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Research Article

### Structural and Conduction Studies of Solid Biopolymer Electrolytes System Based on Carboxymethyl Cellulose

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#### ABSTRACT

This present work discovered on a new proton conducting solid biopolymer electrolytes (SBE) based on biopolymer-carboxymethyl cellulose (CMC) complexed with various concentrations of ammonium thiocyanate (NH<sub>4</sub>SCN). In the polymer-salt complexes system has been prepared via solution-casting method. The ionic conductivity study of the samples was measured using Electrical Impedance Spectroscopy (EIS) and the highest ionic conductivity at room temperature was obtained at  $6.48 \times 10^{-5} \text{ Scm}^{-1}$  for the sample containing with 25 wt.% NH<sub>4</sub>SCN. The temperature dependence of ionic conductivity of the CMC-NH<sub>4</sub>SCN SBE system follow Arrhenius law due to increases of conductivity with increment of NH<sub>4</sub>SCN concentrations. Fourier Transform Infrared (FTIR) spectroscopy was done to study the complexation between CMC and NH<sub>4</sub>SCN. X-ray diffraction study inferred that the samples containing 25 wt.% NH<sub>4</sub>SCN exhibits highest amorphous nature which revealed that highest conductivity in CMC-NH<sub>4</sub>SCN SBE system.

**Keywords:** Solid Biopolymer Electrolytes (SBE); Carboxymethyl Cellulose (CMC); Ammonium Thiocyanate (NH<sub>4</sub>SCN); ionic conductivity

#### INTRODUCTION

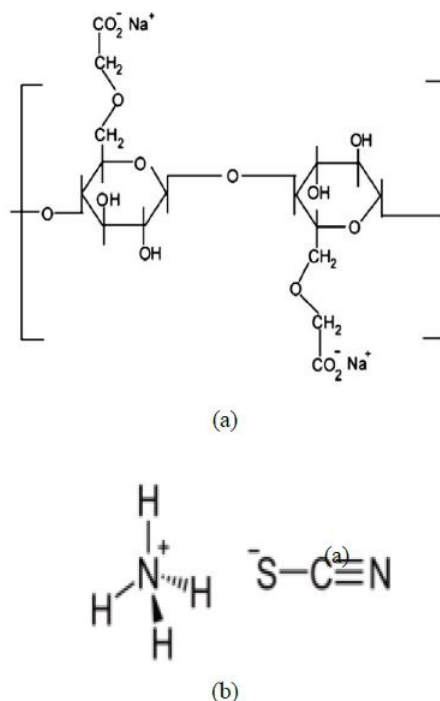
Solid polymer electrolytes with high ionic conductivity have attracted a great deal of researchers and academicians in recent years due to practical importance for the development of solid-state rechargeable batteries, electrochromic display devices and other applications [1]. The most important advantages of polymer electrolytes are favourable mechanical properties, easy of fabrication of thin films of desirable sizes, wide range of composition and hence control of properties, enhanced chemical compatibility and ability to form effective electrode electrolyte contacts [2]. The use of environmental friendly materials as SPE can help

to solve environmental issues. As a result, many effort has been made to develop biopolymer electrolytes by using natural polymer due to their biodegradation properties, richness in nature and low cost [3]. Various renewable resource based natural polymers are suitable to be used as a host polymer in the SPE such as starch, cellulose, chitosan, carrageenan, pectin, chitin, lignocellulosic materials, hyaluronic acid, agarose, polylactides, soy-based plastics, polyhydroxyalkanoates (bacterial polyesters) and so on [4]. Among all the biodegradable polymer materials, carboxymethyl cellulose (CMC) shows superior candidate as a host polymer. CMC was chosen as host polymer due to its superior characteristics, such as being most abundant

