

Original Research Paper

Electrical Studies of Carboxy Methylcellulose-Chitosan Blend Biopolymer Doped Dodecyltrimethyl Ammonium Bromide Solid Electrolytes

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Abstract: In this study, a polymer-blend system consist of Carboxy Methylcellulose (CMC)-Chitosan (CS) as blend biopolymer host and doped with various composition of Dodecyltrimethyl Ammonium Bromide (DTAB) were successfully prepared via solution casting techniques. The new system has been analyzed through Electrical Impedance Spectroscopy (EIS) from temperature 303 K until 393 K to determine the conductivity of biopolymer electrolytes in the frequency range of 50 Hz to 1 MHz and the voltage between 5 to 50 mV. The optimum conductivity ($1.86 \times 10^{-6} \text{ S.cm}^{-1}$) at ambient temperature obtained for composition of 5 wt.% DTAB. The temperature dependence of ionic conductivity was found to obeys the Arrhenius rule where $R^2 \approx 1$ and thermally activated. The dielectric studies show a non-Debye behavior of SBEs based on the analyzed data using complex permittivity, ϵ^* and complex electrical modulus, M^* of the sample at selected temperature.

Keywords: Solid Biopolymer Electrolytes, Dodecyltrimethyl Ammonium Bromide, Biopolymer Blend, Ionic Conductivity, Dielectric Studies

Introduction

In recent years, the electrolyte based on natural polymer has attracted great interest among the academicians. The finding is to spell out the mechanism of conductivity enhancement in the systems (Wach *et al.*, 2001; Chauhan and Lal, 2003; Jung *et al.*, 2006; Isiklan *et al.*, 2008; Peng and Chen, 2010). Most of natural polymer are biodegradable (Huang *et al.*, 2003; Ramlli *et al.*, 2013), easy to be found (Chai and Isa, 2012; Othman *et al.*, 2012) and low in production cost (Rozali *et al.*, 2012) comparable to the current electrolyte systems, they use heavy-metal like lead and mercury which expensive (Khurmi and Sedha, 2010), hazardous (Sit *et al.*, 2012) and non-biodegradable (Rozali *et al.*, 2012). In fact, the earth will run out of these materials if focused solely on it (Calvin, 1979).

Some may use synthetic polymers that derived from petroleum oil like nylon, polyethylene, Teflon, epoxy and polyester as polymer host in SBEs. Unfortunately, most of them are unsolvable in solvents and non-biodegradable which can cause environmental problem compared to natural polymers occurs in nature, often

water-based and can be extracted. For that reason, electrolyte based natural polymer has engrossed much attention due to their potential applications in electrochemical devices such as super capacitors, rechargeable batteries, fuel cells and solar cells (Buraidah and Arof, 2011).

Polymer blend is a mixture of two or more different polymers without covalent bond formation (Shukur *et al.*, 2012). The conductivity of polymer blend is better than the single polymers (Sandoval *et al.*, 2005). Thus, it affects the conductivity of the polymer electrolytes (Utracki, 2002).

Carboxy Methylcellulose (CMC) and Chitosan (CS) (Wan *et al.*, 2006; Kadir *et al.*, 2011; Bakar and Isa, 2014) biopolymer blend have been chosen incorporate as the host due to its mechanical strength and superior properties like good proton, H^+ acceptor from Dopant (DTAB). Hence, the miscibility of the blend with no phase separation between the two polymers has been proven to enhance the ionic conductivity of SBEs (Rajendran *et al.*, 2002; Baskaran *et al.*, 2006). It can form a good electrode-electrolyte surface contact, leakage free and easy for handling compared to liquid

or gel counterparts. Hence, it affects the neatness of the production systems.

This present work aims to discover the electrolyte composition exhibits the highest ambient electrical conductivity in the systems of CMC/CS blend biopolymer doped with DTAB solid electrolytes.

