



# Journal of Applied Sciences

ISSN 1812-5654

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## Structural and Ionic Transport Study on CMC Doped NH<sub>4</sub>Br: A New Types of Biopolymer Electrolytes

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**Abstract:** The development of new solid Biopolymer Electrolyte (BEs) system based on Carboxy Methylcellulose (CMC) is creating opportunity for new types of electrochemical devices which may themselves, in turn, revolutionize many industrial areas. Biodegradable CMC doped with ammonium bromide (NH<sub>4</sub>Br) as BEs were prepared via solution-casting method. The polymer-salt complexes have been analyzed through FTIR spectroscopy, XRD measurement and impedance measurement. The sample contains 25 wt.% NH<sub>4</sub>Br exhibited the highest room temperature conductivity of  $1.12 \times 10^{-4} \text{ Scm}^{-1}$ . Small Polaron Hopping (SPH) model has been found to be most appropriate for fitting the experimental conductivity data.

**Key words:** Solid biopolymer electrolyte, FTIR, ionic conductivity, small polaron hopping

### INTRODUCTION

Polymer Electrolytes (PEs) have attracted much attention due to potential applications in electrochemical devices (Mika *et al.*, 2007; Bozkurt and Meyer, 2001). Many aspects of PEs can be investigated such as ionic conductivity, nature of films and vibrational properties of functional groups. There are several advantages have been discovered on PEs. The main advantages of the PEs are their good mechanical properties, ease of fabrication into thin films of desirable sizes and the ability to form good electrode/electrolyte contact (Armand, 1994; Hashmi *et al.*, 1990). The polymers have been complexed with various salts which provide the ions for conduction. Ammonium salts have already been reported as a good proton donor to the polymer matrix (Stainer *et al.*, 1984; Daniela *et al.*, 1988).

One promising aspirant to act as polymer host for bio-PEs is Carboxy Methylcellulose (CMC). Recently, due to the good biocompatibility and biodegradable, CMC attracted more attentions as representative water-soluble polysaccharide in many research fields (Barbucci *et al.*, 2000; Kulkarni and Sa, 2008; Marci *et al.*, 2006). To the best of our knowledge, there has been no previous study of biopolymer electrolyte based on CMC. The present work aims on developing new type of biopolymer electrolyte with CMC as the host polymer. Ammonium bromide (NH<sub>4</sub>Br) has been chosen as the dopant since ammonium salts are considered as a good proton donor to the polymer matrix (Kumar and Sekhon, 2002). The

prepared polymer electrolytes have been characterized by Fourier Transform Infrared (FTIR), X-ray diffraction (XRD) and by impedance spectroscopic techniques.

### MATERIALS AND METHODS

**Sample preparation:** Two grams of CMC obtained from Acros Organic Co. was dissolved in distilled water. Then, varied amount of NH<sub>4</sub>Br in weight percent (5-35 wt.%) was added. The mixture was stirred continuously until complete dissolution of the NH<sub>4</sub>Br. The mixture was then poured into different Petri dishes and left dried at room temperature for the film to form. The films were kept in desiccators for about 1 month before being characterized to ensure no water present in the BEs system. The CMC-BEs were cut into suitable sizes for further analysis.

**FTIR spectroscopy:** FTIR spectroscopy measurement was carried out using Thermo Nicolet 380 FTIR spectrometer. The spectrometer was equipped with an Attenuated Total Reflection (ATR) accessory with a germanium crystal. The sample was put on germanium crystal and infrared light was passed through the sample with the frequency ranging from 4000 to 675 cm<sup>-1</sup> with spectra resolution of 4 cm<sup>-1</sup>.

**X-ray diffraction:** To study the nature of the BEs system, the X-ray diffraction (XRD) measurements were performed using Rigaku MiniFlex 2. Prior, samples were

cut into suitable sizes (2×2 cm) and then adhered onto a glass slide. The glass slide was then placed at the sample holder of the diffractometer and the samples were directly scanned at 2θ angles between 5 and 80° with X-rays of 1.5406 Å wavelength generated by a Cu Kα source.