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organic substance on the earth, renewable, no toxicity, biocompatible, biodegradable, high hydrophilicity, good film forming ability and cost effective [5,6]. Moreover, it exhibits excellent mechanical and electrical properties [7]. CMC is one of the cellulose or cellulose derivatives has no dangerous effects on human health and is used as highly effective additive to improve the product quality and processing properties in various fields of application such as foodstuffs, cosmetics and pharmaceuticals to products for the paper and textile industries [8]. CMC as shown in Figure 1 contains a hydrophobic polysaccharide backbone and many hydrophilic carboxyl groups, and consequently shows amphiphilic characteristics. The substitution of CH<sub>2</sub>-COONa group is inhomogeneous in both substituted position and degree will increases the

complexity of hydrogen bonds [9]. Consequently, to improve the ionic conductivity of the SPE, the addition of organic or inorganic salt is very significant. Several reported that proton-conducting polymer electrolytes are complexes with strong inorganic acid such as H<sub>3</sub>PO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HCl or ammonium salts such as NH<sub>4</sub>Br, NH<sub>4</sub>SO<sub>4</sub>, NH<sub>4</sub>I and NH<sub>4</sub>ClO with commercially available electron donor polymer such as PEO, PVA, PAA and PEI. However, proton-conducting polymer complexes with inorganic acids suffer from chemical degradation and mechanical integrity making them unsuitable for practical applications [10]. In this present study, NH<sub>4</sub>SCN has been chosen as the dopant salt since ammonium salts are considered as the excellent proton donor to the polymer matrix [11].



**Fig. 1:** The chemical structure of (a) CMC reported by A.S. Samsuddin et al., (b) NH<sub>4</sub>SCN reported by H.J. Woo *et al.*

## 2. Objectives:

The present research aim is to develop the new solid biopolymer electrolyte based on carboxymethyl cellulose (CMC) as the host natural polymer and ammonium thiocyanate (NH<sub>4</sub>SCN) as dopant salt. The prepared samples were characterized by EIS, FTIR and XRD to investigate the effect of NH<sub>4</sub>SCN concentrations on ionic conductivity and structural of CMC-NH<sub>4</sub>SCN SBE system.

## Materials and Methods

### 3.1 Materials:

In this research, CMC was obtained from Acros Organic Co. with molecular weight,  $M_w = 90\,000$  g/mol and viscosity = 400 cp was employed as host

polymer. NH<sub>4</sub>SCN obtained from Merck Co. with  $M_w = 76.11$  g/mol was used as ionic dopant. The proton conducting SBE consisting of CMC complexed with various concentrations of NH<sub>4</sub>SCN had been done via solution casting technique.

### 3.1 Preparation of solid biopolymer electrolytes:

In order to prepare the CMC-NH<sub>4</sub>SCN SBE system films, 2g of CMC was dissolved in 100 ml of distilled water and was stirred until the CMC was completely dissolved. Then, various concentrations of NH<sub>4</sub>SCN were added into CMC solutions and stirred continuously until became homogeneous solutions. The mixtures were poured in different glass petri dishes and left dry at room temperature for drying process until CMC-NH<sub>4</sub>SCN SBE films form.

In order to prevent water content, the films were kept in dessicators for further drying to confirm no presence of water.

### 3.3 Characterization:

#### 3.3.1 EIS spectroscopy:

EIS equipped with HIOKI 3525-50 LCR Hi-Tester was used to measure ionic conductivity of CMC-NH<sub>4</sub>SCN SBE system in the frequency range from 50 Hz to 1 MHz at room temperature (303 K) until 353 K. The films were cut into suitable size and sandwiched between two stainless steel electrode under spring pressure. The diameter of the stainless steel electrode is 2 cm. The conductivity of CMC-NH<sub>4</sub>SCN SBE system were calculated using equation:

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

Here,  $\sigma$  (Scm<sup>-1</sup>) is conductivity,  $t$  (cm) is thickness of the electrolyte film,  $A$  (cm<sup>2</sup>) is the area of surface contact and  $R_b$  ( $\Omega$ ) is the bulk resistance. The bulk resistance,  $R_b$  was obtained from the Cole-Cole plot at the low frequency side at the intersection of the plot the imaginary impedance and the real impedance axis.

