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Ionic Conductivity Studies on Proton Conducting Solid Biopolymer Electrolyte Based on 2-Hydroxyethyl Cellulose (2HEC) Doped with Ammonium Chloride (NH4CL)

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ABSTRACT

Solution casting techniques have been used to create a solid biopolymer electrolyte (SBEs) based on 2-hydroxyethyl cellulose (2HEC) doped with varying amounts of ammonium chloride (NH_4Cl) to investigate the potential of NH_4Cl in enhancing the ionic conductivity of SBE. Electrical impedance spectroscopy (EIS) was used to measure the impedance of the electrolytes between 50 Hz and 1 MHz in frequency. At room temperature, ionic conductivity was at its highest for 16% weight percent of NH_4Cl which was 1.74 x 10^{-3} Scm^{-1}. The temperature dependence data of 2HEC-NH_4Cl SBEs abides Arrhenius behaviour. Complex electrical modulus and complex permittivity were used to assess the dielectric data for the sample at various temperatures.

1. Introduction

Construction, pharmaceuticals, packaging and food processing are just a few of the industries that have benefited from the use of polymer materials, particularly natural polymers [1-8]. Environmentally friendly electronic components are more in demand as technology develops, helping to reduce e-waste. In order to solve the issue and improve the efficiency of the new power sources for electrochemical devices, new electrolytes should be produced [9-12]. This has caused numerous studies to concentrate on solid biopolymer electrolytes (SBEs) [13-15].

Numerous studies have shown that SBEs have good potential in electrochemical devices (as a solid electrolyte component) such as solar cells, batteries, fuel cells and supercapacitors [16-19]. They also have outstanding mechanical stability, are simple to make and have zero leakage features, which are necessary characteristics in any system of electrolytes [20]. A variety of natural polymers, such as chitosan, cellulose derivatives, agar and starch, were investigated for use in various applications

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[21-26]. Despite being more prevalent, secure and affordable than synthetic polymers, natural polymers often have low ionic conductivities at ambient temperature, which limits their potential for use in electrochemical devices [4,11,27,28]. Natural polymers frequently have issues with their relatively low ionic conductivity, which is unsuitable for electrochemical applications where the lowest value ranges from 10^{-11} to 10^{-7} S cm^{-1}.

Researchers also looked for ways to improve them because of their properties and their low conductivity at room temperature. This issue can be resolved by doping the polymer host system with the appropriate proton donor material. Proton donors contribute to a rise in the quantity of free, mobile ions that cause ionic conduction, improving the host polymer's overall ionic conductivity. In addition to adding proton donors, other ways to improve the host polymer include polymer blending, adding organic/inorganic compounds and adding ionic liquids [29]. However, using a doped proton donor is the simplest and least expensive way [4]. Additionally, according to Ramlli *et al.,* [4] and Hafiza *et al.,* [30], the addition of ammonium nitrate and ammonium thiocyanate considerably enhanced the ionic conductivity of pure 2HEC when using the proton donor doping approach. Ammonium salts are commonly used as proton donor materials as the loosely bound proton (H^+) in ammonium has a tendency to move to the polymer host system in studies of solid biopolymer electrolytes. However, not all ammonium salts yield excellent results since certain of their characteristics can alter how they interact with the polymer host. High ion dissociation into the polymer host is provided by low-lattice-energy ammonium salts and substantial anionic groupings, which can aid in improving ionic conductivity [31].

In this study, the polymer of interest is 2-hydroxyethyl cellulose (2HEC). One of the best qualities of this cellulose derivative is its great water solubility, which makes it a suitable thickening and stabilizing agent. As an adhesion promoter organic thickener and among many other uses in the pharmaceutical industry, food industry and manufacturing sector [2,32]. According to Ramlli *et al.,* [33], 2-HEC has also been used in the manufacture of electrodes for use in batteries, where it served as the binder material. Due to these benefits, 2HEC has emerged as a top contender for SBE development for electrochemical applications. Additionally, there aren't many publications on its potential to function as an SBE, so now is the ideal time for our work to add to the corpus of information.