Material and Methods

Sample Preparation

About 1.3333 g of CMC from Acros Organic Co. with purify of >99.9%; average MW = 90,000 and 0.6667 g of chitosan W.A. Hamond Drierite Company LTD were dissolved in 1% of acetic acid solution (Merck). The CMC/CS was stirred until dissolution completely achieved. Then, different composition of DTAB (Magna Value) in wt.% as dopant was added into 1% acetic acid solution and stirred. Then, the CMC/CS solution and DTAB solution were mixed and stirred until it homogenous. The mixtures were casted into Petri dishes and dried in oven at 60°C until SBEs were formed. The SBEs were kept into desiccators for further drying process. Clear and transparent SBEs were obtained for characterization. The designations for SBEs doped with various wt.% of DTAB are shown in Table 1.

Electrical Impedance Spectroscopy (EIS)

The conductivity of SBEs were analyzed by using Electrical Impedance Spectroscopy (EIS) modeled HIOKI 3532-50 LCR Hi-Tester. The machine will be interfaced to a computer in a frequency in the range of 50 Hz to 1 MHz. The electrolytes were cut into a suitable round size and sandwiched in between the stainless steel that act as an electrode of conductivity cell which connected by leads to computer. The bulk resistance (R_b) was obtained from the plot of negative imaginary part (Z_i) versus real part (Z_r) of impedance. The conductivity of the sample was calculated from the Equation 1:

$$\sigma = t / (R_b A) \quad (1)$$

Where:

A = Area of electrolyte-electrode contact (cm²)

t = Thickness of the electrolyte (cm) and

R_b = Bulk resistance (Ω)

Table 1. Designation for SBEs doped with various composition wt.% of DTAB

Sample	Composition (wt.%)
DTAB-0	0
DTAB-1	1
DTAB-2	2
DTAB-3	3
DTAB-4	4
DTAB-5	5
DTAB-6	6
DTAB-7	7

Results and Discussion

Conductivity Studies

Conductivity, σ versus various composition, wt.% of DTAB at ambient temperature was plotted in Fig. 1. It has been observed that the conductivity from 3.15×10^{-9} S.cm⁻¹ increase until it achieved optimum value of 1.86×10^{-6} S.cm⁻¹ at 5 wt.% of DTAB. It shows composition of charge carrier (DTAB) act like a catalyst towards the conductivity of electrolyte.

The increasing of ionic conductivity can be explained by the unification of ions at higher salt concentration, which leads to the enlargement formation of ion clusters and the number of charge carriers and their mobility until H⁺ ion from DTAB has attached optimally to the vacancy in the CMC-CS biopolymer blend host bond (Shukur *et al.*, 2012).

Afterward, the conductivity of the SBEs starts to fall after the addition of 6 wt.% of DTAB. According to Aziz *et al.* (2010) the decreasing of conductivity can be clarified by accumulation of ion that contribute to the overcrowded system, thus it conveys to the decreasing number of mobile charge carriers and limitation towards mobility ion (Selvasekarapandian *et al.*, 2005).

Figure 2 shows the temperature dependence of conductivity for SBEs at selected temperatures. The temperature-dependence of ionic conductivity measurements were used to analyze the mechanism of ionic conduction of SBEs systems and even the small changes has been detected. According to Vieira *et al.* (2007), the dependence of ionic conductivity on the salt composition provides information on the specific interaction among salt and polymer matrix.

It shows that as the temperature increase, the conductivity will also increase as it proves temperature, T is directly proportional to the conductivity, σ as shown in the Equation 2. According to Samsudin and Isa (2012a; 2012b) the pattern proves that the conductivity is thermally assisted. The regression value are near to 1 which is $R^2 \approx 1$ that supported by (Samsudin *et al.*, 2012) the temperature dependent of ionic conductivity for this complexes systems obeys an Arrhenius behavior by the expression of the Equation 2.

$$\sigma = \sigma_o \exp(-E_a / kT) \quad (2)$$

Where:

σ = Conductivity

σ_o = Pre-exponential factor

E_a = Activation energy and

K = Boltzmann constant

Based on the equations that applied, the value of E_a will lower at the highest conductivity. This phenomenon

is due to the increment of ions in the SBEs systems and the addition of DTAB that leads to the decrement of energy barrier for the ion transport that causes the reduction of E_a as shown in Fig. 3.

