2-HYDROXYETHYL CELLULOSE-AMMONIUM THIOCYANATE SOLID BIOPOLYMER ELECTROLYTES: IONIC CONDUCTIVITY AND DIELECTRIC STUDIES

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Abstract: There is demand for application of polymer materials in electrochemical devices, especially natural polymers, because of their superiority in mechanical integrity, affordability and biodegradability. In this work, solid biopolymer electrolyte (SBEs) comprising 2-hydroxyethyl cellulose (2-HEC) doped with different weight percentage of ammonium thiocyanate, NH_4SCN (0 – 44 wt.%) were prepared using a facile solution casting technique. The effects of NH_4SCN on ionic conductivity and dielectric properties of SBEs were investigated using electrochemical impedance spectroscopy (EIS). The ionic conductivity recorded at room temperature showed massive improvement for pure 2-HEC from the value of 5.93×10^{-8} S cm^{-1} to 1.16×10^{-4} S cm^{-1}, comprising 36 wt.% NH_4SCN. Meanwhile, at elevated temperatures, the ionic conductivity revealed the Arrhenius behaviour, where it increased proportional to the temperatures. In addition, by introducing NH_4SCN content as a proton donor, it also effectively reduced the activation energy of the SBEs, which further support enhancing the ionic conductivity. In dielectric permittivity study, the ε_r and ε_i increased as the NH_4SCN content increased, revealing the non-Debye dependency of the SBEs, which indicates that the SBEs are ionic conductors. The addition of the optimum value of NH_4SCN content showed good characteristic for electrochemical devices applications.

Keywords: Solid biopolymer electrolytes, ionic conductivity, dielectric permittivity, temperature dependence, ionic conductor.

Introduction

Polymer materials especially natural polymers have many contributions in industries such as construction, pharmaceuticals and food manufacturing (Tanti *et al*., 2016; Attaran *et al*., 2017; Dmour & Taha, 2018; Yu *et al*., 2018; Balla *et al*., 2019; Rajak *et al*., 2019). As the technology advances, environmentaly friendly electronic components also increased in demand in order to combat e-waste. This has led to many works focus on solid biopolymer electrolytes (SBEs) (Aziz *et al*., 2020; Kumar *et al*., 2020). Numerous works have revealed that SBEs display good capability as a solid electrolyte component in electrochemical devices such as fuel cells, batteries, solar cells and supercapacitors (Liew *et al*., 2014; Monisha *et al*., 2017; Kannadhasan *et al*., 2019; Perumal *et al*., 2019; Singh & Singh, 2019). In addition, they have excellent mechanical stability, easy to fabricate and have non-leakage properties, which are crucial characteristics for electrolyte systems (Rasali & Samsudin, 2018; Mahalakshmi *et al*., 2019). Various kinds of natural polymers were studied for SBE applications including chitosan, cellulose derivatives, agar and starch (Nwanya *et al.,* 2015; Selvalakshmi *et al*., 2017; Zainuddin *et al*., 2018; Abdullah *et al*., 2018; Asnawi *et al*., 2020). Even though natural polymers are abundant, safe and inexpensive compared to synthetic polymers, they usually have low ionic conductivity at room temperature, which hinder

the potential for application in electrochemical devices.

A common problem with natural polymers is their relatively low ionic conductivity at around $\times 10^{-11}$ - $\times 10^{-7}$ S cm^{-1}, which is not suitable for electrochemical applications, where the minimum value for consideration is $(1 \times 10^{-4}$ S cm$^{-1})$. However, this problem can be solved by doping appropriate proton donor material into the polymer host system. Proton donors help increase the number of free mobile ions responsible for the occurrence of ionic conduction, hence, enhancing the overall ionic conductivity of the host polymer. Besides doping proton donors, there are also methods like polymer blending, addition of or/inorganic materials and addition of ionic liquids could also be used to enhance the host polymer (Noor & Isa, 2019). However, doping proton donor is the easiest and most affordable method (Pandi *et al.*, 2016). Hafiza and Isa (2017) also mentioned that by utilizing the proton donor doping method, the ionic conductivity of pure 2-HEC was significantly increased after introducing ammonium nitrate (NH_4NO_3). Ammonium salts were commonly used as a proton donor material in solid biopolymer electrolytes studies by many researchers because of the characteristic of the loosely bound proton (H^+) in the ammonium, which tends to migrate to the polymer host system. Even so, not all ammonium salts produce great results because there are some properties that can affects their behaviour with the polymer host. Ammonium salts with low lattice energy and have large anionic offer high dissociation of ions into the polymer host, which can help in improving ionic conductivity (Brza *et al.,* 2020).

