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Potential of Ionic Conductivity and Transport Properties Solid Biopolymer Electrolytes Based Carboxy Methylcellulose/ Chitosan Polymer Blend Doped with Dodecyltrimethyl Ammonium Bromide

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Abstract

The production of an electrolyte via solution casting techniques has been applied in carboxy methylcellulose (CMC)/ chitosan (CS) biopolymer blend doped with different composition of dodecyltrimethyl ammonium bromide(DTAB). Conductivity of the electrolytes at the ambient temperature (303K) containing 5wt. % of DTAB was increased 1.85 x 10^{-6} Scm^{-1}. The Electrical Impedance Spectroscopy (EIS) shows the temperature dependence of ionic conductivity has obeys the Arrhenius Rule where increasing the temperature will increase the conductivity of the electrolytes. The transference number measurement (TNM) shows conductivity of the electrolytes was relate with the ionic mobility, μ and the diffusion coefficient, D of cations and anions in the SBEs systems. The systems show more cationic than anionic conductor reveals that this system is a proton conductor.

Keywords: Polymer blend, dodecyltrimethyl ammonium bromide, carboxy methylcellulose, chitosan, transference number measurement.

Introduction

Solid biopolymer electrolytes (SBEs) are a type of electrolyte that has been targeted to be widely used in batteries because of the low-cost production[1,2], biodegradable properties[3,4] and natural based product compared to commercial batteries thathazardous[5,6]and non-biodegradable[7-10].

In this research, natural biopolymers such as CMC and CS[11-14] have been chose due to its superior properties as a blend biopolymer host and DTABwas chosen as dopant to encourage the enhancement of ionic conductivity in this systems[15,16].

The interaction of biopolymer blend is one of the best techniques to improve the mechanical strength, thermal stability and ionic conductivity of the electrolyte[17,18]. In fact, the miscibility of the blends has been proved that no phase separation between two polymers hence increasing the conductivity[19,20].

This research was focusing on type of proton conducting in the biopolymer blend systems based DTAB dopant. SBEs were characterized by EIS where the conductivity data was obtained including the relation of composition, temperatures and frequency towards blending systems[7]. The ionic mobility and diffusion of systems has been analyzed through TNM.

Material and Methods

Sample Preparation: CMC (Acros Organic Co.) and chitosan (W.A. HamondDrieriteCompany LTD) were dissolved in 1% acetic acid solution (Merck). The CMC/CS was stirred until dissolution complete achieved. Then, different composition of DTAB (Magna Value) in wt. % was added into 1% acetic acid solution and stirred. The CMC/CS solution and DTAB solution were mixed and stirred until homogenous solution were obtained. The mixture solutions were casted into Petri dishes and dried in oven at 60 ºC until SBEs were formed. The SBEs were kept into desiccators (with silica gel) for further drying process and stabilization ion. The designation and composition of SBEs doped with different wt. % DTAB are shown in table 1.

Table-1
Designation and composition of SBEs with different wt. % DTAB

Sample	CMC/ CS (±0.0001g)	DTAB (wt. %)
DTAB – 0	2.0000	0
DTAB – 1		1
DTAB – 2		2
DTAB – 3		3
DTAB – 4		4
DTAB – 5		5
DTAB – 6		6
DTAB – 7		7

Electrical Impedance Spectroscopy (EIS): Electrical Impedance Spectroscopy (EIS) HIOKI 3532-50 LCR Hi-Tester has been used to analyze the conductivity of CMC/CS – DTAB solid biopolymer electrolytes. The electrolytes were cut into a suitable size and placed between the blocking stainless steel electrodes.EISwas interfaced to a computer in the frequency range of 50Hz to 1MHz. 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),

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

where A = area of electrolyte-electrode contact (cm²), t = thickness of the electrolyte (cm) and R_b is the bulk resistance (Ω).

Transference Number Measurement (TNM): The transference number was measured the diffusion of ionic (t_{ion}) or electron (t_e) which brings the conductivity behavior in SBEs phenomena. SBEs were characterized via dc polarization method where the dc current was monitored as a function of time on the application of a fixed dc voltage (1.5 V).