According to Chai and Isa (2013) the conducting ions easily excited to free ion-like state which affects the increment conductivity of Solid Biopolymer Electrolytes (SBEs) systems. The conductivity behavior of SBEs can be deeply explained from the dielectric studies where it is comes from the fundamental knowledge regarding the electrical studies of electrolytes (Chai and Isa, 2011).

Dielectric Studies

The dielectric constant is a basic knowledge in the ability of the biopolymer to disband added salts which may increase the conductivity of the electrolytes. Dielectric constant also known as stored charge in

material. The loss of energy represents the dielectric loss, ϵ_i which normally produces a rise in temperature of a dielectric placed in an alternating electrical field. The dielectric constant (the real part of complex permittivity, ϵ_r , Equation 3) and dielectric loss (the imaginary part of complex permittivity, ϵ_i , Equation 4) are defined as:

$$\epsilon_r = Z_i / \omega C_o (Z_r^2 + Z_i^2) \quad (3)$$

$$\epsilon_i = Z_r / \omega C_o (Z_r^2 + Z_i^2) \quad (4)$$

where, Z_i is the imaginary part of the complex permittivity, Z_r is the real part of the complex permittivity, $\omega = 2\pi f$ (f is frequency) and $C_o = \epsilon_o A/t$ (ϵ_o is permittivity of free space). The dielectric constant, ϵ_r and dielectric loss, ϵ_i for DTAB-5 are shown in Fig. 4a and b.

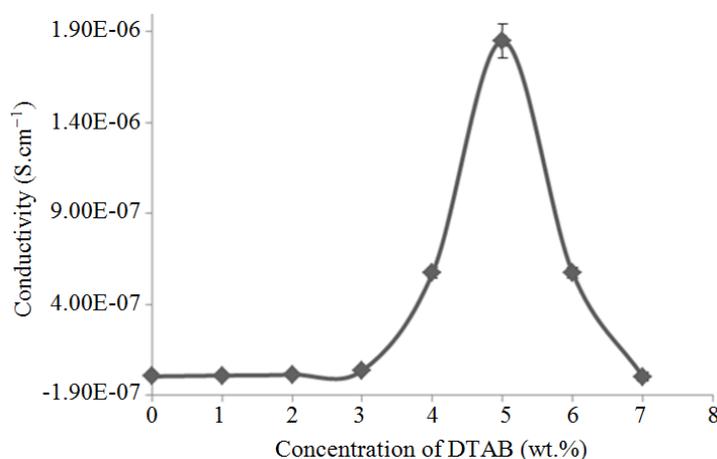


Fig. 1. Conductivity, σ versus various composition, (in wt.%) of DTAB at ambient temperature

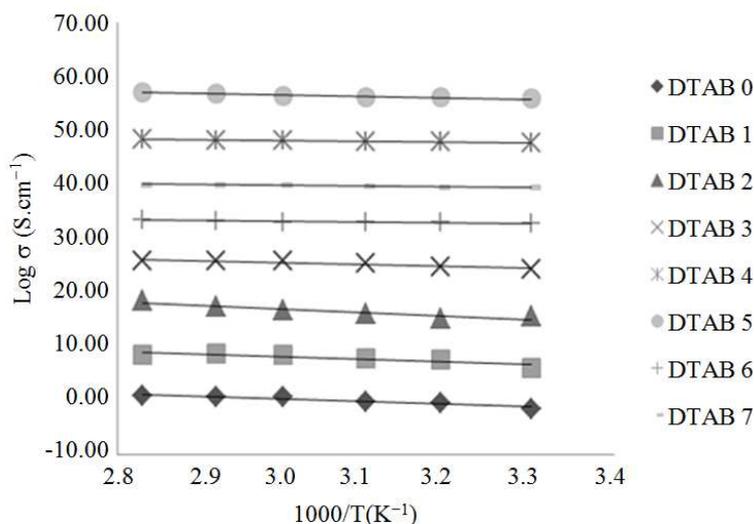


Fig. 2. Temperature dependence of conductivity for SBEs sample at different composition of DTAB (wt.%)