In this work, 2-hydroxyethyl cellulose (2-HEC) has been selected as the polymer of interest. It was one of the cellulose derivatives that has excellent properties such as good thickening and stabilizing agent, good film-forming ability and highly water-soluble. It also used in many other applications such as natural thickener, suspension and as an adhesive agent in pharmaceutical, food and manufacturing industries (El Fawal *et al.,* 2018; Kozlowska,

Stachowiak & Sionkowska, 2018). 2-HEC also has been utilized in electrode fabrication, as reported by Ramlli *et al.* (2018), where it was used as the binder material in electrodes for battery application. These advantages have made 2-HEC a great candidate to be developed into SBE for electrochemical applications. Plus, reports on its capability to serve as a solid biopolymer electrolyte is still limited and this is the perfect opportunity for this work to contribute to the body of knowledge. Ammonium thiocyanate (NH_4SCN) was used as a proton donor and it was selected because of its low lattice energy of ~ 605 kJ mol^{-1} and has large anions (SCN^-) which could help in dissociations of mobile ions. This work focused on the effect of different NH_4SCN contents on 2-HEC in terms of ionic conductivity, temperature dependence, activation energy, dielectric permittivity and modulus analysis of the new SBEs. The samples were prepared by simple solution casting technique and all tests were done by using Electrochemical Impedance Spectroscopy (EIS) at room temperature.

Materials and Methods

Sample Preparation

The SBE films were prepared using a facile solution casting technique. 2-HEC polymer and NH_4SCN salt were used as received. 2 grams of 2-HEC was dissolved in 70 ml of distilled water and doped with various weight percentages (0 – 44 wt.%) of NH_4SCN at 4 wt.% interval. The solution was stirred until homogenous, then, cast into several Petri dishes and dried in an oven at 55°C until a thin film is formed. All samples were kept in a desiccator to prevent moisture contamination prior to characterization. Table 1 lists the samples designation, polymer and salt content used in this work.

Sample Characterization

Electrochemical impedance spectroscopy (EIS) model HIOKI 3532-50 LCR Hi-tester EIS with computer interface was used to determine the ionic conductivity and electrical properties of

Table 1: Sample designation, polymer and salt content in SBE films

Sample	2-HEC (g)	NH$_4$SCN (g)	NH$_4$SCN (wt.%)
HEAT-0		0.000	0
HEAT-4		0.083	4
HEAT-8		0.174	8
HEAT-12		0.273	12
HEAT-16		0.381	16
HEAT-20	2.000	0.500	20
HEAT-24		0.632	24
HEAT-28		0.779	28
HEAT-32		0.941	32
HEAT-36		1.125	36
HEAT-40		1.333	40
HEAT-44		1.571	44

the SBE films. The sample was cut into a suitable size and then sandwiched between two stainless steel electrodes connected to the EIS. The EIS measurement was recorded in a frequency range of 50 Hz to 1 M Hz at temperature between 303 K and 373 K. The ionic conductivity, σ of SBE film was determined by using equation:

$$\sigma = \frac{t}{R_b \times A} \quad (1)$$

where t is the thickness of the SBE film, R_b is the bulk resistance determined from the intercept of x-axis of Cole-Cole plot and A is the surface contact area of SBE film and electrodes. The activation energy, E_a can be determined from the Arrhenius rule:

$$\sigma = \sigma_0 exp \frac{-E_a}{kT} \quad (2)$$

Here, σ_0 is the pre-exponential factor, k is the Boltzman constant and T is the absolute temperature. The dielectric permittivity (ε) and electrical modulus (M) can be determined by using the equations below:

$$\varepsilon_r = \frac{z_i}{\omega C_0(z_r^2 + z_i^2)} \quad (3)$$

$$\varepsilon_i = \frac{z_r}{\omega C_0(z_r^2 + z_i^2)} \quad (4)$$

$$M_r = \frac{\varepsilon_r}{(\varepsilon_r^2 + \varepsilon_i^2)} \quad (5)$$

$$M_i = \frac{\varepsilon_i}{(\varepsilon_r^2 + \varepsilon_i^2)} \quad (6)$$

where $C_0 = \frac{\varepsilon_0 A}{t}$, $\varepsilon_0 = 8.85 \times 10^{-12}$ Fm^{-1} and ω is the angular frequency = $2 \pi f$ (f is the frequency in Hertz).

