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# A Study on Dielectric Properties of The Cellulose Derivative-$NH_4Br$-Glycerol-Based The Solid Polymer Electrolyte System

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## Abstract

The characterization of biopolymer-based solid polymer electrolytes (SPEs) has been carried out in this present work. Cellulose derivative was chosen due to its superior physical attributes. In this work, $NH_4Br$-doped glycerol plasticized carboxyl methylcellulose-based SPEs were successfully prepared via the solution casting method. The conductivity and dielectric properties of the prepared films were investigated using the impedance analysis which presented ~$1.91\times10^{-3}$ $Scm^{-1}$ (with addition of 6 wt% of glycerol). In addition, the studied SPE system shows a non-Debye behaviour without a single relaxation time. The findings of the research indicate that the complexes of $NH_4Br$ and glycerol in the cellulose derivative influence the ionic conductivity and dielectric properties of the SPE system.

## Abstrak

**Kajian Sifat Dialektik dari Gliserol Turunan Selulosa-NH4Br- Berdasarkan Sistem SPEs**. Perkembangan elektrolit polimer pepejal (SPEs) berdasarkan bahan bio-polimer telah dilakukan dalam kajian sekarang ini. Bio-polimer dari turunan selulosa dipilih karena sifatnya yang unggul. Dalam karya sekarang ini, SPEs berdasarkan karboksil metilselulosa didopkan dengan $NH_4Br$ dan terplastikkan dengan gliserol telah berhasil disiapkan melalui metode tebaran larutan. Sifat unggul film telah diselidiki dalam terma konduktivitas mereka dan juga sifat dielektrik menggunakan teknik impedansi. Nilai ionik tertinggi untuk nilai konduktivitas yang ditemui ialah $1,91 \times 10^{-3}$ S $cm^{-1}$ ketika 6 wt.% gliserol ditambahkan. Sifat dilektrik dari sistem SPEs menunjukkan tren yang signifikan di mana sistem ini secara tepatnya dapat disebut perilaku non-Debye tanpa waktu relaksasi tunggal. Interaksi dari $NH_4Br$ dan gliserol dalam turunan selulosa telah menunjukkan bahawa ianya mempengaruhi konduktivitas ionik dan sifat dielektrik dalam sistem SPEs.

*Keywords: solid polymer electrolytes, carboxyl methylcellulose, ionic conductivity, dielectric studies, non-Debye behavior*

## 1. Introduction

Electrolyte is an important component of electronic devices, which became the main focus of the research on the application of electrochemical devices [1] due to the establishment of ionic conductivity-performance correlation in a poly (ethylene oxide) (PEO)/$Na^+$ SPE system in 1973 [2]. Polymer electrolytes are grouped into three classes, namely solid, liquid, and gel. Solid polymer electrolytes possess superior properties (i.e., compatibility with anode and cathode, no outflow, low self-discharge in battery, lightweight, minimal risk of leakage, mechanical stability, and flexibility) in com-parison with that of the liquid and gel-based electrolytes [3,4]. Synthetic polymer-based SPEs present high ionic conductivity which could be one of the best candidates. However, as the non-biodegradable synthetic polymers lead to environmental issues, biodegradable natural polymers could be the best substitute to minimize the risk [5].

Natural polymer hosts, such as sago, starch, chitosan, and cellulose are suitable to be used [6-9]. One of the most widely explored candidates as a polymer host is the non-toxic, biocompatible, and biodegradable carboxyl methyl cellulose (CMC) which could be dissolved in water for various purposes [10-15]. In the present work, the CMC was utilized as a proton-conductor in the SPE system. Bare CMC shows poor conductivity; however, the ionic conductivity increased to $10^{-4}$ $Scm^{-1}$ after the addition of $NH_4Br$, which originated from the effect of the ammonium salt [16-18].

The doped-SPEs, however, are yet to show significant ionic conductivity which attracted various attempts and techniques to enhance the ionic conductivity e.g., blending, copolymerization, and plasticization. Chai and Isa [19] prepared proton conducting glycerol plasticized CMC-based SPEs using the solution casting method. This improved not only the ionic mobility but also the

mechanical properties of the SPE film. Other works also reported that the addition of plasticizers such as ethylene carbonate (EC) [20,21], propylene carbonate (PC) [22], glycerol [23], polyethylene glycol (PEG) [24] leads to the enhancement of ionic conductivity.