Since ammonium chloride (NH_4Cl) has a low lattice energy of just 705 kJ mol-1, which may aid in the dissociation of mobile ions, it was chosen as a proton donor. Regarding the research of ionic conductance, temperature reliance and activation energy, dielectric permittivity, and modulus research of the novel SBEs, this work concentrated on the impact of various NH_4Cl concentrations on 2HEC. Electrochemical Impedance Spectroscopy (EIS) at room temperature was used for all tests after the samples were manufactured using a straightforward solution casting procedure.

2. Methodology

2.1 SBE Preparation

Using the solution casting approach, 2.0 g of 2-Hydroxyethyl Cellulose or 2HEC (Sigma-Aldrich Inc., 99.0% purity), was dissolved in distilled water to create a thin sheet-like of solid biopolymer electrolyte. After that, different concentrations of ammonium chloride or NH_4Cl, from Sigma Aldrich were added to the 2HEC solution and stirred together until the mixture was homogeneous (Table 1). After complete dissolution, the mixture was put in a petri dish and heated for a short period of time in an oven set at a constant temperature of 50°C. After that, the films were put in a desiccator filled with silica gel to finish drying.

2.2 Sample Characterization

The ionic conductivity and electrical characteristics of the SBE films were assessed using the electrochemical impedance spectroscopy (EIS) model HIOKI 3532-50 LCR Hi-Tester EIS with computer interface. The SBE film was divided into an appropriate size of 2cm x 2cm before being placed between two stainless steel electrodes that were attached to the EIS. The EIS measurement was made between 303 K and 373 K, with a 50 Hz to 1 M Hz frequency range. Eq. (1) was used to calculate the ionic conductivity of the SBE film.

$$\sigma = \frac{t}{R_b A} \tag{1}$$

where A is the region of surface contact of the SBE sample and electrodes and t is the thickness (mm) of the SBE film. When analysing the impedance properties of materials like solid polymer electrolytes, electrochemical impedance spectroscopy (EIS) frequently used the Cole-Cole plot, also referred to as the Nyquist plot. This graphic can be used to calculate the electrolyte's bulk resistance (R_b).

For instance, the semicircle seen in the Nyquist plot might be utilised to determine the bulk resistance, according to a study by Huggins [34]. The bulk resistance of the electrolyte is represented by the point at which the semicircle at the high-frequency end intercepts the real axis (Z). The data was plotted in the Cole-Cole plot form, where the imaginary part of impedance, $-Z_i$, was plotted on the y-axis and the real part of impedance, Z_r, was plotted on the x-axis of the chart to estimate the bulk resistance or Rb value. The Arrhenius rule (Eq. (2)) can be used to calculate the activation energy, Ea,

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \tag{2}$$

Here, σ_0 is the pre-exponential factor, k is the Boltzmann constant and T is the absolute temperature. The dielectric permittivity (ε) can be determined by using Eq. (3) and Eq. (4):

$$\varepsilon_r = \frac{Z_i}{\omega C_o (Z_r^2 + Z_i^2)} \tag{3}$$

$$\varepsilon_i = \frac{Z_r}{\omega C_o (Z_r^2 + Z_i^2)} \tag{4}$$

Where $C_0 = \frac{\varepsilon_o A}{t}$, ε_o= 8.85 x 10^{-12} Fm^{-1}. ω is the angular frequency = 2πf, where f is the frequency (Hz). By using the value obtained from dielectric permittivity (ε), we can calculate the value for electrical modulus (M) by using Eq. (5) and Eq. (6).

$$M_r = \frac{\varepsilon_r}{\varepsilon_r^2 + \varepsilon_i^2} \tag{5}$$

$$M_i = \frac{\varepsilon_i}{\varepsilon_r^2 + \varepsilon_i^2} \tag{6}$$

Table 1
Designation and weight percentage NH_4Cl salt for SBE samples

Sample	2HEC (g)	NH_4Cl (wt%)	NH_4Cl Weight (g)
2HECAC0	2	0	0.0000
2HECAC4	2	4	0.0833
2HECAC8	2	8	0.1739
2HECAC12	2	12	0.2727
2HECAC16	2	16	0.3809
2HECAC20	2	20	0.5000
2HECAC24	2	24	0.6315