Results and Discussion

Figure 1 depicts the Cole-Cole plots for all SBEs at different NH$_4$SCN content. From the figure, a semicircle plot emerges for sample SBE-0, which indicates a high bulk resistance across the sample (Aziz *et al*., 2020). As the NH$_4$SCN content increases, the semicircle has reduced in size and inclined spike has appeared in the plot. The reduction of semicircle signifies that only the resistivity element of the SBE remains (Hema *et al*., 2009). The appearance of semicircle in the plot can be caused by the parallel combination of bulk resistance and bulk capacitance of the SBEs (Samsudin *et al.,* 2014). The formation of inclined spike can be due to the formation of capacitive region in between the SBE and the two electrodes' interface (Shukur *et al.*, 2013). An ideal capacitance would show a 90° angle spike in the impedance plot, however, in this work it appears less than 90° and can be attributed to the imperfection of the stainless steel electrode's surface and SBE interface (Tang *et al*., 2016).
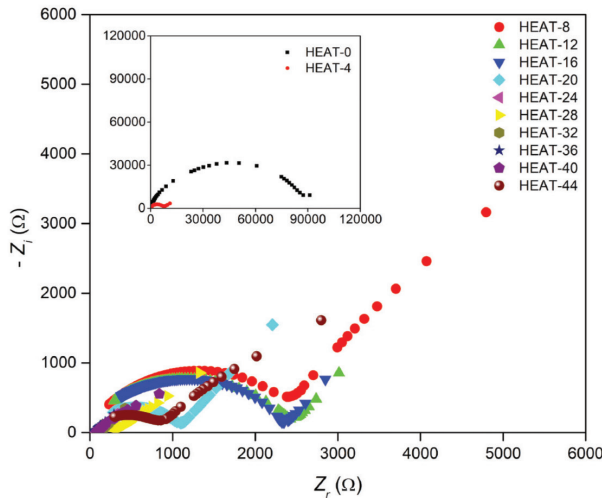
Figure 1: Cole-Cole plots for all SBEs measured at room temperature

An equivalent circuit can be used to describe the phenomenon in the Cole-Cole plots for all SBE samples except HEAT-0, as shown in Figure 2. Based on the figure, the R_b represents the bulk resistance, C_b is the bulk capacitance and CPE is the constant phase element for the non-ideal capacitor. The R_b can be attributed to the rearrangement of ions in the free volume of the polymer matrix and C_b can be referred to the polarization effect of immobile polymer chain (Hema *et al.*, 2008). The CPE represents the capacitive behaviour which occurred between the electrode and electrolyte interface (Muchakayala *et al.*, 2017).

The room temperature ionic conductivity of the SBEs was calculated using Equation 1 and plotted in Figure 3. Referring to the figure, the ionic conductivity increased proportionally to the content of NH_4SCN until optimum content at HEAT-36. The ionic conductivity of pure 2-HEC at room temperature is 5.93 x 10^{-8} S cm^{-1} (HEAT-0). The first significant increase in ionic conductivity can be found at

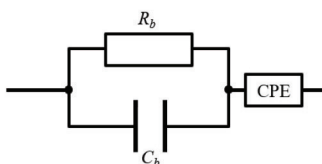HEAT-24, after which the value decreases at HEAT-28 before another rise until reaching the optimum at HEAT-36. The highest ionic conductivity was observed to be 1.16 x 10^{-4} S cm^{-1} for HEAT-36. Beyond 36 wt.% NH_4SCN, the ionic conductivity gradually dropped to 1.45 x 10^{-5} S cm^{-1} (HEAT-44). At higher salt content (>44 wt.% NH_4SCN), the SBEs were observed to inherit poor mechanical stability and can be neglected. Table 2 summarized several previous reports on the highest ionic conductivity at room temperature for solid biopolymer electrolytes which are related to the current work. From the table, the ionic conductivity of the current work is comparable to the previous studies, which indicates good compatibility between the 2-HEC and NH_4SCN.