The plasticizer-cellulose-salt complexes (glycerol-CMC-$NH_4Br$) are initially hypothesized to show improved ionic conductivity in comparison with that of the bare CMC. The effects of ionic conductivity and dielectric properties have been investigated to understand the electrical behaviour of the SPE system. In addition, the effects of the concentration of glycerol as a plasticizer on the conductivity of CMC-$NH_4Br$ were also studied using an electrochemical impedance spectroscopy.

## 2. Methods

**Sample preparation** The CMC was dissolved in 100 ml distilled water and 25wt. % $NH_4Br$ solution was added. The mixture was stirred continuously until it is thoroughly blended. Various amounts of glycerol were added i.e., 2, 4, 6, 8, and 10wt. %, and labelled with A1-A5 respectively as shown in Table 1. The solution was poured into petri dishes and dried at room temperature until plasticized polymer film is formed. The semi-dried plasticized film was then placed in a desiccator for the next drying process.

**Electrical impedance spectroscopy (EIS)** The electrical impedance spectroscopy analysis was carried out using HIOKI 3532-50 LCR Hi-Tester at different temperatures between 303 and 373K to study the ionic conductivity of the SPE films. The ionic conductivity $\sigma$ was calculated using the equation (1) below:

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

where $t$ is the thickness, $R_b$ is the bulk resistance, and $A$ ($cm^2$) is the electrode-electrolyte contact area of the SPE films. The Arrhenius behavior can be expressed with the equation below:

$$\sigma = \sigma_o \exp(-E_a/kT) \tag{2}$$

where $\sigma_o$ is the pre-exponential factor, $E_a$ is the activation energy, k is the Boltzmann constant and T is the absolute temperature.

**Table 1. Designation for CMC-$NH_4Br$–glycerol of SPE System**

| Sample | Designation | Glycerol composition (wt. %) |
|---|---|---|
| 1 | A1 | 2 |
| 2 | A2 | 4 |
| 3 | A3 | 6 |
| 4 | A4 | 8 |
| 5 | A5 | 10 |

**Dielectric study** The dielectric study is needed to describe the mechanism and interactions of ions in the SPEs [25]. The dielectric constant $\varepsilon_r$ and dielectric loss $\varepsilon_i$ can be determined using the following equations:

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

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

**Modulus study** The real modulus $M_r$ and imaginary modulus $M_i$ were determined using equation (5) and equation (6):

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

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

## 3. Results and Discussion

**Conductivity study** Table 2 presents the ionic conductivity of samples A1-A5 in the present work. The graphs of activation energy and ionic conductivity as a function of salt concentration are shown in Figure 1.

**Table 2. Room Temperature Ionic Conductivity**

| Sample | Glycerol (wt. %) | Conductivity σ ($Scm^{-1}$) |
|---|---|---|
| A1 | 2 | $6.05 \times 10^{-4}$ |
| A2 | 4 | $2.73 \times 10^{-5}$ |
| A3 | 6 | $1.91 \times 10^{-3}$ |
| A4 | 8 | $2.34 \times 10^{-4}$ |
| A5 | 10 | $3.82 \times 10^{-5}$ |