Results and Discussion

Conductivity Studies on CMC/CS – DTAB SBEs: Figure-1 shows the plot of conductivity, σ and activation energy, E_a of SBEs based CMC/CS - DTAB. The highest conductivity of SBEs was found at 5wt. % DTAB of 1.86 x 10^{-6} Scm^{-1}in ambient temperature. It can be seen that the conductivity of the sample increased with the increasing of wt. % of DTAB. The increasing of the concentration of DTAB leads to the increase of dipole-dipole interaction between the proton (H^+) and the channel of CMC/CS – DTAB which can caused the number of mobile ions and its mobility in an optimum state. The activation energy, E_a was found inversely proportional to the conductivity. The lowest Ea value gives the highest conductivity value. According to Nik Aziz et., al[20], the conductivity of SBEs generally linked to the number of ions and the ability of the conducting species in the SBEs complexes. Above 5 wt. % of DTAB, the conductivity starts to decrease gradually due to the disassociation of the ions into neutral aggregate[21]. Thus, it leads to the formation of ion cluster and reduce the number of mobile ions and its mobility[22].

Figure 2 shows the plot of temperature dependence of conductivity obtained at 303K – 353K according to equation (2).

$$\sigma = \sigma_o \exp\left(\frac{-E_a}{kT}\right) \quad (2)$$

$\sigma_o$is the pre – exponential, E_a is the activation energy, T is an absolute temperature and k is the Boltzmann constant. The plot shows the conductivity of SBEs obey the Arrhenius behavior and thermally activated where the regression value, R^2 nearly to 1. The ions jump into the vacant sites of neighbor that caused to increase the ionic conduction in SBEs. Surprisingly, the nature of cations transport is quite similar to that occurring in ionic crystals[19]. The activation energy, $E_a$as listed in equation (2) is important to the ions in order to supply the minimum energy required by the ions to move and pass the barrier[23, 24].It can be seen the conductivity increase as the E_a decrease. The ionic conductivity of SBEs depends on the number of mobile and mobility of ions and can be expressed by the Nernst equation (3).

$$\sigma = nq\mu \quad (3)$$

where$\sigma$is the ionic conductivity, n is the number of mobile ions,μ is mobility of mobile ion and q is the electron charge. It is very important parameters in order to understanding the transport properties of SBEs systems. The number of mobile ions was estimated from Rice and Roth[25] equation (4).

$$\sigma = \left(\frac{2(Ze)^2}{3kTm}\right) nE_a\tau\exp^{(-E_a/kT)} \quad (4)$$

where Z, E_a, m are the valency, activation energy and mass of the conducting ions, respectively, l is mean free path or distance between coordinating[26].

$$l = (\sigma n)^{-1} \quad (5)$$

where$l$ is the mean free path, n is the number of target particles per unit volume and σ is the effective cross sectional area for collision. Mean free path is the average distance travelled by a moving particle such as an atom, a molecule, a photon between successive impacts collisions which modify its direction or energy or other particle properties.

Transference Number Measurement Studies on CMC/CS – DTAB SBEs: Figure 3 shows the normalized polarization current versus time from DTAB – 5 samples which exhibitthe highest conductivity. The initial current was observed to decrease with the increase of time. It will become constant when it completely in depleted situation. According to Samsudinet., al.[26], the cell polarized and the current flow at the steady state caused electron migrates across the systems. The diffusion coefficients mobility of electrode in SBEs system can be calculated from the Nernst – Einstein[25-27]equation of transference number:

The mobility ion, μ and the diffusion coefficient, D can be calculated following equations,

$$t_+ = \frac{D_+}{D_+ + D_-} \quad (6)$$

$$D = D_+ + D_- = \frac{kT\sigma}{ne^2} \quad (7)$$

According to Tan and Arof[27], the ionic mobility can be defined to the equation as follows:

$$\mu = \mu_+ + \mu_- = \frac{\sigma}{nq} \quad (8)$$

$$t_+ = \frac{\mu_+}{\mu_+ + \mu_-} \quad (9)$$

Where μ_+ is the ionic mobility of cations and μ_- is the ionic mobility of anions. Table 2, shows selected ionic mobility and diffusion coefficient of cations and anions in the SBEs systems. The value of cations of μ_+ and D_+ was revealed to be greater than anions. The interaction relates to the conductivity principle that proves the system is more cationic than anionic conductor[21, 28,29]. Hence, it reveals that CMC/CS – DTAB SBEs systems is a proton conductor.