The increased ionic conductivity can be related to the increased number of free mobile ions which dissociated from NH_4SCN into the 2-HEC polymer host. With the increased number of ionic dopants, the occurrence of ionic conductions in the polymer system also increased, hence, improving the overall ionic conductivity of SBE (Kovarsky *et al.*, 2011; Sohaimy & Isa, 2017). The addition of NH_4SCN salt provides more free mobile ions (NH_4^+ and SCN^-) to be dissociated in the polymer host system. According to Hafiza and Isa (2017), the dissociated cations could also interact with
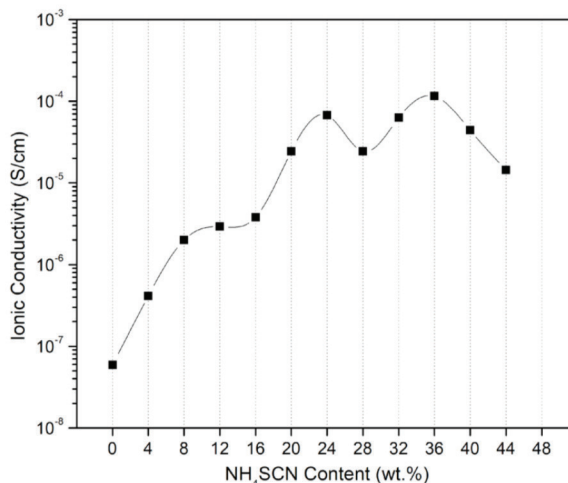

Figure 2: The corresponding equivalent circuit for Cole-Cole plots in Figure 1

Figure 3: The ionic conductivity versus NH$_4$SCN content at room temperature

Table 2: List of the ionic conductivity at room temperature with the optimum NH$_4$SCN content from previous works compared to the current work

Solid Biopolymer Electrolyte Systems	Salt (wt.%)/Ratio	Ionic Conductivity (S cm^{-1})	Reference
PVA/MC-NH$_4$SCN	40	1.45×10^{-4}	(Shamsuri *et al.*, 2020)
CMC-NH$_4$SCN	25	6.48×10^{-5}	(Isa & Noor, 2015)
i-Carrageenan-NH$_4$SCN	1:0.3	3.56×10^{-3}	(Moniha *et al.*, 2018)
Tamarind seed polysaccharide-NH$_4$SCN	1:0.4	2.85×10^{-4}	(Premalatha *et al.*, 2016)
2-HEC-NH$_4$NO$_3$	12	4.50×10^{-4}	(Hafiza & Isa, 2017)
2-HEC-NH$_4$SCN	36	1.16×10^{-4}	Current work

the lone pair of electrons of oxygen atom in the 2-HEC. Meanwhile, the decrease in ionic conductivity can be related to the formation of ion clusters due to the aggregation of free mobile ions. As the number of free mobile ions increase, the space inside the polymer matrix has become smaller, hence the ions start moving closer to each other and finally becoming ion clusters due to the small gravity pull towards each other (Ramya *et al.*, 2007; Shamsuri *et al.*, 2020). With fewer free mobile ions available, it will reduce the occurrence of ionic conduction, thus leading to the decrease of ionic conductivity of SBEs.

The plot of ionic conductivity at elevated temperatures for all SBEs is depicted in Figure 4. As can be seen from the figure, the ionic conductivity increases as the temperature

increases and this can be related to the increasing migration of ions through the polymer matrix (Monisha *et al.*, 2017; Moniha *et al.*, 2018). At higher temperatures, the segmental motion receives enough energy and allows them to vibrate. This made the side polymer chain more flexible and turns out to be closer to each other, hence, allowing for more ion migrations and consequently increase the ionic conductivity of the SBEs (Aziz & Abidin, 2013). Similar phenomena can also be observed in ionic crystals (Kumar *et al.,* 2012). The temperature-dependent ionic conductivity analysis confirms that the increase of ionic conductivity obeys the Arrhenius rule, where the regression value is close to unity (R2 ≈ 1). There is also no sudden rise or drop of ionic conductivity, which shows that the increase in ionic conductivity was only

