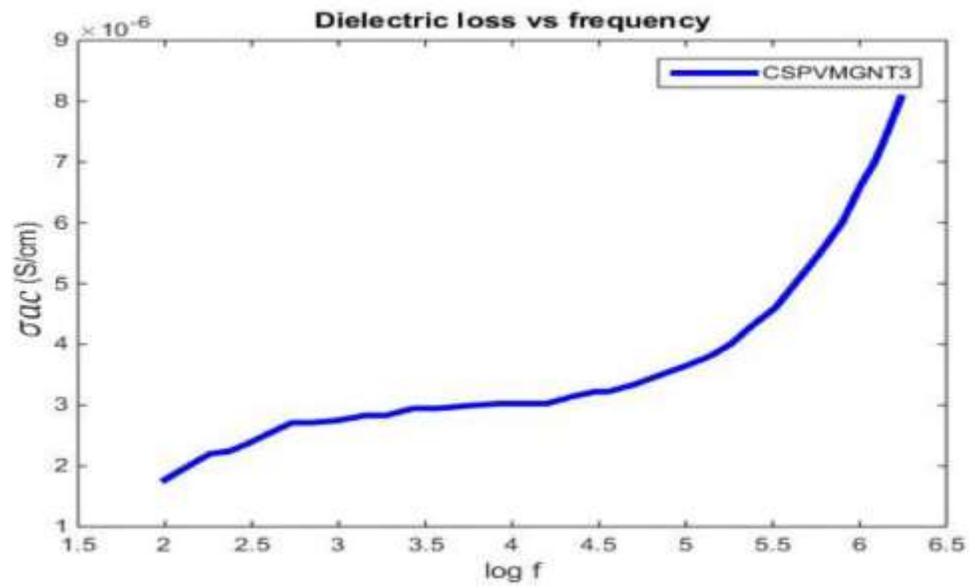
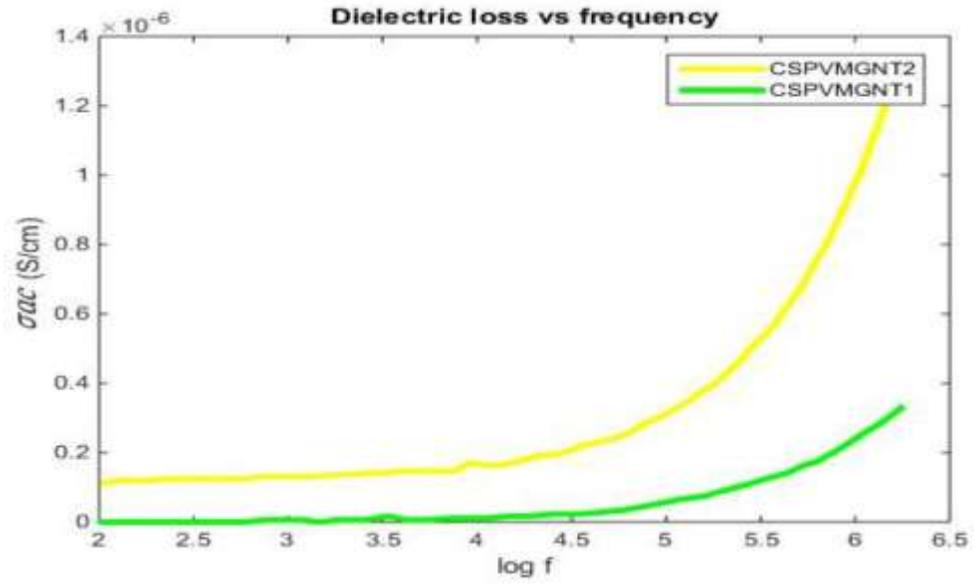


Fig. 3.5. Imaginary portion of electric modulus (M'') with respect to frequency for plasticized CS:PVA:Mg(NO₃)₂ biopolymer blend electrolyte systems at ambient temperature



