

## Immittance Response on Carboxymethyl Cellulose Blend with Polyvinyl Alcohol-Doped Ammonium Bromide-Based Biopolymer Electrolyte

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### Abstract

The blended carboxymethyl cellulose (CMC) and polyvinyl alcohol (PVA) doped with various compositions of ammonium bromide (NH<sub>4</sub>Br)-based solid biopolymer electrolytes (SBEs) were prepared by using the casting method. In this present work, CMC/PVA-NH<sub>4</sub>Br SBE thin film was used to investigate the electrical conductivity via electrical impedance spectroscopy. The maximum conductivity obtained was  $3.21 \times 10^{-4} \text{ S cm}^{-1}$  for sample AB20 at ambient temperature (303 K), and this result might be due to the increased number of charge carrier. A dielectric study was conducted to understand the conductivity behavior. The electrical properties have been measured as a function of frequency of  $\epsilon_r$ ,  $\epsilon_i$ ,  $M_r$ , and  $M_i$ , indicating a non-Debye type behavior.

### Abstrak

**Respon Imitansi pada Campuran Karboksimetil Selulosa dengan Elektrolit Biopolimer Berbasis Amonium Bromida yang Didoping dengan Polivinil Alkohol.** Campuran karboksimetil selulosa (CMC) dan polivinil alkohol (PVA) yang didoping dengan berbagai komposisi elektrolit biopolimer padat (SBE) berbasis amonium bromida (NH<sub>4</sub>Br) dibuat dengan menggunakan metode pengecoran. Di dalam karya tulis ini, film tipis CMC/PVA-NH<sub>4</sub>Br SBEs yang digunakan untuk menginvestigasi konduktivitas listrik melalui Spektroskopi Impedansi Listrik (*Electrical Impedance Spectroscopy* (EIS)). Konduktivitas maksimum yang diperoleh dari hasil tersebut adalah  $3,21 \times 10^{-4} \text{ S cm}^{-1}$  untuk sampel AB20 pada temperatur lingkungan (303K) dan hal ini bisa jadi berupa jumlah pembawa muatan yang meningkat. Suatu studi dielektrik dilaksanakan dengan maksud untuk memahami perilaku konduktivitas. Sifat-sifat listrik telah diukur sebagai suatu fungsi frekuensi  $\epsilon_r$ ,  $\epsilon_i$ ,  $M_r$  dan  $M_i$  menunjukkan suatu perilaku tipe non-Debye.

*Keywords: solid biopolymer electrolytes, ammonium bromide, conductivity, non-Debye behavior, EIS*

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### 1. Introduction

Electrolytes are substances that can be produced electrically by conductive solution when dissolved in solvent and regarded as the main components in electrochemical devices. In 1975, Wright discovered ionic conductivity in polyethylene-based solid polymer electrolytes (SPEs) [1]. Since then, SPEs became popular among researchers in improving ionic conductivity due to its superior potential application in various ionic devices, such as super capacitors, batteries, solar cells, and fuel cells [2]. SPEs also feature several advantages, such as good electrode contact, absence of leakage, and the use of a simple method to prepare their various forms, over liquid and gel-based electrolytes [3]. Synthetic polymers, such as polyvinyl alcohol (PVA) [4] and polyvinylidene fluoride [5], receive considerable attention as host polymers in research owing to their

relatively high conductivity. However, synthetic polymers are nonbiodegradable polymers that result in environmental crisis [6].

The use of natural polymers, such as carboxymethyl cellulose (CMC) [2] and chitosan [7], as host polymers is more suitable for the green world as these materials are biodegradable polymers. Cellulose is also known as the most abundant organic compound on earth, and it possesses good electrical properties [8]. However, the performance of CMC in terms of conductivity can be improved further by adopting a recently widely used blending approach [9]. This popularity is due to the easy preparation of the polymer blend and easy control of the physical properties of the films [10]. As reported by El-Sayed et al. [11], the 50/50 blended CMC/PVA (wt%/wt%) showed the lowest dielectric constant at different temperatures, a condition that is suitable in applications.