due the migration of ions and not by water (Parameswaran *et al.,* 2017). The slight drop in ionic conductivity at higher temperatures at HEAT-24 and HEAT-36 may be due to the influence of either one or a combination of transport parameters, such as the number of free mobile ions or the ionic mobility and diffusion coefficient in the polymer electrolyte system (Muchakayala *et al*., 2017; Hafiza & Isa, 2020) and will be reported elsewhere. The activation energy (E_a) of SBEs was determined from Equation 2. Table 3 summarizes the ionic

conductivity at 303 K and 373 K, activation energy and regression values determined from temperature dependence plot in Figure 4.

From Table 3, it can be observed that the E_a value is inversely proportional to the value of ionic conductivity where the highest conductive SBE has the lowest value of E_a, which is commonly found in polymer electrolytes. A low value of E_a signifies the minimum energy required by the ions to break the energy band gap is lower, hence making them easier to hop to another vacant site. This leads to the increase of
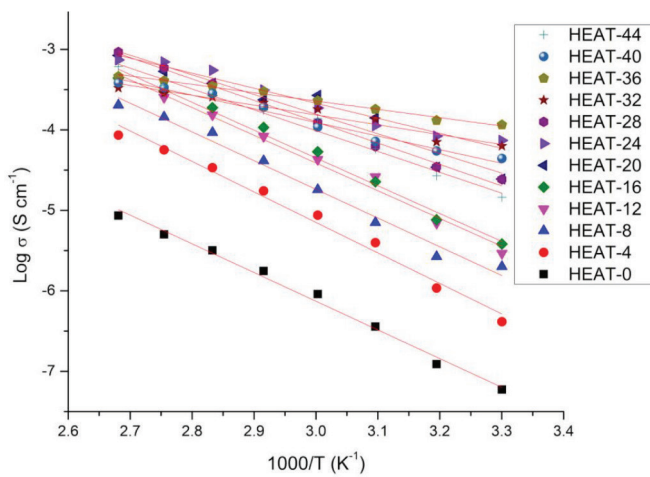

Figure 4: Temperature dependence of ionic conductivity for all SBEs in range from 303 K to 373 K

Table 3: The ionic conductivity, activation energy and regression value of SBEs

Sample	σ (S/cm)		E_a (eV)	R^2
	303 K	373 K		
HEAT-0	5.93×10^{-8}	8.60×10^{-6}	0.46	0.99
HEAT-4	4.13×10^{-7}	8.63×10^{-5}	0.42	0.99
HEAT-8	2.00×10^{-6}	1.95×10^{-4}	0.38	0.99
HEAT-12	2.92×10^{-6}	4.03×10^{-4}	0.37	0.99
HEAT-16	3.82×10^{-6}	4.41×10^{-4}	0.36	0.99
HEAT-20	2.45×10^{-5}	8.42×10^{-4}	0.30	0.93
HEAT-24	6.75×10^{-5}	7.17×10^{-4}	0.27	0.97
HEAT-28	2.43×10^{-5}	9.28×10^{-4}	0.30	0.99
HEAT-32	6.29×10^{-5}	3.32×10^{-4}	0.26	0.95
HEAT-36	1.16×10^{-4}	4.62×10^{-4}	0.23	0.99
HEAT-40	4.41×10^{-5}	3.84×10^{-4}	0.28	0.98
HEAT-44	1.45×10^{-5}	6.13×10^{-4}	0.30	0.98

ionic conductivity in SBEs (Hafiza & Isa, 2018). The dielectric permittivity was used to further analyze the ionic conductivity behaviour in this work.

Figure 5 shows the frequency-dependent dielectric constant (ε_r) and dielectric loss (ε_i) plots for all SBEs at 303 K and at elevated temperatures (303 K – 373 K) for sample HEAT-36. Dielectric constant is a measure of the ability of the material to store charge, whereas dielectric loss is a measure of energy losses due to the movement of ions in a rapidly changing electric field (Woo *et al.*, 2012). Based on Figure 5 (left side), high values of both ε_r and ε_i plots can be seen at low frequency, before its gradually decreases as the frequency increase. No significant relaxation peak was seen from these plots, which indicates that the ionic conductance was mainly due to the increase in number of free mobile ions in the polymer matrix

(Majid & Arof, 2007; Nithya *et al.*, 2011). The high value of both ε_r and ε_i at lower frequencies, which decreases as the frequency increases, can be ascribed to the occurrence of electrode polarization and space charge effect and also confirm the non-Debye dependence of the SBEs (Kumar *et al.*, 2012; Isa & Ahmad, 2018). The high value of ε_i also indicates a large value of losses during the dipole orientation (Hemalatha *et al.*, 2015).