**Impedance spectroscopy:** The polymer electrolyte samples were cut into small discs of 2 cm diameter and sandwiched between two stainless steel electrolytes under spring pressure. The samples were characterized via Electrical Impedance Spectroscopy (EIS) using HIOKI 3532-50 LCR Hi-Tester interfaced to a computer in a frequency range between 50 Hz and 1 MHz. The measurements were carried out at room temperature of 303 until 383K. The conductivity of electrolyte can be calculated from the equation:

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

Here, A (cm<sup>2</sup>) is the electrode-electrolyte contact area of the film and t its thickness. R<sub>b</sub> is bulk resistance obtained from the complex impedance plot at the intersection of the plot and the real impedance axis.

## RESULTS AND DISCUSSION

**FTIR spectroscopic analysis:** Figure 1 shows the spectra of CMC-NH<sub>4</sub>Br complexes in the region from 1200 to 1700<sup>-1</sup>. In the present work, the band at 1592 cm<sup>-1</sup> is assigned to asymmetrical COO<sup>-</sup> stretching of the carboxylate anion in the CMC (Pushpamalar *et al.*, 2006). With the addition of AB in the system, this peak is expected to be affected due to the lone pair electrons will attract the salt molecules to be attached to it. Upon addition of AB salt, the gap for 1592 cm<sup>-1</sup> due to COO<sup>-</sup> is observed to decrease up to 35 cm<sup>-1</sup>. In ammonium bromide, the hydrogen bonding occurs with the N-H bond within the tetrahedral ion, NH<sub>4</sub><sup>+</sup>, pointing directly toward the bromide ion, Br<sup>-</sup> and forming an N-H...Br hydrogen bond (Reed and Williams, 2006). Two of the four hydrogens of NH<sub>4</sub><sup>+</sup> ions are bound identically, one hydrogen is bound more rigidly and the fourth more weakly. The weakly bound H of NH<sub>4</sub><sup>+</sup> can easily be dissociated under the influence of a dc electric field (Hema *et al.*, 2008). These H<sup>+</sup> ions can hop via each coordinating site (oxygen) at the band 1592 cm<sup>-1</sup> of the host polymer (CMC) and thus conduction takes place. The conduction occurs through structure diffusion (Grotthus mechanism), i.e., the conduction occurs through the exchange of ions between complexed sites (Hashmi *et al.*, 1990). Hence from FTIR

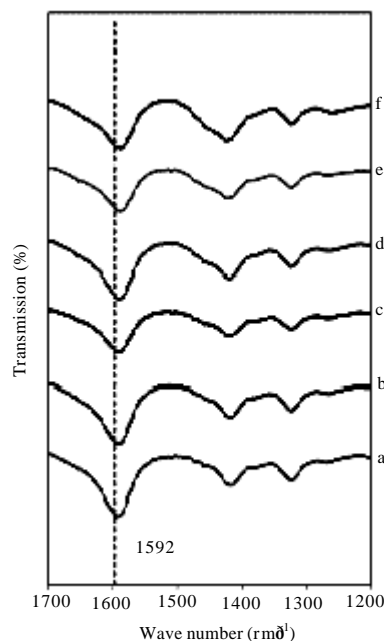


Fig. 1: FTIR spectra of (a) pure CMC film (b) 5 wt.% NH<sub>4</sub>Br (c) 10 wt.% NH<sub>4</sub>Br (d) 15 wt.% NH<sub>4</sub>Br (e) 20 wt.% NH<sub>4</sub>Br and (f) 25 wt.% NH<sub>4</sub>Br

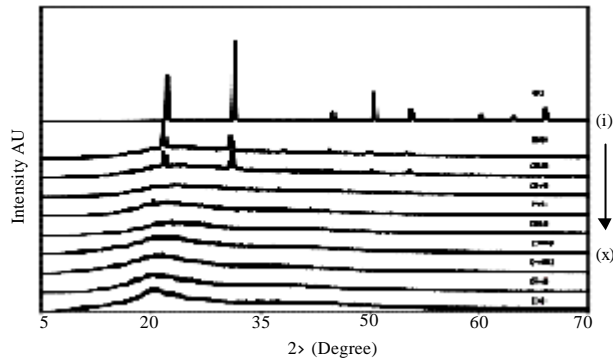
spectroscopy the interaction between CMC and NH<sub>4</sub>Br has been confirmed and the conduction mechanism in the polymer electrolytes has been well established.