3. Results

3.1 Ionic Conductivity Studies

Eq. (1) was used to determine the SBEs' ionic conductivity at room temperature, which was then shown in Table 2. By referring to the table, the ionic conductivity rose according to the amount of NH_4Cl present until it reached its ideal concentration at 16 wt%. Pure 2HEC (2HECAC0) sample has an ionic conductivity of 7.45 x 10^{-6} S cm^{-1} at ambient temperature. Ionic conductivity begins to noticeably climb after the addition of 4 wt% NH_4Cl and so forth, then reaches its peak at 16 wt%. 2HECAC16 was found to have the maximum ionic conductivity, 1.74 x 10^{-3} S cm^{-1}. As the addition of salt continues, the ionic conductivity tends to decrease to 6.5 x 10^{-4} S cm^{-1} for the sample with 20 wt% NH_4Cl and finally to 2.95 x 10^{-4} S cm^{-1} at 24 wt%. The SBEs were shown to inherit weak mechanical stability and can be disregarded at increasing salt contents (>24 wt% NH_4Cl).

The increased amount of free mobile ions that dissociated from NH_4Cl which entered the 2HEC polymer host may be the cause of the improved ionic conductivity. The prevalence of ionic conduction in the polymer system increased with the number of ionic dopants, enhancing the SBE's total ionic conductivity [35]. More free mobile ions (NH_4^+) are capable of being separated in the polymer host system thanks to the addition of NH_4Cl salt. The dissociated cations may potentially interact with the oxygen atom's single pair of electrons in the 2-HEC, claimed by Hafiza and Isa [36]. Numerous studies lend evidence to this theory. For example, according to Kulkarni *et al.,* [37] reported a considerable increase in conductivity in polymer electrolytes with NH_4Cl addition. They attributed this to the dissociation of NH_4Cl and the ensuing free NH_4^+ ions. Similar to this, Varshney *et al.,* [38] found that ammonium salt-doped polymer electrolytes have increased ionic transport, emphasizing the function of free NH_4^+ ions. Furthermore, studies by Kulkarni and Frech [39] showed the contribution of dissociated NH_4^+ ions to the ionic conductivity in ammonium salt-based polymer electrolytes. The suggested process was supported by Prasad *et al.,* [40] who also reported higher ionic conductivity in PEO-based electrolytes with NH_4Cl addition. In the meantime, as the concentration of NH_4Cl increases, the accumulation of free mobile ions might lead to the creation of ion clusters, which can explain why ionic conductivity is decreasing. The interior space of the polymer matrix has shrunk as the number of free mobile ions has increased; as a result, the ions begin to move closer to one another and eventually form ion clusters because of the weak gravitational attraction they have on one another [41]. The aforementioned phenomenon has strong support in the literature, as evidenced by the research conducted by Lu *et al.,* [42]. Their findings showed that ion clustering results in a decrease in ionic mobility because it reduces the free volume within the polymer matrix. According to Zhu *et al.,* [43], the creation of ion clusters can hinder the growth of ionic conductivity in polymer electrolytes by obstructing ion transport and resulting in a reduction in conductivity. The availability of free mobile ions will decrease, which will limit ionic conduction and result in a drop in the ionic conductivity of SBEs. The work done by Ahmad *et al.,* [44] for the polymer

electrolyte Carboxymethyl Cellulose doped with NH_4Cl also experiences the effect of ion clustering, leading to a decrease in ionic conductivity.

Table 2
Designation, thickness, bulk resistance and ionic conductivity of SBE

Sample	Thickness (mm)	Bulk resistance, R_b	Ionic conductivity, σ (S cm^{-1})
2HECAC0	0.0174	7.43×10^{2}	7.45×10^{-6}
2HECAC4	0.0122	1.42×10^{2}	2.73×10^{-5}
2HECAC8	0.0106	1.13×10^{1}	2.99×10^{-4}
2HECAC12	0.0122	5.67	6.85×10^{-4}
2HECAC16	0.0200	3.66	1.74×10^{-3}
2HECAC20	0.0170	8.33	6.50×10^{-4}
2HECAC24	0.0150	1.62×10^{1}	2.95×10^{-4}