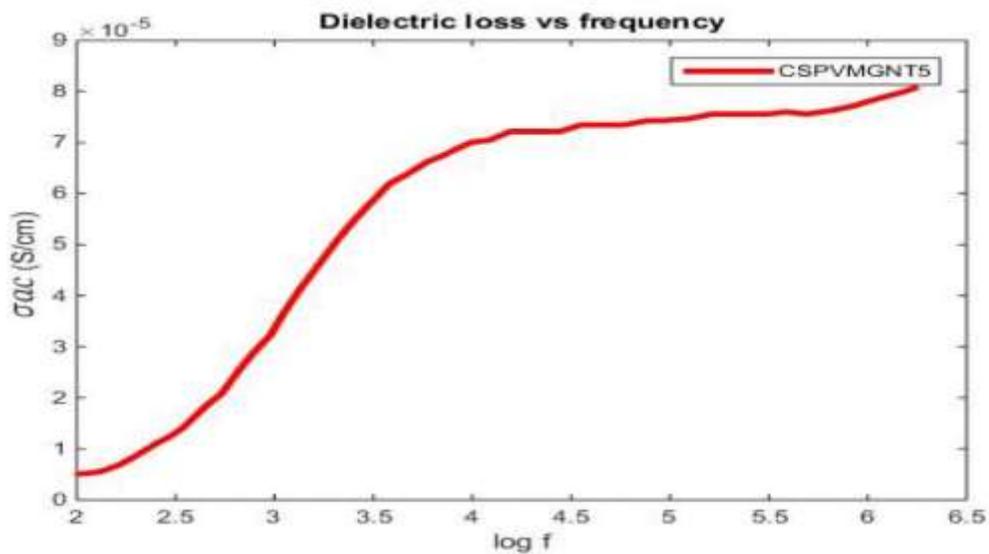
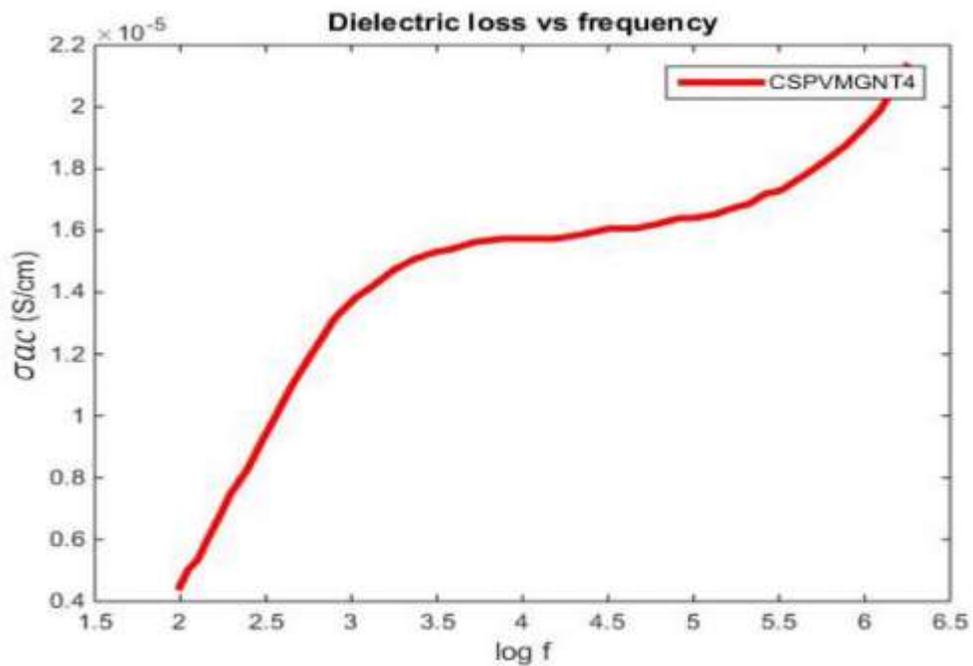


Fig.3.6. AC conductivity spectra for all plasticized CS:PVA:Mg(NO₃)₂ biopolymer blend electrolyte systems at ambient temperature.

Conclusion

Plasticized biopolymer blend electrolytes based on CS:PVA:Mg (NO₃)₂ with varying amounts of glycerol which were fabricated using a solution casting method to facilitate the transport of magnesium ions. The peak appearance for the current compounds displayed a non-Debye type.

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