Figure 2 shows the XRD patterns for the various electrolyte films. It can be inferred from the X-ray diffractograms, the amorphousness of the polymer electrolyte decreased after addition of more than 25 wt.% NH<sub>4</sub>Br. Conductivity increases with the increase in amorphous domain of the sample (Shuhaimi *et al.*, 2010). It can be predicted that the sample containing 25 wt.% salt exhibits the highest conductivity at room temperature. However, with increment of salt composition above 25 wt.%, new peaks at 2θ = 22.25 and 31.20° corresponding to the undissociated salt have been observed and the sample has become more crystalline. Changes in amorphousness of the CMC-NH<sub>4</sub>Br BEs system contribute to the change of conductivity of the samples. This amorphous nature is responsible for greater ionic diffusivity resulting in high ionic conductivity (Shuhaimi *et al.*, 2010; Balasubramanyam *et al.*, 2007). This observation confirms that complexation has taken place in the amorphous phase.

**Impedance studies:** The conductivity of the CMC-NH<sub>4</sub>Br based BEs system at room temperature is tabulated in Table 1. It can be observed that the ionic conductivity of

**Table 1:** Transport parameters of the CMC-NH<sub>4</sub>Br biopolymer electrolytes at room temperature

NH <sub>4</sub> Br (wt.%)	$\sigma$ (Scm <sup>-1</sup> ) ( $\times 10^{-3}$ )	$\tau$ (s) ( $\times 10^{-22}$ )	$\eta$ (cm <sup>3</sup> )	$\mu$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ) ( $\times 10^{-16}$ )	D (cm <sup>2</sup> s <sup>-1</sup> ) ( $\times 10^{-18}$ )	E <sub>a</sub> (eV)
0	0.00126	0.862	5.66 $\times 10^{27}$	0.139	0.363	0.24
5	0.00211	0.898	6.40 $\times 10^{27}$	0.206	0.538	0.23
10	0.01310	0.908	3.30 $\times 10^{28}$	0.248	0.649	0.22
15	0.15100	0.930	2.62 $\times 10^{29}$	0.361	0.942	0.21
20	1.01000	0.967	9.69 $\times 10^{29}$	0.651	1.700	0.20
25	11.2000	1.160	1.47 $\times 10^{30}$	4.770	12.50	0.14
30	6.53000	1.100	1.27 $\times 10^{30}$	3.210	8.380	0.16
35	1.97000	1.010	9.97 $\times 10^{29}$	1.240	3.230	0.18



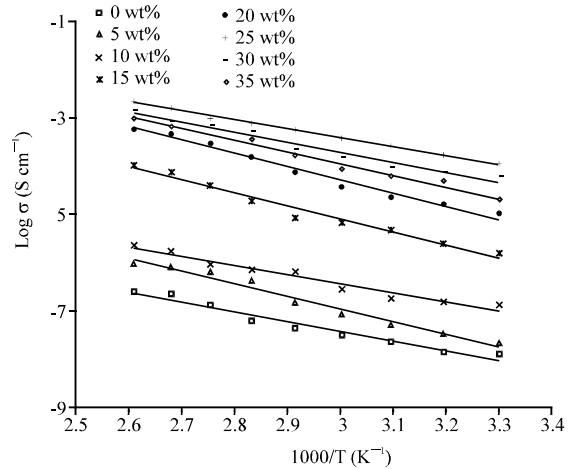
**Fig. 2:** XRD patterns for (i) pure NH<sub>4</sub>Br, (ii) CMC-35 wt.% NH<sub>4</sub>Br, (iii) CMC-30 wt.% NH<sub>4</sub>Br, (iv) CMC-25 wt.% NH<sub>4</sub>Br, (v) CMC-20 wt.% NH<sub>4</sub>Br, (vi) CMC-15 wt.% NH<sub>4</sub>Br, (vii) CMC-10 wt.% NH<sub>4</sub>Br, (viii) CMC-5 wt.% NH<sub>4</sub>Br, (xi) pure CMC film and (x) CMC powder