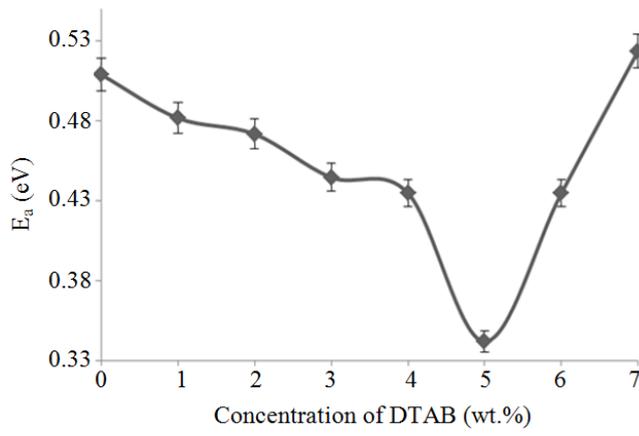


Fig. 3. Activation energy, E_a versus composition of DTAB (wt.%)

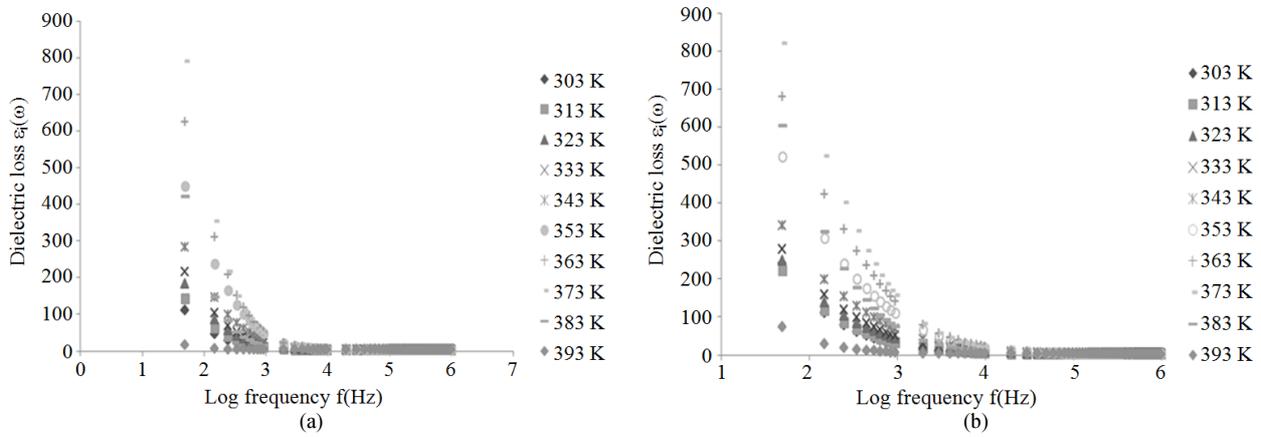


Fig. 4. (a) Dielectric constant versus log frequency for DTAB-5 (b) Dielectric loss versus log frequency for DTAB-5