In addition, the increment of ε_r at low frequency as the NH₄SCN content increases may be attributed to the enhancement of the charge stored in the SBEs. This also indicates that the increase of number of free mobile ions in the SBEs, which leads to the increase of ionic conductivity (Yusof *et al.,* 2014). The value of ε_r and ε_i decrease gradually as the frequency increases and can be referred to the rapid reversal of the electrical field, in which

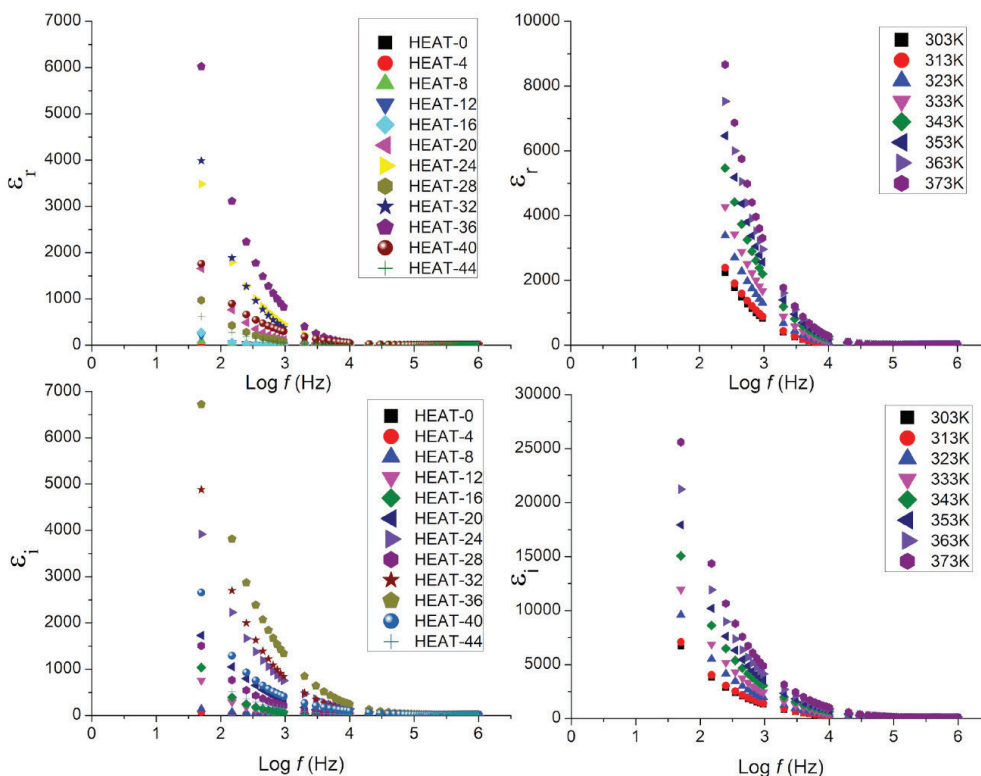Figure 5: Frequency-dependant of ε_r and ε_i at 303 K for all SBEs (left side) and at elevated temperatures for sample HEAT-36 (right side)

ion diffusion is not possible, hence, reducing the charge accumulated at the electrode and resulting in lowered value of ε_r (Vieira *et al.*, 2007; Aziz, 2015).

Figure 5 (right side) shows the value of ε_r and ε_i for HEAT-36 measured at elevated temperatures. Both of ε_r and ε_i increase with the rising temperature which indicates the ionic conductivity increases at higher temperature due to the increase of the number of free mobile ions in the polymer electrolyte system (Khiar & Arof, 2010; Chai & Isa, 2011). The increment of ε_i with the temperature may also be due to the large number of losses during the dipole orientation. Thus, this may increase the number of free mobile ions and its random interactions, which eventually leads to a longer relaxation time (Hemalatha *et al.*, 2015). Further analysis of dielectric modulus give better understanding on the effect of electrode polarization.