3.2 Temperature-Dependent Conductivity Analysis

Figure 1 shows how the 2HEC-NH_4Cl SBE system's ionic conductivity varies with temperature across the range of 303 to 353 K for 0 wt% - 20 wt%. As for the 24 wt% sample, it was not included due to the sample becoming crystalline and brittle at high temperatures. Figure 1 shows that for all electrolytes, the conductivity of the system rises linearly with an increase in temperature. Increased ionic mobility in the SBE can explain this phenomenon. By exerting force against the hydrostatic pressure while moving the polymer portion, exerted from the close-by atoms as a result of the vibrational energy, tiny voids are produced as the temperature rises [45]. By creating free space, the ensuing conductivity makes it possible for ions, solvated molecules or polymer segments to flow. The free available volume surrounding the polymer chain affects the overall mobility of the ion and polymer. Due to the rise in temperature, it also enhances segmental ion mobility and also lead to an increase in free volume. As a result, it leads to an increase in conductivity [46]. According to the Arrhenius behaviour of the DC conductivity values (Regression value, R^2), the conductivity mechanism is a thermally activated process [45].

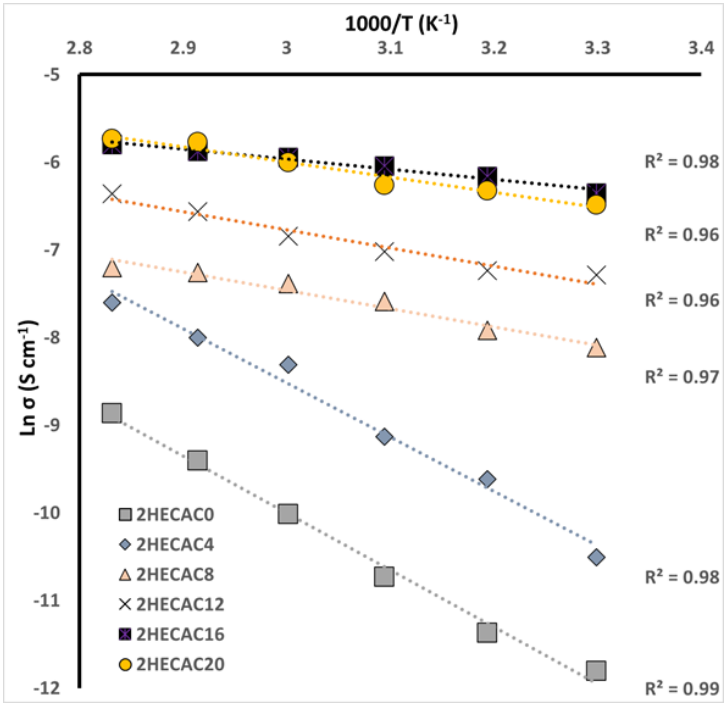

Fig. 1. 1000/T versus Ln σ for the SBE sample

The Arrhenius plot's linear fit is used to determine the activation energy of the sample. In Figure 2, the activation energy is shown. As the NH_4Cl concentration rises, it can be observed that the activation energy decreases. The electrolyte with the highest conductivity has the lowest activation energy, which suggests that charge carriers in higher conducting electrolytes need less energy to start the migration process. Studies by Li *et al.,* [47], Chen *et al.,* [48], Feng and Zhang [49], Smith *et al.,* [50] and Li *et al.,* [51] provide evidence that although moderate concentrations of salt generally lower activation energy and improve ion conductivity in polymer electrolytes, high concentrations can cause ion aggregation and disrupt the structural order of the polymer matrix. This behaviour leads to a decrease in conductivity even with the expected rise in salt content because it promotes ion-pairing actions and hinders ion mobility, which raises activation energy. These results highlight the possibility that the rise in activation energy resulting from ion clustering and structural alterations brought on by high salt concentrations is related to the conductivity decrease observed with increased NH_4Cl concentration.