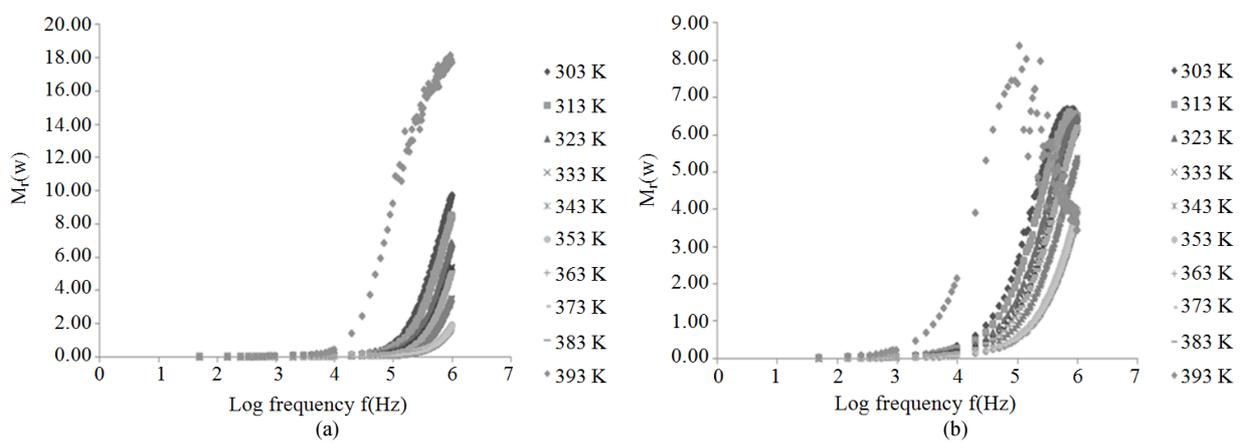


Fig. 5. (a) Real part of electrical modulus versus log frequency for DTAB-5 (b) Imaginary part of an electrical modulus versus log frequency for DTAB-5

Figure 4a and b shows the lowest dielectric constant and dielectric loss in the range of 3 to 6 Hz of DTAB-5. The appreciable relaxation peaks was not found in the range frequency that been used in this study. Both ϵ_r and

ϵ_i have a sharp rise at the low frequencies due to the electrode polarization and space charge effects have occurred and confirming that as non-Debye dependence (Chai and Isa, 2011).

According to Khair and Arof (2010) the polarization that occurs due to the charge accumulation will lead to the decreasing in the value of dielectric loss. The increment of frequency consume will increase the rate of reversal of the electric field. As a result, no time for charge to build up at the interface. The increment of frequency consume will 'increase the rate of reversal of the electric field. As a result, no time for charge to build up at the interface.

Modulus Studies

In the modulus study, the real part of electrical modulus, M_r and imaginary part of electrical modulus, M_i was calculated by using the Equation 5 and 6:

$$M_r(\omega) = \varepsilon_r / (\varepsilon_r^2 + \varepsilon_i^2) \quad (5)$$

$$M_i(\omega) = \varepsilon_i / (\varepsilon_r^2 + \varepsilon_i^2) \quad (6)$$

Figure 5a and b show both M_r and M_i are low and nearest to zero at low frequency but it starts to increase as frequency increased from 3 Hz until 6 Hz with no relaxation peaks. According to (Khair *et al.*, 2006; Hafiza *et al.*, 2014) the appearance of this long tail at low frequencies is perhaps due to the large capacitance applied with the electrodes which confirmed the non-Debye behavior in the SBEs system.

Modulus value will be increase with frequency due to the bulk effect (Carlson *et al.*, 1997). Bulk effect has been discovered by (Gunn, 1963) there are two elements regarding to bulk effect: Transferred by electron and avalanche transit-time. In this research, the bulk effects were because of transferred by electron happen in the systems (Murayama *et al.*, 1974).

Conclusion

Transparent Solid Biopolymer Electrolytes (SBEs) of CMC/CS-DTAB were prepared with no phase separation. The miscible blending of CMC with Chitosan (CS) doped with DTAB has improved the conductivity of the electrolyte from $3.15 \times 10^{-9} \text{ S.cm}^{-1}$ to $1.86 \times 10^{-6} \text{ S.cm}^{-1}$ and this systems show the highest ionic conductivity at room temperature (303 K). The ionic conductivity results as a function of temperature display an Arrhenius rule and the value of activation energy is capsized of conductivity. The dielectric study suggests that samples show non-Debye dependence. The performance of this SBEs system can be improvised by introducing plasticizer to the system.

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Author's Contributions

Nur Yasmin Abu Bakar: Participated in overall experiments from sample preparation until data-analysis and contributed to the writing of the manuscript.

Nur Hafiza Mr. Muhamaruesa: Participated in further data-analysis.

Nur Ain Bashirah Aniskari: Participated in reporting data and eradicate the problem.

Mohd Ikmar Nizam Mohamad Isa: Participated in overall experiments from sample preparation until data-analysis and contributed to the writing of the manuscript.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved.

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