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To cite this article: A F Fuzlin *et al* 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **342** 012080View the [article online](#) for updates and enhancements.

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Effect on Ammonium Bromide in dielectric behavior based Alginate Solid Biopolymer electrolytes

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Abstract. This paper present the development of solid biopolymer electrolytes (SBEs) system which has been accomplished by incorporating various composition of ionic dopant namely ammonium bromide (NH_4Br) with alginate solution casting method. The prepared sample of SBEs has been analyzed via electrical impedance spectroscopy (EIS) showed that the ionic conductivity at room temperature was increased from $4.67 \times 10^{-7} \text{ S cm}^{-1}$ for un-doped sample to optimum value at $4.41 \times 10^{-5} \text{ S cm}^{-1}$ for composition of 20 wt. % NH_4Br . The SBEs system was found to obey the Arrhenius characteristics with $R^2 \sim 1$ where all sample is thermally activated when increasing temperature. The dielectric behavior of the alginate- NH_4Br SBEs system were measured using complex permittivity (ϵ^*) and complex electrical modulus (M^*) and shown the non-debye behavior where no single relaxation was found for present SBEs system.

1. Introduction

Nowadays, solid biopolymer electrolytes (SBEs) system already been used in battery industry to avoid hazardous in environment. Biopolymer (natural polymer) is one of the biodegradable product which made from waste material that been used in electrolyte study. Biopolymer is the host polymer in the proton-conducting solid biopolymer electrolytes (SBEs) system because of it safety issues and low-cost in battery production [1]. The examples of host polymer that been study are carboxymethyl cellulose (CMC) [2-4], chitosan [5-7], cornstarch [8], and 2-hydroxyethyl cellulose (2-HEC) [9].

Alginic acid, or called alginate, is the cell wall extraction of brown seaweed, which considered being biocompatible, non-immunogenic, biodegradability and having low toxicity [10, 11]. The pure alginate shows empirical formula, which is $\text{NaC}_6\text{H}_7\text{O}_7$ [12]. Alginate is highly water absorbing that consist of (1-4)-linked β -d-mannuronic acid (M) and α -l-gluronic acid (G) units [11]. Alginate can be host polymer in SBE system but its conductivity is low. Therefore, the addition of dopant system was found to be a suitable way to enhance the ionic transports and conductivity performances.

In proton-conducting solid biopolymer electrolyte (SBEs) system, ammonium bromide (NH_4Br) is good proton donor which could approve the proton conduction through solid polymer electrolyte matrix as well as could enhance the ionic conductivity to the higher value [9] [13-16]. NH_4Br is ammonium halide type that consists of NH_4^+ ion and Br^- ion. Ionic salt will doped with biopolymer to increase the ionic conductivity. There are many research proved that used of ammonium salt can increase conductivity such as carboxymethyl cellulose (CMC) doped with ammonium thiocyanate (NH_4SCN) [17].



In the present study, the proton conducting SBEs films based on Alginate incorporating with NH_4Br have been prepared via solution casting technique with various compositions. The ionic conductivity and dielectric behaviour of alginate- NH_4Br based biopolymer electrolytes (BEs) system was observed by using electrical impedance spectroscopy (EIS).

2. Material and methods

2.1. Preparation of SBEs thin films

The preparation of the sample was started by dissolving 2 g of alginate into 98 ml of distilled water. Then, different amount of NH_4Br (5 – 30 wt. %) were added into the alginate solution. The alginate- NH_4Br solution is then was stirred slowly until a homogeneous solution is obtained. The mixture of alginate- NH_4Br was casted into different petri dishes and left to dry until film completely formed. The film is then transferred into a desiccator filled with silica gel to further up drying and also prevent water content appear in the film [18] [19].

2.2. Preparation of SBEs thin films

The alginate- NH_4Br electrolytes will be press and sandwiched between two stainless steel electrodes of a conductivity holder. The dielectric properties of the proton conducting SBEs system were tested using HIOKI 3532–50 LCR Hi-tester interfaced to a computer in a frequency range of 50 Hz to 1 MHz and were tested with different temperature from 303K to 353K. The value of bulk resistance (R_b) was determined from the Cole-Cole plots imaginary impedance (Z_i) versus real impedance (Z_r) which obtained from the impedance measurement. The ionic conductivity, σ of the electrolyte was measured using the following equation:

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

where t is the thickness of the electrolytes and A is the electrode–electrolyte contact area (cm^2).