the sample increases with addition of salt content. The highest conductivity is  $1.12 \times 10^{-4}$  Scm<sup>-1</sup> for the sample containing 25 wt.% NH<sub>4</sub>Br. Above 25 wt.% NH<sub>4</sub>Br the conductivity decreases and can be attributed to the reassociation of the ions into neutral aggregates (Schantz and Torell, 1993; Teeters *et al.*, 1996) and also the excess salt recrystallized out of the polymer as previously proven by XRD result in Fig. 2.

The log  $\sigma$  versus 1000/T plot for the CMC-NH<sub>4</sub>Br systems shown in Fig. 3 confirms that the ionic conductivity of the biopolymer electrolyte increase with increasing temperature for all compositions. Since all polymer complexes do not show any abrupt jump with temperature, it indicates that these electrolytes exhibit a completely amorphous structure (Rajendran and Uma, 2000). The regression values are close to unity, ( $R^2 = 1$ ) suggesting that the temperature-dependent ionic conductivity for all complexes obeys Arrhenius behavior (Micheal *et al.*, 1997) by the relation,

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad (2)$$

where,  $\sigma_0$  is the pre-exponential factor,  $E_a$  the activation energy and  $k$  is the boltzman constant.



**Fig. 3:** Temperature dependence of ionic conductivity

The activation energy (combination of the energy of defect formation and the energy for migration of ion) listed in Table 1 was calculated by linear fit of the Arrhenius plot. It shows that  $E_a$  for the conduction decreased gradually with the increase in the salt content implying that the ions in highly conducting samples require lower energy for migration. In the situation of biopolymer electrolyte, when the ion has acquired enough energy, it is able to split away from the donor site and travel to another donor site. The movement from one site to another result in the conduction of charge and the energy for this conduction is the  $E_a$  (Buraidah *et al.*, 2009). Thus, in order to analyze quantitatively the conductivity trend observed, the number of free ions,  $\eta$  has been calculated based on the Rice and Roth model (Rice and Roth, 1972). Knowing  $\eta$  and combining the result with conductivity, the mobility of the ionic charge carrier,  $\mu$  can then be determined. Table 1 lists the transport parameters at room temperature for complexes of CMC-NH<sub>4</sub>Br BEs system.

Table 1 depict the values of number density of mobile ions,  $\eta$ , ionic mobility,  $\mu$  and the diffusion coefficient,  $D$ . The transport parameters were found to be related to the conductivity of the samples. It can be explained that as the conductivity increase, the  $E_a$  as mentioned before require lower energy to move the ion

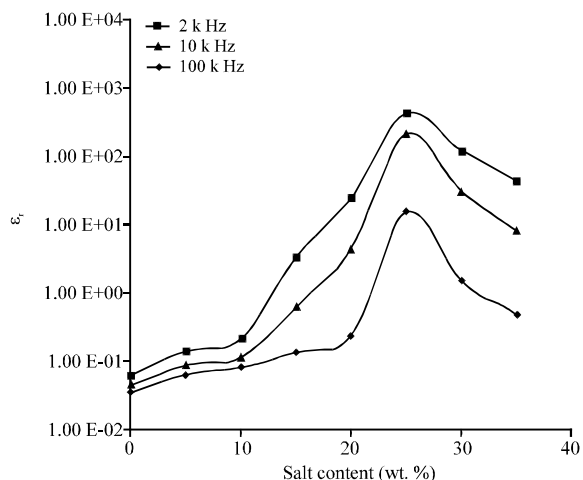


Fig. 4: Salt content dependence of dielectric constant  $\epsilon_r$  at selected frequencies