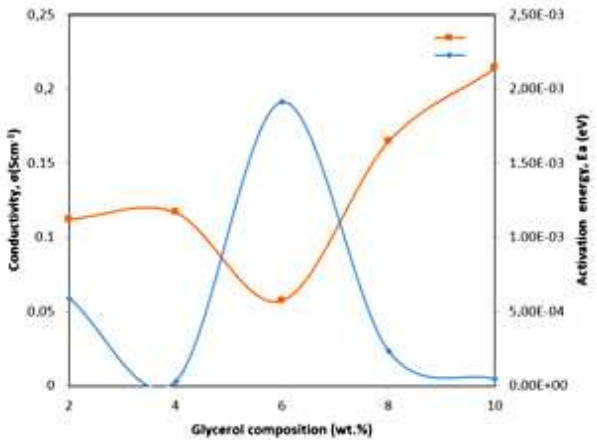


**Figure 1. Ionic Conductivity σ and Activation Energy $E_a$ Against Glycerol Composition of CMC-$NH_4Br$-Glycerol**

Sample A3 which comprises of CMC-$NH_4Br$-glycerol at room temperature (303K) shows the highest conductivity ~1.91 x $10^{-3}$ $Scm^{-1}$. The trend is clearly observed in the region of A1-A3 i.e., with the increment of glycerol, the conductivity increases; which could be described with the association of ions at a high concentration of plasticizer. The result supports the findings of a study by Ibrahim *et al*. (2012) which show that the dissociation of salt is contributed by the addition of plasticizer [26].

Further increment of glycerol above 6wt. % has caused the conductivity to decrease, which is due to low ion mobility caused by two factors viz. (i) excess of free mobile ions [27] and (ii) re-association of the ions into neutral aggregates [28,29].

The activation energy $E_a$ decreases as the plasticizer composition increases (samples A1-A3). Sample A3 (6wt. % glycerol) shows the lowest activation energy. The decrease in the activation energy strongly supports the increment of the electrical conductivity where a low activation energy system would need a smaller amount of energy to support the migration of ions compared with that of the high activation energy system [30].

The $E_a$ was calculated from the gradient of the log of the conductivity *vs.* temperature plot (Figure 2). The temperature dependence ionic conductivity study was carried out to understand the mechanism of ionic conduction in the temperature ranging from 303 to 373 K. The result shows a linear relationship i.e., the conductivity increased along with the increasing temperature. The observation suggests that the conductivity obeys the Arrhenius behavior and is thermally assisted [31-33]. According to Ramesh *et al.*, the main mechanism which contributes to the ionic conductivity of Arrhenius-behaved SPEs is the movement of an ion jumping from one site to its neighbouring vacant sites [34].

**Dielectric study** The amount of stored charge in a material is represented with complex permittivity (ε) or dielectric constant [35-36]. The dielectric constant $\varepsilon_r$ and dielectric loss $\varepsilon_i$ curves of sample A3 are shown in Figure 3 (a) and (b); delivered by two graphs at various temperatures and compositions of glycerol. A sudden increase in dielectric constant and dielectric loss at low