Dielectric constant also called as amount of charge stored in material. The loss of energy represents the dielectric loss, ϵ_i that normally produces a rise in temperature of a dielectric placed in an alternating electrical field. The amount of energy losses represents to the dielectric loss, ϵ_i where the movement of ions began when the polarity of electric field reverses rapidly during increasing temperature [20,21].

The dielectric constant (the real part of modulus, ϵ_r) and dielectric loss (the imaginary part of modulus, ϵ_i) is calculated using the following equation:

$$\epsilon_r = \frac{Z_i}{\omega C_o (Z_r^2 + Z_i^2)} \quad (2)$$

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

The complex electric modulus (M^*) is used to investigate the conductivity relaxation phenomena. It also needed to suppress the effects of electrode polarization and bulk dielectric properties of the SBE system. The real modulus, M_r and imaginary modulus, M_i was calculated using the following equation:

$$M_r = \frac{\epsilon_r}{(\epsilon_r^2 + \epsilon_i^2)} \quad (4)$$

$$M_r = \frac{\epsilon_r}{(\epsilon_r^2 + \epsilon_i^2)} \quad (5)$$

3. Results and discussion

3.1. Conductivity studies

The variation of ionic conductivity values of alginate samples containing with different amounts of NH_4Br was shown in Figure 1. The ionic conductivity at ambient temperature was found to increase from $4.67 \times 10^{-7} \text{ S cm}^{-1}$ for un-doped sample towards optimum value with six magnitudes order at $4.41 \times 10^{-5} \text{ S cm}^{-1}$ for composition of 20 wt. % NH_4Br . The increment of ionic conductivity with increasing of NH_4Br concentration can be related to the increment of number of mobile charge carriers [21]. This is because the complexation between alginate and NH_4Br gives to the high dispersion of H^+ , therefore will effect towards the increment of ionic conductivity [22, 23]. It clearly can be seen that with the addition above than 20 wt. % NH_4Br , the ionic conductivity start to decreased and this can be attributed due to neutral aggregation of the ions re-associated and also lead to formation of ion cluster as reported by other researcher [14, 24].

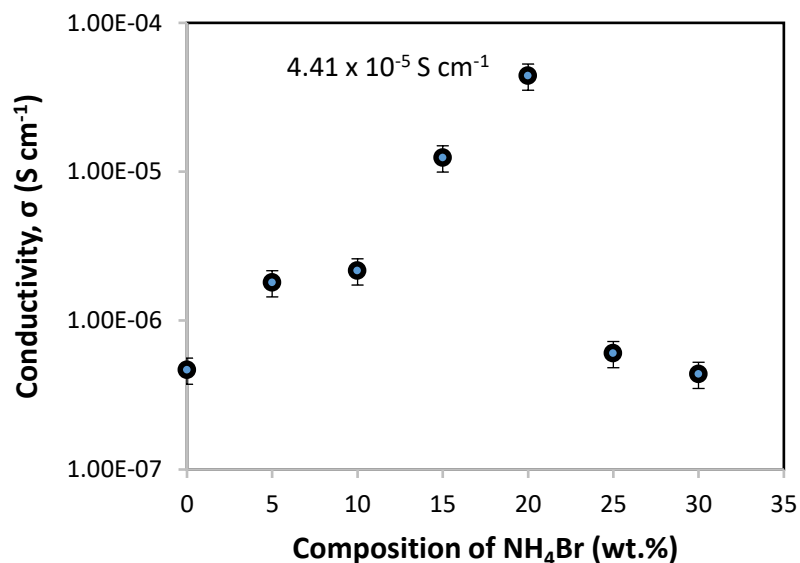


Figure 1. Ionic conductivity of alginate- NH_4Br SBEs system at room temperature.