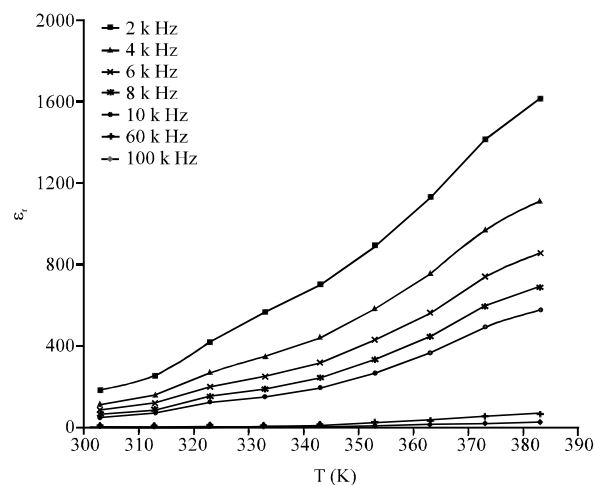


Fig. 5: Temperature dependence of dielectric constant  $\epsilon_r$  for sample containing 25 wt.%  $\text{NH}_4\text{Br}$  at selected frequencies

due to increasing of  $\eta$ ,  $\mu$  and  $D$  in this BEs system. The mechanism of transport parameter can be more describe in dielectric studies.

**Dielectric studies:** The dielectric constant is representative for the stored charge in a material. In polymer electrolytes, the charge carriers are ions. The dielectric constant (the real part of complex permittivity,  $\epsilon_r$ ) is given by:

$$\epsilon_r = \frac{Z_i}{\omega C_0 (z_i^2 + z_i^2)} \quad (3)$$

Here,  $C_0 = \epsilon_0 A/t$  and  $\omega = 2\pi f$ .  $\epsilon_0$  is permittivity of free space,  $Z_i$  and  $Z_r$  is the imaginary and real parts of the complex permittivity and  $f$  is frequency. The salt content dependence of the dielectric constant ( $\epsilon_r$ ) at selected frequencies is shown in Fig. 4. It can be observed that the  $\epsilon_r$  increase with increment of salt content for every frequency until after 25 wt.%  $\text{NH}_4\text{Br}$  when the value of  $\epsilon_r$  drops. This implies that, as the salt content increase, the stored charge in the sample rise which means that the number density of mobile ions has increased. Decrement in dielectric constant at 30 wt.%  $\text{NH}_4\text{Br}$  is due to decrement in density of charge carriers which is attributed to the reassociation of ions. Results shown in Fig. 5 imply that the phenomenon of polarization rise with temperature in this system. As temperature increases, the degree of salt dissociation an redissociation of ion aggregates start to grow resulting in the increase in number of charge carrier density.

**Frequency dependence AC conductivity:** The ac conductivity can be obtained from dielectric loss,  $\epsilon_i$  at every frequency according to:

$$\sigma_{ac} = \epsilon_0 \epsilon_i \omega \quad (4)$$

The phenomenon of ac conductivity can be analyzed using Jonscher's Universal Power Law (UPL) (Winie and Arof, 2004).

$$\sigma(\omega) = \sigma_{dc} + A\omega^s \quad (5)$$

$$\sigma_{ac} = A\omega^s \quad (6)$$

Here,  $\sigma(\omega)$  is the total dc and ac conductivity. The dc conductivity,  $\sigma_{dc}$  is the frequency independent component,  $A$  is a parameter dependent on temperature and  $s$  is the power law exponent with value in the range between 0 and 1. From Eq. 4 and 6:

$$\ln \epsilon_i = \frac{\ln A}{\epsilon_0 + (s-1) \ln \omega} \quad (7)$$

Where:

$$\epsilon_i = \frac{Z_i}{\omega C_0 (Z_i^2 + Z_r^2)} \quad (8)$$

Figure 6 depicts the frequency dependence of dielectric loss,  $\epsilon_i$  at selected temperatures for higher conductivity. Form the plot, the value of exponent  $s$  can be obtained from the slope at the higher frequency region where there is no or minimal space charge polarization