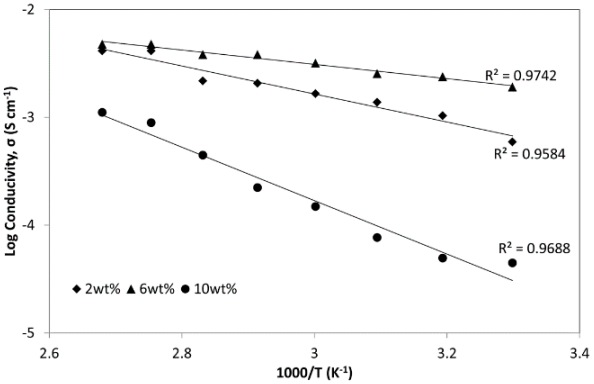


**Figure 2. Arrhenius plots for CMC-$NH_4Br$-Glycerol**

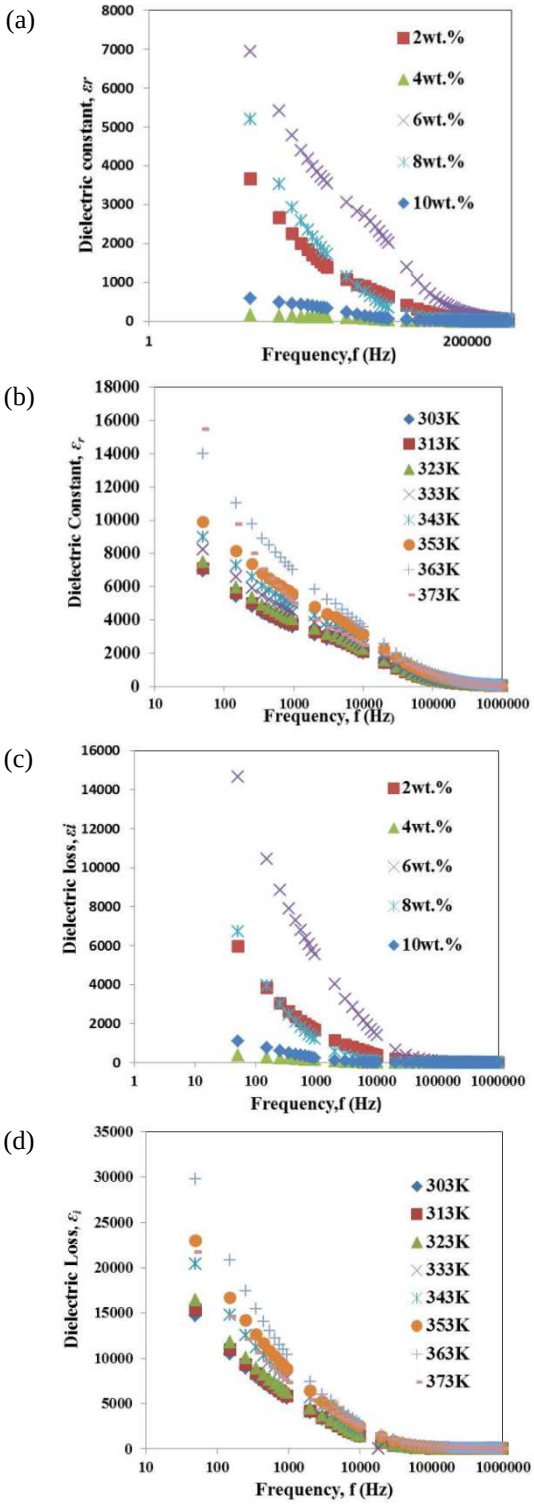


**Figure 3. Variation of Dielectric Constant $\varepsilon_r$ versus $f$ (Hz) in (a) wt.% of Glycerol and (b) at Various Temperatures, Dielectric loss $\varepsilon_i$ versus $f$ (Hz) in (c) wt.% of Glycerol and (d) at Various Temperatures for Sample A3**