The effect of temperature on the properties of the ionic conductivity in alginate- NH_4Br SBE system can be analysed using temperature dependence study of ionic conductivity. The log conductivity versus $1000/T$ for various samples at the temperature range from 303 K to 353 K are shown in Figure 2. It shows that the ionic conductivity increased linearly with temperature, which showing that the conductivity is thermally assisted for the present system. The regression value, R^2 was found close to unity ($R^2 \sim 1$) suggesting that all composition for alginate- NH_4Br SBE system in ionic study of

temperature-dependence obey Arrhenius behaviour [14]. From the plot of log conductivity versus $1000/T$, the activation energy, E_a was calculated using the Arrhenius relationships equation:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \quad (6)$$

where E_a is the activation energy, σ is the conductivity of SBEs system, σ_0 is the pre-exponential factor, k is the Boltzmann constant, and T is the temperature in Kelvin.

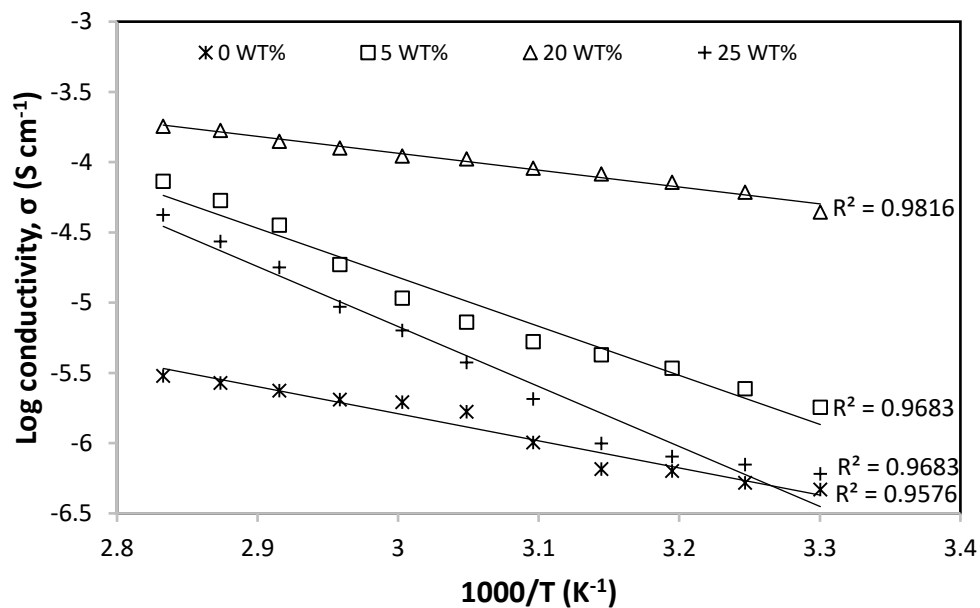


Figure 2. Temperature dependence of alginate-NH₄Br SBEs system.

The activation energy, E_a is the energy needed an ion to migrate from one site to another and can be due to the defect formation [18, 25]. The activation energy, E_a for selected sample of the alginate-NH₄Br of SBE system is shown in Figure 3. It can be observed that the increment of ionic conductivity SBE system lead to decrease the E_a value and this suggesting the ions which correspond to H⁺ only require lower energy to migrate to polymer backbone thus will enhanced the ionic mobility.