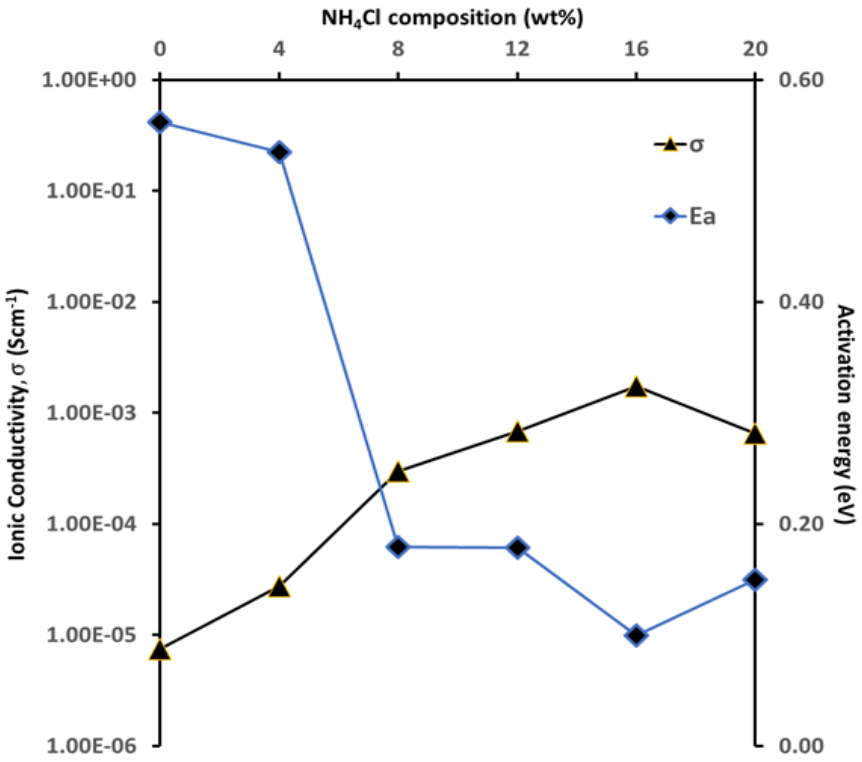

Fig. 2. NH_4Cl composition versus ionic conductivity and activation energy

3.3 Dielectric Studies

For SBEs with a range of 0 wt% to 20 wt% at 303 K, the frequency-dependent dielectric constant (ε_r) and dielectric loss (ε_i) graphs are shown in Figure 3 and Figure 4. The ability of a material to hold a charge is measured by its dielectric constant, whereas the energy lost as a result of the flow and motion of ions in a rapidly varying electric field is measured by its dielectric loss [52]. According to Figure 3 and Figure 4, high values of the ε_r and ε_i plots are visible at low frequencies before they progressively decline as frequency rises. These graphs revealed no discernible relaxation peak, indicating that the ionic conductivity was mostly caused by the rise in the amount of vacant mobile ions in the polymer matrix [4,53]. The presence of electrode polarisation and the space charge effect at lower frequencies may be explained by the high value of both ε_r and ε_i, which diminishes as the frequency goes up. This confirms that the SBEs are not Debye-dependent [22,54,55]. The high value

of ε_i also suggests that there was a significant reduction during the dipole orientation [4]. The improvement of the charge stored in the SBEs may also be responsible for the increment in ε_r at low frequency as the NH_4Cl concentration rises. This further suggests that an increase in the number of free mobile ions in SBEs causes an increase in ionic conductivity [56]. The value of ε_r and ε_i steadily decreases with frequency and this may be attributed to the electrical field's quick reversal, which prevents ion diffusion and reduces the charge that builds up at the electrode, lowering the value of ε_r. [21,57]. The rises at higher temperatures are a result of the polymer electrolyte system's increased quantity of free mobile ions [16,58,59] The significant amount of loss experienced during the alignment of the dipole may potentially be contributing to the increase in ε_i with temperature. This might result in more vacant mobile ions and their random contacts, which ultimately results in a higher relaxation time [4].