In this work, CMC and PVA were selected as host polymers owing to their superior mechanical and good charge storage capacity. Ammonium bromide (AB) (NH<sub>4</sub>Br) was selected as a dopant as it serves as a good proton donor to the biopolymer matrix and is suitable in the application of low-energy density devices [12]. This present system used CMC/PVA doped with AB-based solid biopolymer electrolytes (SBEs) for the evaluation of electrical properties.

## 2. Experimental Methods

Sample preparations CMC and PVA were obtained from Acros Organic Co. and Merck Co., respectively. The CMC/PVA with a 80/20 ratio was used as the biopolymer-blended host and dissolved in distilled water (highest conducting sample as reported in [13]). Then, varied amounts of NH<sub>4</sub>Br (5 wt.% to 35 wt.%) were added to the CMC/PVA blended solution. The solutions were then stirred continuously until homogeneity. The solutions were then cast into several petri dishes at room temperature for future drying until film formation.

Electrical impedance spectroscopy HIOKI 3532-50 LCR HiTESTER was used to analyze the ionic conductivity of SBE thin film-based blended CMC/PVA doped with various compositions of NH<sub>4</sub>Br. The frequency ranges of 50 Hz to 1 MHz at ambient temperature (303 K) with elevated temperature from 30 °C to 100 °C were selected for the present study. The thin film of biopolymer electrolytes was then cut into smaller sizes with a 2 cm diameter of the sample contact surface and sandwiched between two stainless steel electrodes. The bulk resistance (*R<sub>b</sub>*) value was obtained from the imaginary impedance (*Z<sub>i</sub>*) versus real impedance (*Z<sub>r</sub>*) plot, and the ionic conductivity  $\sigma$  was determined using Equation (1):

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

where *t* refers to the sample thickness, and *A* (cm<sup>2</sup>) denotes the cross-sectional area of the biopolymer electrolyte film. The thickness of the SBE system was measured via a digital thickness gage (DML3032) and ranged between 0.0285 cm and 0.0696 cm.

**Table 1. Designation of CMC/PVA-NH<sub>4</sub>Br SBE System**

Design	NH <sub>4</sub> Br composition (wt. %)
AB0	0
AB5	5
AB10	10
AB15	15
AB20	20
AB25	25
AB30	30
AB35	35

The dielectric constant,  $\epsilon_r$  also known as the real part of complex permittivity, is defined as follows [14]:

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

where  $C_o = \epsilon_o A/t$  ( $\epsilon_o$  is permittivity of free space),  $\omega = 2\pi f$  (*f* is frequency), *Z<sub>i</sub>* represents the imaginary part of the complex permittivity, and *Z<sub>r</sub>* is the real part of the complex permittivity.

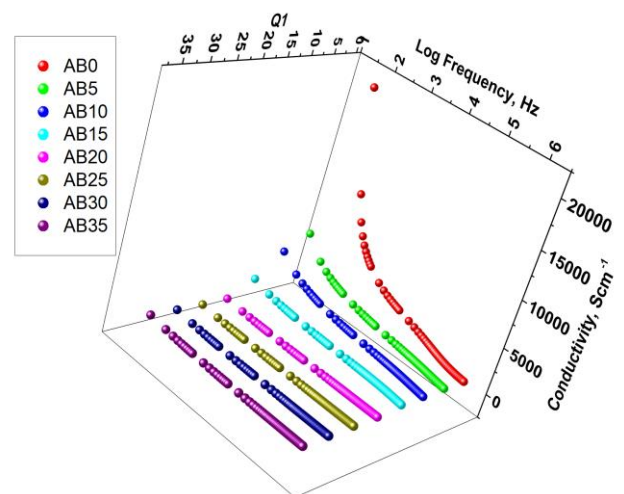
The real modulus *M<sub>r</sub>* and imaginary modulus *M<sub>i</sub>* were determined as follows:

$$M_r = \frac{\epsilon_r}{(\epsilon_i^2 + \epsilon_r^2)} \tag{3}$$

$$M_i = \frac{\epsilon_r}{(\epsilon_i^2 + \epsilon_r^2)} \tag{4}$$

## 3. Results and Discussion

Conductivity studies. Figure 1 depicts the conductivities of various NH<sub>4</sub>Br compositions at room temperature versus the selected frequencies. The results showed that the conductivity of CMC/PVA-NH<sub>4</sub>Br SBE system has decreased with increasing frequency, with the electrode polarization effect dominating the high-frequency region [15]. Figure 2 illustrates the various conductivities for each NH<sub>4</sub>Br composition. The ionic conductivity increased with increasing salt content. As observed in Figure 1, the highest conductivity at room temperature was 3.21 X 10<sup>-4</sup> S cm<sup>-1</sup> for the sample containing 20 wt.% NH<sub>4</sub>Br. This increment in conductivity can be related with the ion dissociation at low salt composition. The present study is supported by that of Samsudin *et al.* [16], who observed that NH<sub>4</sub>Br interacted with the carboxyl anion group from the CMC polymer host, producing more sites for ion hopping and that exchange



**Figure 1. Conductivity Versus Frequency at Selected Frequencies**

can occur to increase the ionic conductivity. After the addition of the AB20, the conductivity decreased, and this result may be attributed to the association of ions at high salt composition, leading to the formation of neutral aggregates [17]. The decrement of conductivity can also be explained in terms of the re-association of salt, which supplied more proton ( $H^+$ ) ions with the increasing salt content, causing the reduction in ionic mobility and increase in the ion mobility [18].

**Dielectric study.** The study of dielectric constant aims to measure the reduction of coulomb interaction of the ion pair in polymer electrolytes, whereas dielectric loss is a direct measure of the energy dissipated and generally consists of contributions from the ionic transport and charge or dipole polarization [19]. Figure 3 shows the salt composition dependency of the dielectric constant  $\epsilon_r(\omega)$  of selected samples at the selected frequencies curves. The graph shows an almost similar pattern with the conductivity plot in Figure 2. This trend mainly occurred due to the increasing charge carrier number [20]. As the charge carrier is related with the movement of ions, the increment in charge carrier causes the increase in the ion density, hence increasing the conductivity [21]. However, beyond sample AB20, the dielectric constant and dielectric loss decreased due to the decrement in the density of charge carrier, leading to ion re-association [12].

**Modulus study.** Further analysis in electrical behavior has focused on the dielectric moduli, including the real

modulus ( $M_r$ ) and imaginary modulus ( $M_i$ ), which exhibited the effect of electrode polarization, indicating the electrical property of the polymer electrolyte. Figure 4 shows the frequency dependence of real and imaginary moduli. From Figures 4(a) and 4(b), at low frequencies, the values of  $M_r$  and  $M_i$  were low and nearest to zero. However, the values increased as frequency increased from 3 Hz to 5 Hz. Increasing modulus ( $M_r$  and  $M_i$ ) values at higher frequencies might be assigned to the bulk effect [22], [23]. The appearance of this long tail at low frequencies is due to the large capacitance applied with the electrodes [22], [24]. The modulus values are at zero vicinity, indicating a small polarization, which is the main advantage of  $M_r$  and  $M_i$  modulus studies.

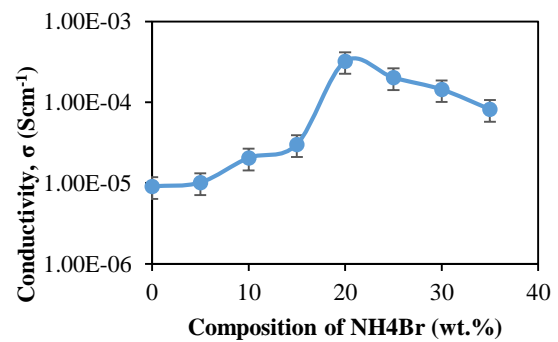
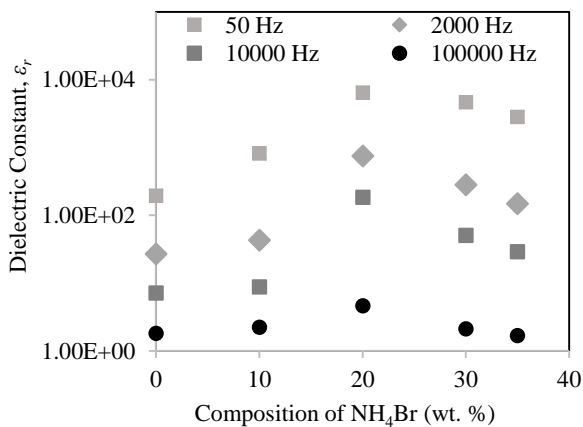
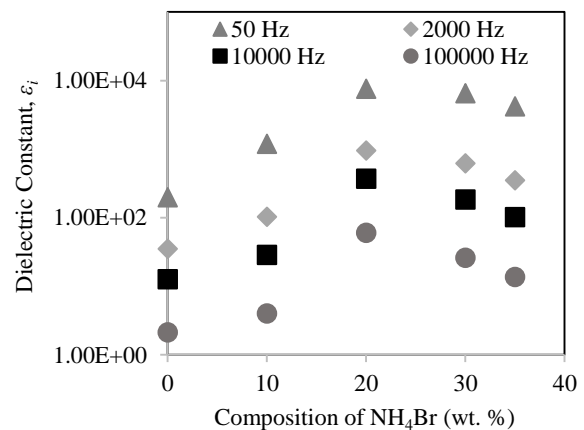