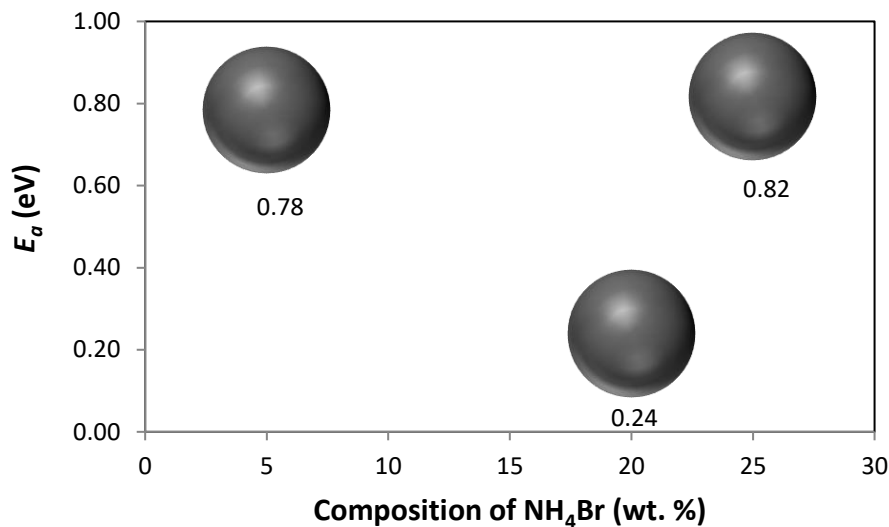


Figure 3. Activation energy for selected sample of alginate-NH₄Br SBEs system.

3.2. Dielectric studies

The dielectric constant is the amount of charge stored in material. In polymer electrolyte study, the charge carrier is ions. Figure 4 shows the study of the dielectric constant for different concentration at selected frequency. It can be observed that increased in concentration of salt, the dielectric constant, ϵ_r also increased for every frequency until 20 wt. % when the ϵ_r value decreased rapidly. This implies that as the concentration of salt is increased, the stored charge also increased which reflected the increasing number of ions in SBE system [26]. Therefore, the reducing of dielectric constant at 25 wt. % NH₄Br is due to decrement in number of density of charge carriers which attributed to the re-association of ions [14]. In Figure 5, the result shown that rising in temperature also increased the dielectric constant value. This is because the re-dissociation of ion starts to aggregates starting to grow resulting in the increment of number of charge carrier density [14].

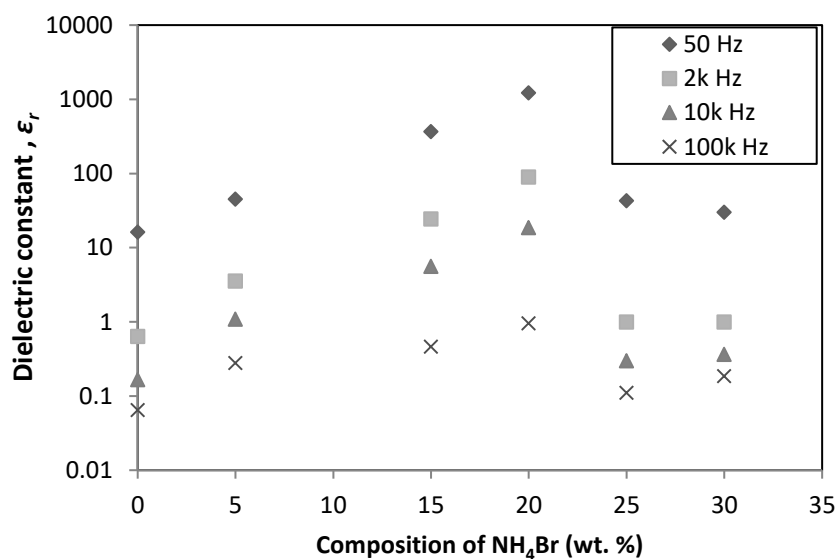


Figure 4. Dielectric constant of alginate-NH₄Br SBEs system.

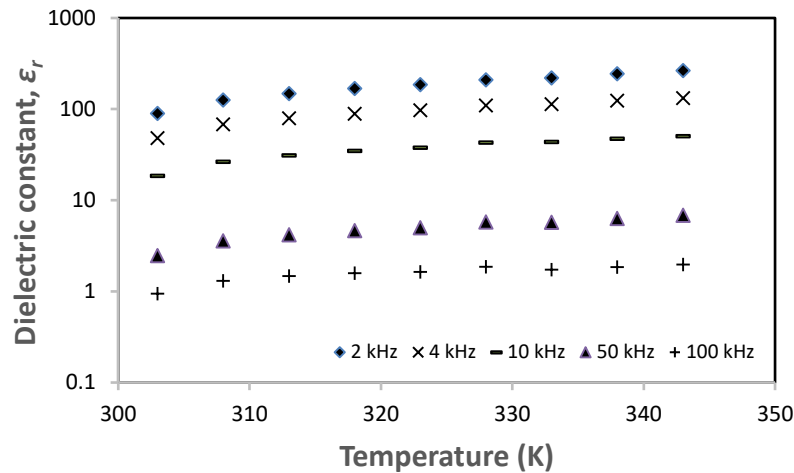


Figure 5. Dielectric constant for the highest sample of SBEs system.