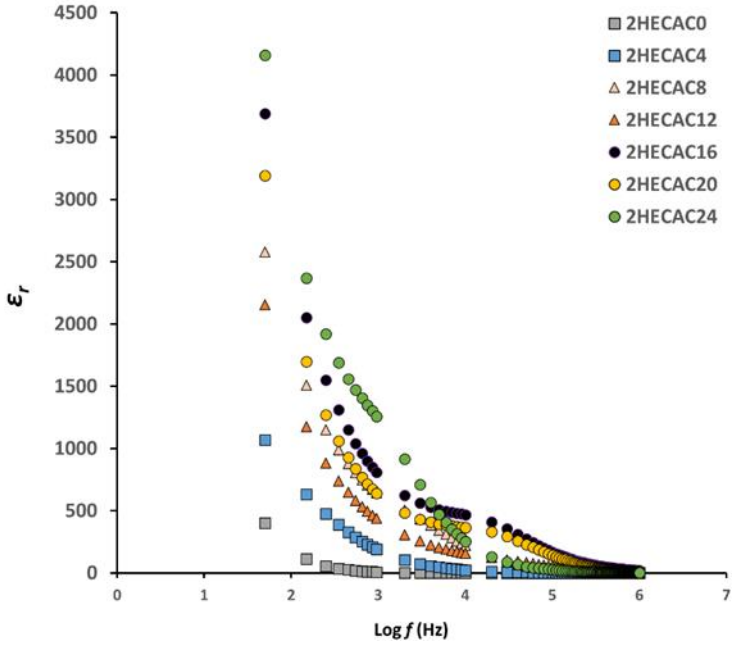

Fig. 3. Frequency-dependant of ε_r at 303 K for all SBEs

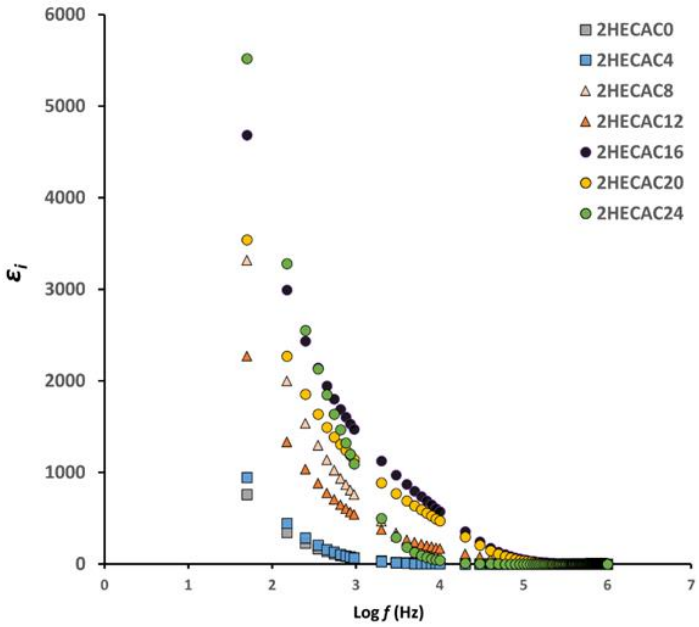

Fig. 4. Frequency-dependant of ε_i at 303 K for all SBEs

A further examination of the dielectric modulus helps to clarify the impact of electrode polarisation. Figure 5 and Figure 6 depict the fluctuation of the real component (M_r) and imaginary part (M_i) of the dielectric modulus for all SBE samples. The figure shows that the value of M_r and M_i is virtually nil at lower frequencies and increases as the frequency rises without a discernible relaxation peak. A large decrease in electric double layer capacitance (EDLC) at the electrode/electrolyte interface is shown by the long tail observed around the area of low frequencies, further supporting the non-Debye behaviour of the SBEs. The influence of electrode polarisation can also be disregarded due to M_r low value [4,59,60]. The ionic conduction was caused by the short-ranged mobility ion carriers of the SBEs, as indicated by the rising value of M_r at higher frequencies [4]. Additionally, it has been discovered that the M_r decreases as the concentration rises.