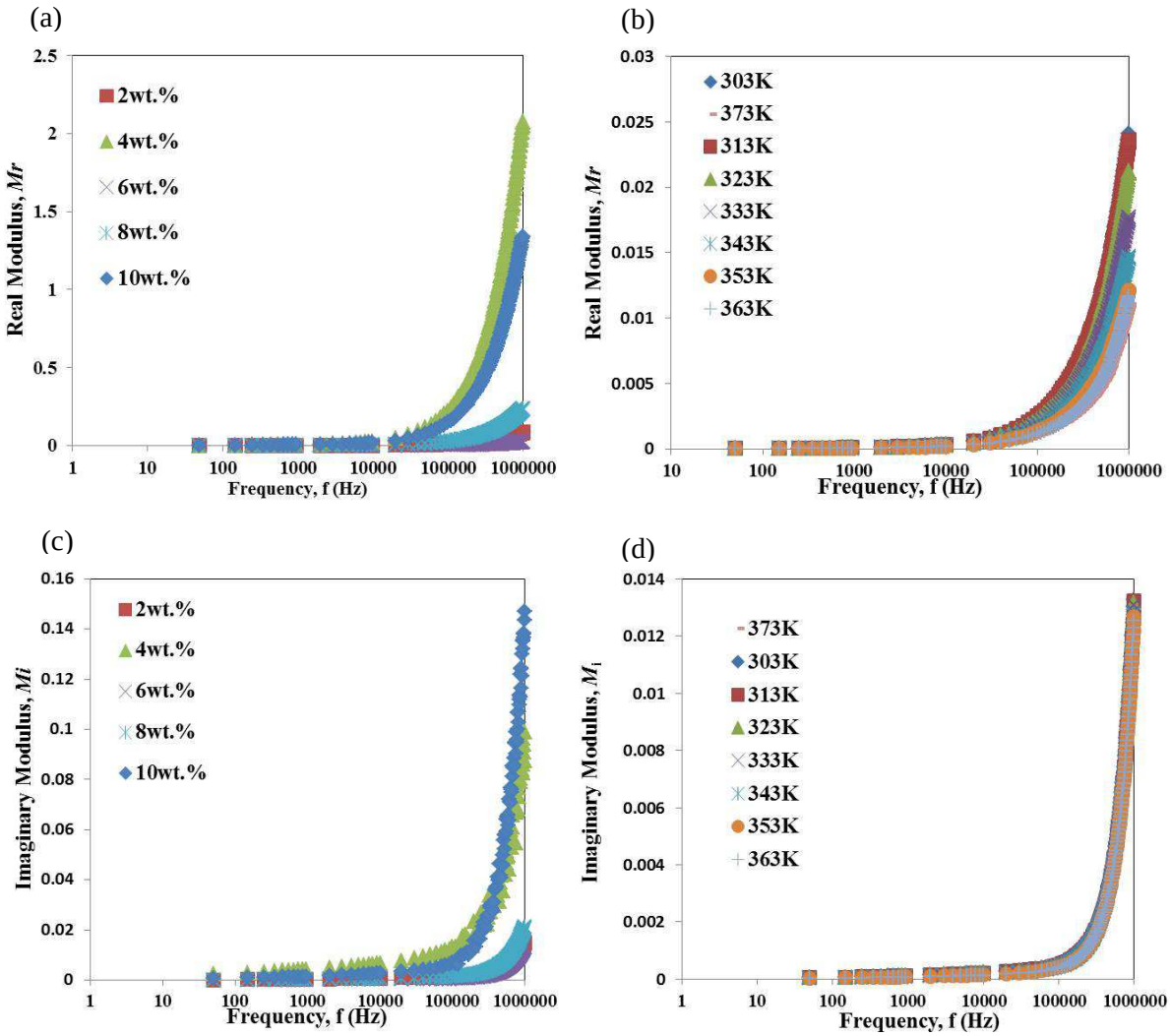


**Figure 4. Variation of Imaginary Modulus *Mi* versus *f* (Hz) in (a) wt.% of Glycerol and (b) at Various Temperatures, Real Modulus *Mr* versus *f* (Hz) in (c) wt.% of Glycerol and (d) at Various Temperatures for Sample A3**

frequency and high temperature was observed, which can be correlated to the anode and cathode polarity effects [36] in the SPE system. At high frequency, the periodic reversal of the electric field occurs rapidly where there is no excess ion diffusion in the path of the field [37]. Majid and Arof [38] state that charge build-up at the boundary will be suppressed at high frequency. The polarization due to the charge accumulation decreased, which lowered the value of real and imaginary part of dielectric constant [39]. The $\varepsilon_r$ increased as the glycerol increased from 2 to 6 wt.%. Furthermore, it can be observed from Figure 3 (b), as the temperature increased, the stored charge also increased due to the large number of charge carriers indicated by an asymptotic rise in dielectric constant values [40].

Furthermore, the absence of relaxation trend in the graph strengthened the observation [41]. The observed trend could be recognized as a non-Debye behavior [42-44]. A detailed analysis of the dielectric behavior is presented in the next section using dielectric modulus to draw a salient conclusion.

Modulus formalism was used for further analysis due to a non-observable loss peak in the dielectric plots. The variation of modulus studies is listed in Figure 4(a) and (b).

From Figure 4, the real modulus and imaginary modulus increased proportionally to the increment of frequency. According to Ramesh *et al.* [43], when the real modulus and imaginary modulus approach zero in a low frequency region, the anode and cathode polarity phenomena are negligible. The slope of each curve for the imaginary electrical modulus exhibits a long tail extending into the region of a longer relaxation time. These show that the samples are highly capacitive and a non-Debye behavior system is confirmed [45-47]; those tally with the absence of relaxation peak in Figure 3.

## 4. Conclusion

The CMC-$NH_4Br$-Glycerol-based SPE is success fully fabricated with optimized glycerol (6wt. %) which presented maximum ionic conductivity ca. $1.91x10^{-3}$ $Scm^{-1}$ at room temperature. The addition of glycerol in the SPE system was identified to have a salient effect that increases the conductivity. The temperature dependence ionic conductivity of the SPE system confirms the Arrhenius behavior. The dielectric behavior of the studied SPEs was found to be dependent on the ionic conductivity, frequency, and temperature caused by the non-Debye behavior.

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