Figure 6 shows that the dielectric loss, ϵ_i for SBEs system. Dielectric loss, ϵ_i is the measure of dispersed energy and mostly contributes in the ionic transport and the polarization of the charge [17, 27]. Based on Figure 6, it can be found that the value of dielectric loss increases rapidly at low frequencies and gradually drops at higher frequencies for all samples. There were no appreciable relaxation peaks observed in the frequency range that was used in this study. The value of ϵ_i increases sharply at the low frequencies due to enhancement in the mobility of charge carriers and can be related to the free charge motion within the electrolytes [17]. Meanwhile, the value of ϵ_i decreases at higher frequencies because of the lesser ions that can pile up at the interface, which have a faster rate in the direction of the electric field change [17, 29]. The value of ϵ_i reduces at higher frequencies due to the periodic reversal of the electric field occurring so fast that there is no excess ion diffusion in the direction of the field [19, 21].

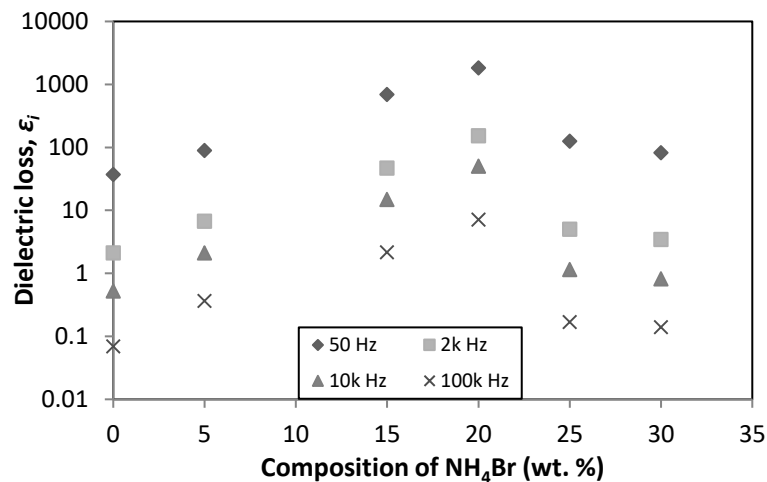
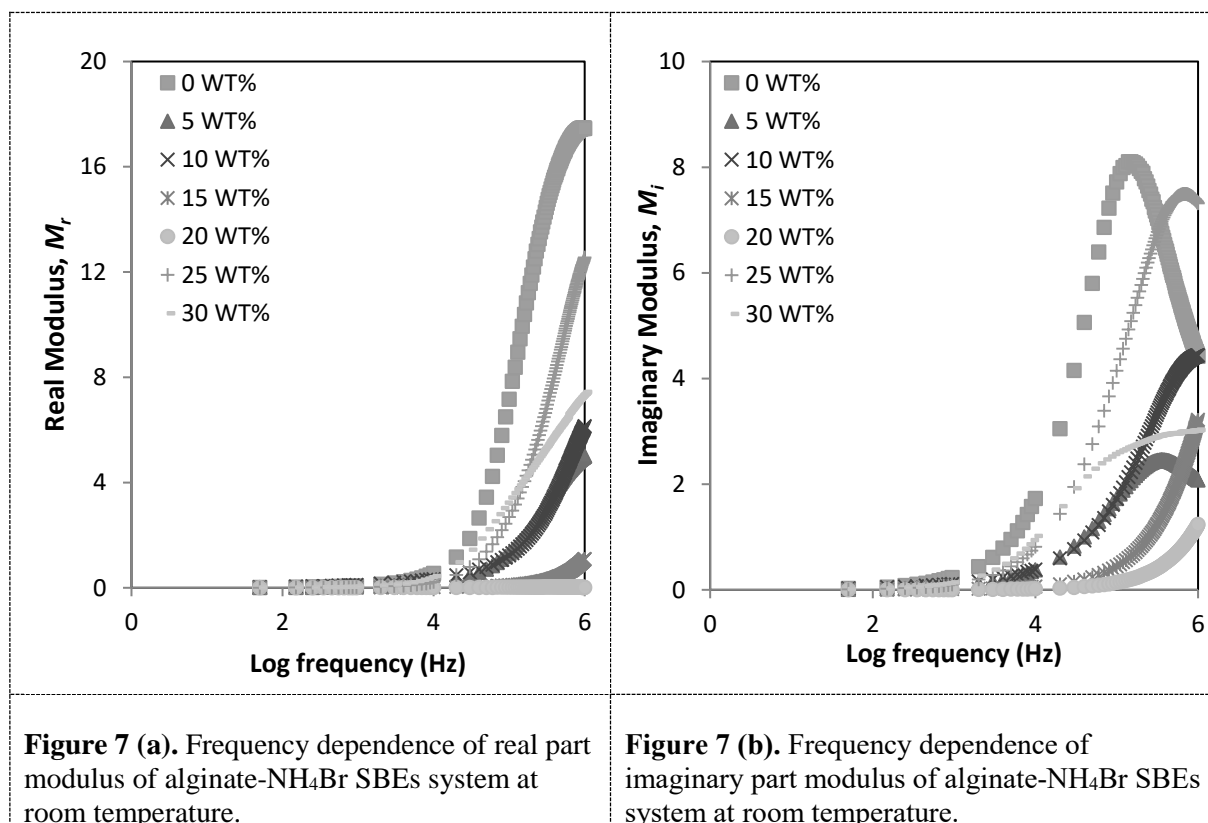