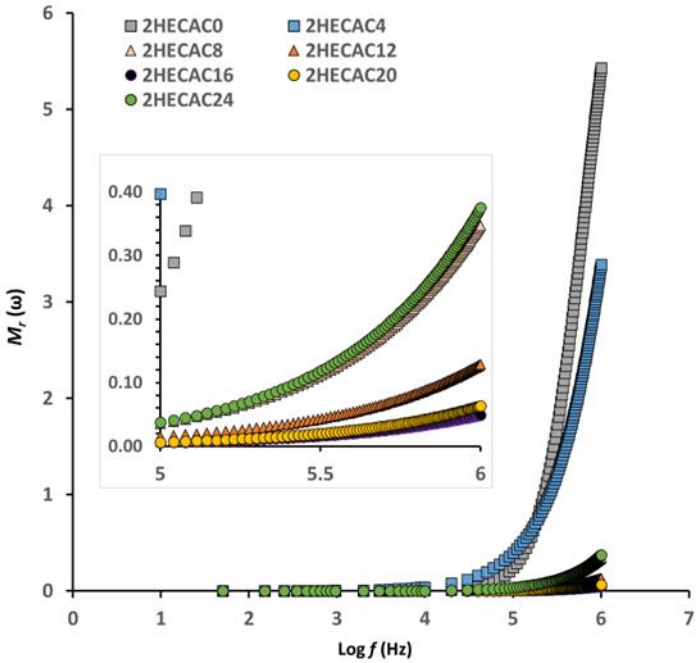

Fig. 5. Frequency-dependant of M_r at 303 K for all SBEs

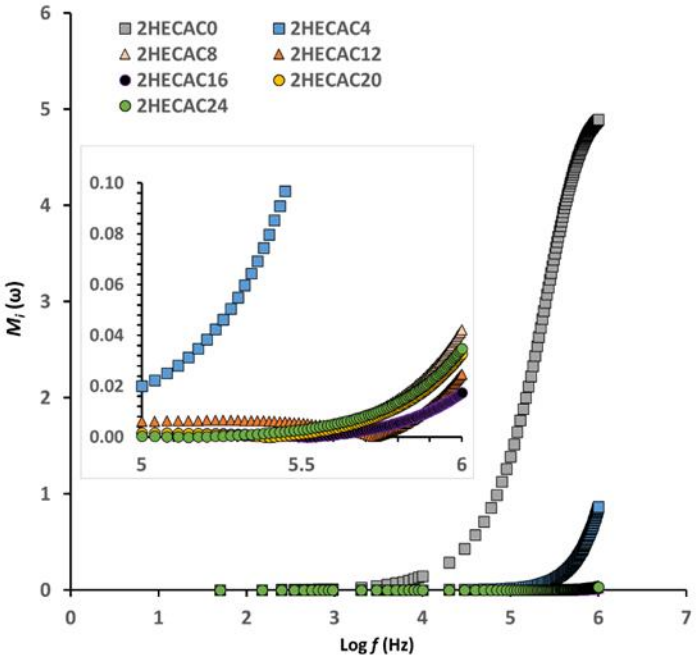

Fig. 6. Frequency-dependant of M_i at 303 K for all SBEs

4. Conclusions

An innovative solid biopolymer electrolyte system based on 2HEC doped with several NH_4Cl contents (wt.%) has been properly developed by utilizing the solution casting technique. According to the EIS study, the sample containing 16 weight percent NH_4Cl has an optimal value of room temperature ionic conductivity of 1.74 x 10^{-3} S cm^{-1}. In ionic conductor solid biopolymer electrolyte systems, the ionic conductivity also seems to be temperature-aided, which is a feature of Arrhenius behaviour. In addition, the ionic conductivity was influenced by the activation energy (E_a), where a lower value of E_a yields higher ionic conductivity. The SBEs exhibit non-Debye behaviour, which supports the idea that the movement of free mobile ions causes ionic conduction in the polymer system, according to dielectric permittivity studies. Analysis of dielectric constant (ε_r) and dielectric loss (ε_i) display a high value at low frequency and rise with increasing NH_4Cl content as well as temperature, indicating high dissociations of mobile ions into the polymer system. The ionic conductive property of the SBEs was further validated by modulus analysis. These findings lead to the conclusion that the 2HEC-NH_4Cl SBEs have a great deal of promise for use in electrochemical devices.

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