Figure 2. Ionic Conductivity of CMC/PVA-NH<sub>4</sub>Br SBEs

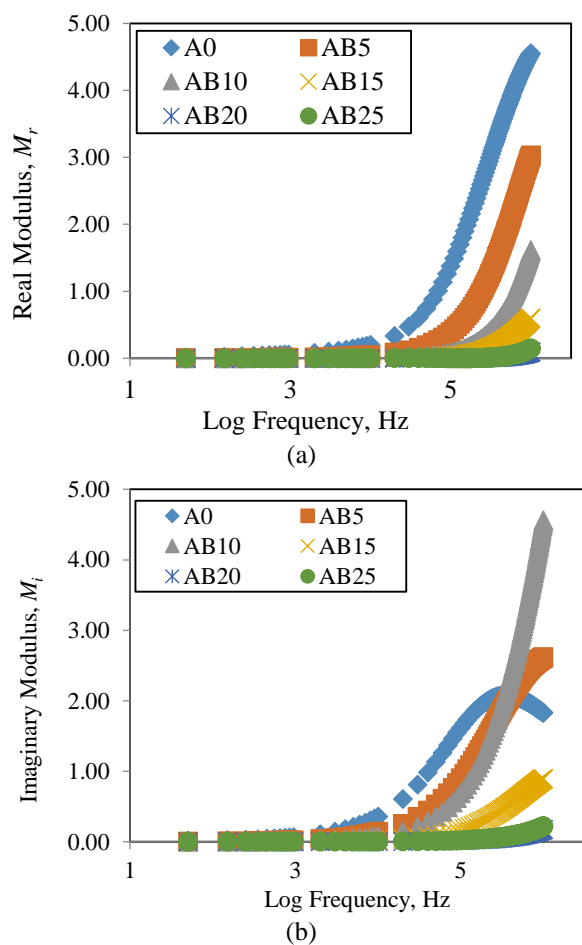


(a)



(b)

Figure 3. (a) Dielectric Constant and (b) Dielectric Loss Versus Various Composition of NH<sub>4</sub>Br (wt.%) at Selected Frequencies



**Figure 4. Frequency Dependence of (a) Real Modulus and (b) Imaginary Modulus at Various Compositions of NH<sub>4</sub>Br at Room Temperature (303 K)**

#### 4. Conclusion

The SBE-based CMC blended with PVA doped with various compositions of NH<sub>4</sub>Br has been prepared by using casting method. The highest ionic conductivity achieved at room temperature was  $3.21 \times 10^{-4} \text{ S cm}^{-1}$  for sample AB20. This increment in conductivity until AB20 is attributed to ion dissociation, which created more space for the ions to move from one site to another, thus increasing the mobile charge carrier. The decrement occurred beyond sample AB20 mainly due to ion association. A higher ion density indicates a higher charge carrier, which can reflect the increase in the ionic conductivity. Thus, the value of ionic conductivity strongly depends on the number of charge carrier.

#### Acknowledgement

The authors would like to thank MOHE for FRGS (RDU170115), Faculty of Industrial Sciences and

Technology, University Malaysia Pahang, for the help and support given for the completion of this work.

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