Figure 6. Dielectric loss of alginate-NH₄Br SBEs system at room temperature.

3.3. Modulus studies

Electrical modulus study is a study of the dielectric behaviour of the alginate-NH₄Br SBEs system that suppresses the effect of electrode polarization [25]. Figure 7 shows the frequency dependence of the real and imaginary parts of the modulus formalism, respectively, as a function of frequency for all compositions of the alginate-NH₄Br SBEs system at room temperature. Figure 7 (a) and (b) show that both M_r and M_i approach zero at low frequencies but begin to rise sharply as frequency increases [17, 27, 28]. At

highest conductivity, the real and imaginary part modulus becomes lowest at higher frequency. The presence of peaks in the modulus formalism for all the polymer system shows that the polymer electrolyte films are ionic conductor at higher frequencies [18]. Figure 7 show long tail at low frequencies due to the large capacitance applied with the electrodes and also removal of electrode polarization [18, 29-32]. This confirmed the non-Debye behaviour in the alginate-NH₄Br SBE system.



4. Conclusion

Solid biopolymer electrolytes (SBEs) system based on alginate as host and doped with NH₄Br at various salt composition were successfully prepared via solution cast technique. The highest ionic conductivity at ambient temperature was obtained at $4.41 \times 10^{-5} \text{ S cm}^{-1}$ for sample containing 20 wt. % NH₄Br. Temperature dependence shows that the SBEs system in the present work following Arrhenius behaviour where the R^2 were found closed to unity. The calculated activation energy were found to be inversely proportional with ionic conductivity of SBEs system where only require small amount of energy for ions migration. The dielectric and modulus properties shown that the alginate-NH₄Br SBEs system can be described with non-Debye behaviour where non-single relaxation of ions were observed in the present work. Based on the results, it shows that the biopolymer namely alginate has a good potential to be use as an electrolytes system for application in electrochemical devices.

Acknowledgement

The authors would like to thank Universiti Malaysia Pahang for the financial via internal grant (RDU1703189), Faculty of Industrial Sciences and Technology, University Malaysia Pahang for the support given in this work.

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