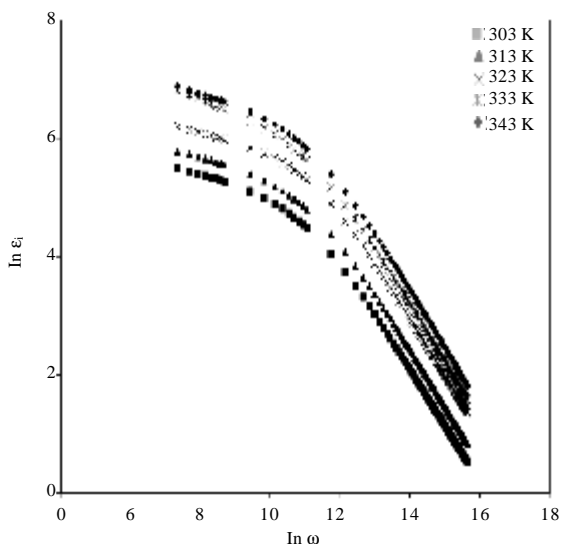


Fig. 6:  $\ln \epsilon_1$  versus  $\ln \omega$  at elevated temperatures

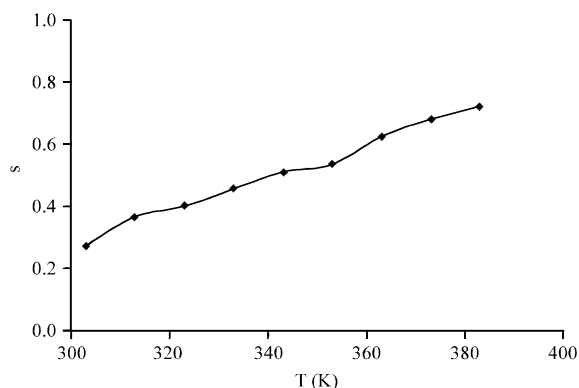


Fig. 7: Variation of exponent  $s$  versus temperature

(Buraidah *et al.*, 2009). The variation of  $s$  with temperature for biopolymer electrolyte system is plotted in Fig. 7.

From Fig. 7, it can be observed that  $s$  increase with increasing temperature. Thus, the frequency dependence of sample can be explained in terms of Small Polaron Hopping (SPH) model due to the variation of the index  $s$  with temperature (Mott and Davis, 1979). In this model, a small polaron is formed by the addition of a charge carrier to a site which results in large degree of local lattice distortion.

### CONCLUSION

The development of new solid biopolymer electrolytes based on CMC doped with  $\text{NH}_4\text{Br}$  has been prepared by solution cast technique. FTIR spectroscopy

provides an insight into the possible interaction between CMC and  $\text{NH}_4\text{Br}$  which confirm via Grotthuss mechanism and the ionic species in the polymer electrolytes has been well established as a proton conductor ( $\text{H}^+$ ). XRD measurements confirmed that the BEs system predominantly amorphous in nature. The highest conductivity obtained was  $1.12 \times 10^{-4} \text{ cm}^{-1}$  at room temperature. The temperature dependence of ionic conductivity of the BEs system exhibits Arrhenius behavior where the samples conductivity exclusively affected by the temperature and composition of  $\text{NH}_4\text{Br}$ . From the calculations carried out, it can be inferred that the conductivity is governed by the number density of ions, mobility of ions and diffusion coefficient. The conduction mechanism studies shown the biopolymer electrolyte can be best represented by the SPH model.

### ACKNOWLEDGMENT

The authors would like to thank MOHE for the FRGS Vot59185, Faculty Sciences and Technology and University Malaysia Terengganu for the technical and research support.

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