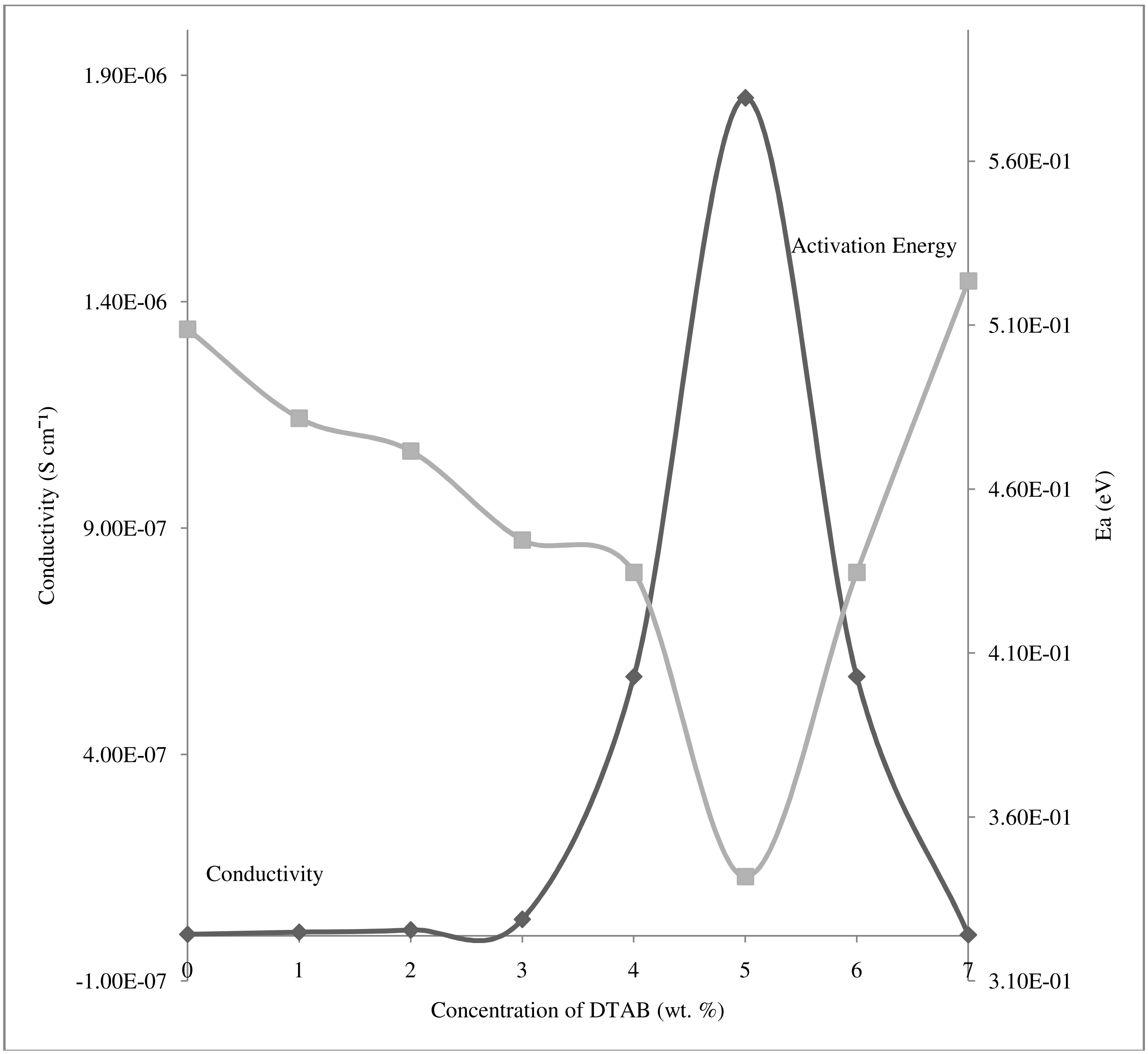

Figure-1
Plots of conductivity and activation energy vs. concentration of DTAB at ambient temperature (303K)