The variation of real part (M_r) and imaginary part (M_i) of dielectric modulus at various temperatures for HEAT-36 is shown in Figure 6. From the figure, it is observed that at lower frequencies, the value of M_r and M_i is almost zero and rises up as the frequency increases without noticeable relaxation peak. The presence of the long tail at low frequencies indicates a great suppression of electric double layer capacitance between the electrode and electrolyte interface, which further confirms the non-Debye behaviour of the SBEs. With the low value of M_r, the contribution of electrode polarization can also be neglected (Kavitha *et al.*, 2016; Selvalakshmi *et al.,* 2018). The increasing value of M_r at higher frequencies indicates that the ionic conduction was due to the short, ranged mobility ions carrier of the SBEs (Rozali *et al*., 2012). It is also observed that the M_r decrease with increased temperature.

Conclusion

A new type of solid biopolymer electrolytes system based on 2-HEC doped with several NH_4SCN contents (wt.%) has been successfully developed by utilizing solution casting technique. EIS analysis revealed that the optimum value of room temperature ionic conductivity is 1.16
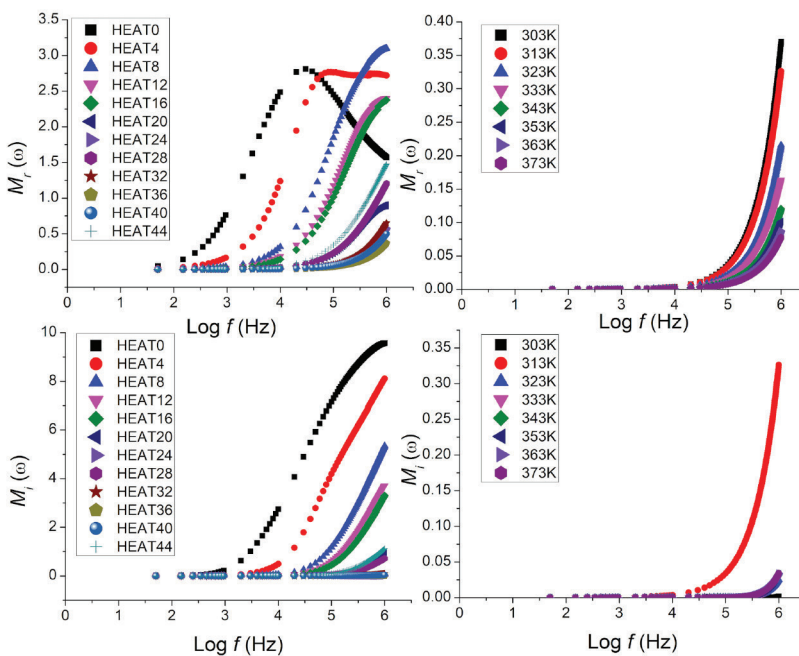

Figure 6: Frequency-dependant of M_r and M_i at 303 K for all SBEs (left side) and at elevated temperatures for sample HEAT-36 (right side)

x 10^{-4} S cm^{-1} for sample containing 36 wt.% NH$_4$SCN. The ionic conductivity also appears to be temperature assisted, which is a characteristic of Arrhenius behaviour, a characteristic found in ionic conductor solid biopolymer electrolytes system. This also denies any conductions by water molecule in the polymer system. In addition, the ionic conductivity was affected by the value of activation energy (E_a), where the low value of E_a yields high ionic conductivity. From dielectric permittivity analysis, the SBEs show non-Debye behaviour, which further support the ionic conduction in the polymer system was due to the movement of free mobile ions. Analysis of dielectric constant (ε_r) and dielectric loss (ε_i) displays high value at low frequency and rises with increasing NH$_4$SCN content as well as temperature, indicating high dissociations of mobile ions into the polymer system. Modulus analysis also confirmed the ionic conductive characteristic of the SBEs. Based on these results, it is believed that the 2-HEC-NH$_4$SCN SBEs has great potential for application in electrochemical devices, however, further analysis on the structural and physical integrity of the SBEs can be beneficial for better understanding of it.

Acknowledgements

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