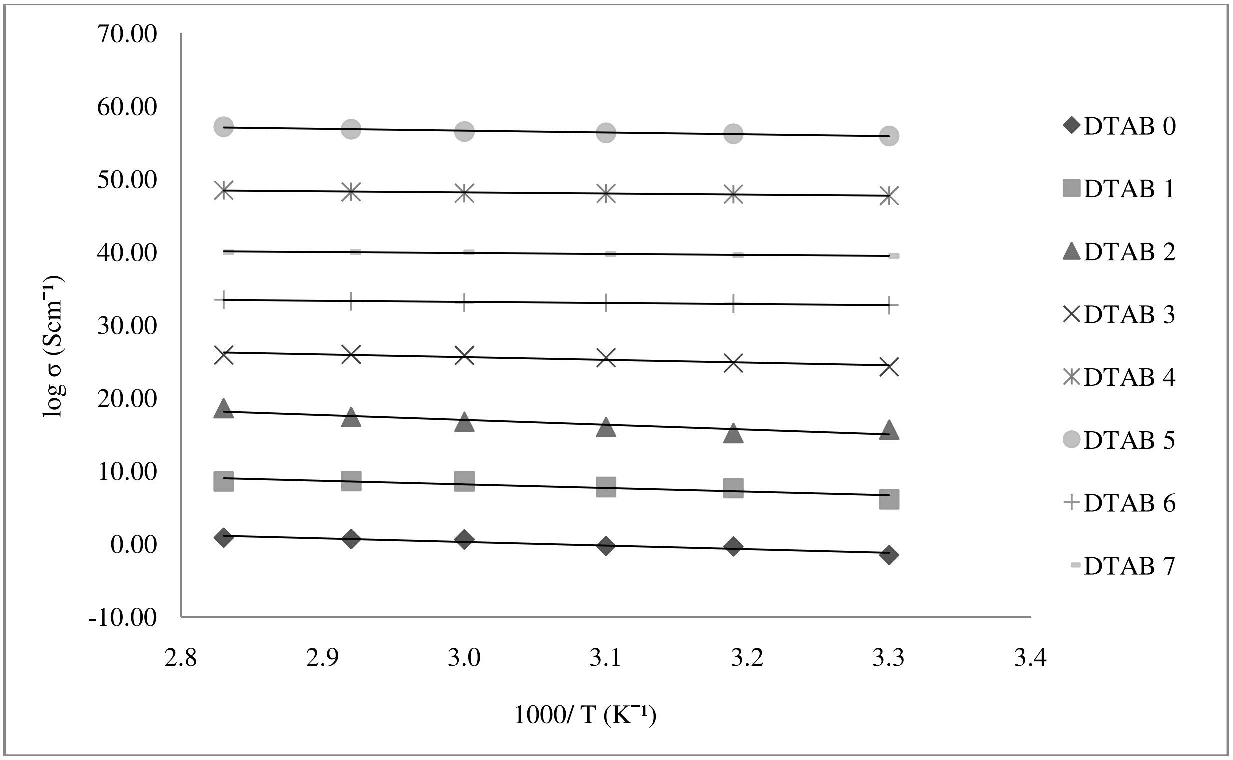

Figure-2
Temperature dependence of the ionic conductivity

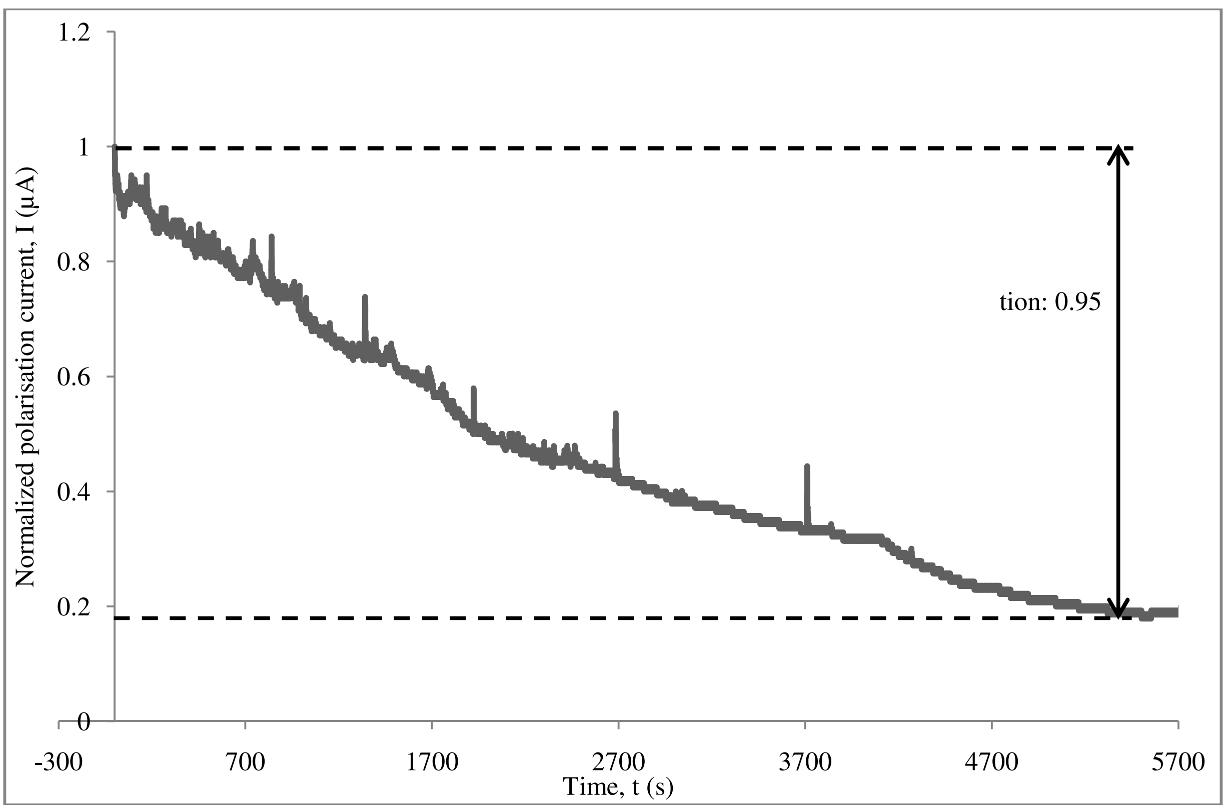

Figure-3
Normalized polarization current vs. time for DTAB - 5 samples

Table-2
Ionic mobility and diffusion coefficient of cations and anions on selected sample

Sample	tion	$\mu_+ \times 10^{-10}$ ($cm^2 V^{-1} s^{-1}$)	$\mu_- \times 10^{-10}$ ($cm^2 V^{-1} s^{-1}$)	$D_+ \times 10^{-11}$ ($cm^2 s^{-1}$)	$D_- \times 10^{-11}$ ($cm^2 s^{-1}$)
DTAB-1	0.94	196	12.7	0.004400	0.000286
DTAB-3	0.81	801	42.4	0.018100	0.000955
DTAB-5	0.95	302	72.1	0.680000	0.162000

Conclusion

Solid biopolymer electrolytes (SBEs) systems based on CMC/CS – DTAB have been prepared using solution casting techniques. The increment composition of DTAB has been found can influence the conductivity of the system where the ionic conduction value is1.86 x 10^{-6} $S.cm^{-1}$ at 5 wt. % has been obtained from the systems. Besides, it also increases the mobility and diffusion coefficient of ions. The proven has been shown in TNM studies where the charge transports in SBEs predominantly due to protons where the value of cations μ_+ and D_+ is found to be higher than the value of $\mu_-$and D_-.

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