#### 3.3.2 FTIR spectroscopy:

Fourier Transform Infrared (FTIR) spectroscopy was carried out using Thermo Nicolet Avatar 380 FTIR spectrometer to study the interaction and complexation in the CMC-NH<sub>4</sub>SCN SBE system. The spectrometer was equipped with an attenuated total reflection (ATR) accessory with a germanium crystal. The films was put on a germanium crystal and infrared light through the sample in frequency range from 4000 to 700 cm<sup>-1</sup> with spectra resolution of 4 cm<sup>-1</sup>.

#### 3.3.3 X-ray diffraction:

X-ray diffraction (XRD) measurement model with Rigaku Mini Flex II diffractometer prepared with an X<sup>c</sup>elerator, to study the nature of the CMC-NH<sub>4</sub>SCN SBE system. The films were cut into a suitable size and put onto glass slide. Then, the glass slide was placed in the sample holder of the diffractometer and the films were directly scanned at  $2\theta = 5^\circ$  until  $80^\circ$  with X-rays of  $1.5406\text{\AA}$  wavelength generated by CuK $\alpha$  source.

## Results and Discussion

### 4.1 Conductivity analysis:

The ionic conductivity depends on some factors such as ionic conducting species concentration, cationic or anionic types of charge carriers, the charge carriers mobility and the temperature [12,13]. Table 1 presents the ionic conductivity at room temperature of CMC-NH<sub>4</sub>SCN SBE system as a function of the NH<sub>4</sub>SCN concentrations. It can be observed that the ionic conductivity of the sample increases with increment of the salt concentration until a optimum is reached at 25 wt.% of NH<sub>4</sub>SCN. The dependence of ionic conductivity with NH<sub>4</sub>SCN concentration provides information on the specific interaction between the polymer matrix and the dopant salt. According to Nik Aziz N.A. et al., enhancement in ionic conductivity with increasing salt concentration can be associated to the increase in the number of mobile charge carriers and the interaction between NH<sub>4</sub><sup>+</sup> ion with carboxyl group bring to high dispersion of H<sup>+</sup> that increases the conductivity of the CMC-NH<sub>4</sub>SCN SBE system [14].

**Table 1:** Ionic conductivity for CMC-NH<sub>4</sub>SCN SBE system at room temperature.

Sample	Salt concentration (wt.%)	Conductivity, $\sigma$ (Scm <sup>-1</sup> )	Standard deviation
AT-0	0	$9.41 \times 10^{-8}$	$1.38 \times 10^{-9}$
AT-5	5	$3.21 \times 10^{-7}$	$2.01 \times 10^{-9}$
AT-10	10	$1.30 \times 10^{-6}$	$9.02 \times 10^{-9}$
AT-15	15	$3.80 \times 10^{-6}$	$4.00 \times 10^{-8}$
AT-20	20	$1.04 \times 10^{-5}$	$1.78 \times 10^{-7}$
AT-25	25	$6.48 \times 10^{-5}$	$1.47 \times 10^{-6}$

The temperature-dependent of ionic conductivity measurements are carried out to analyze the mechanism of ionic conduction in CMC-NH<sub>4</sub>SCN SBE system. Figure 2 presents the Arrhenius plots of CMC-NH<sub>4</sub>SCN SBE system in the temperature range of 303-353 K. The regression values of all samples are close to unity where  $R^2 \approx 1$ , indicating that the temperature-dependent ionic conducting for this CMC-NH<sub>4</sub>SCN SBE system obeys Arrhenius law, suggesting that conductivity is thermally assisted [15].

According to Arrhenius behavior, the nature of cation transport can be deduced to be similar to that

in ionic crystals, where ions jump into neighbouring vacant sites [16]. From Figure 3, it can be observed that the conductivity increases as the temperature increases. An increase in ionic conductivity with temperature may be interpreted as a hopping mechanism between coordinating sites together with local structural relaxations and segmental motions of the polymer salt complexes. As the temperature increases the polymer chain hopping and intra-chain ion movements, which the conductivity of electrolyte will increase [17].

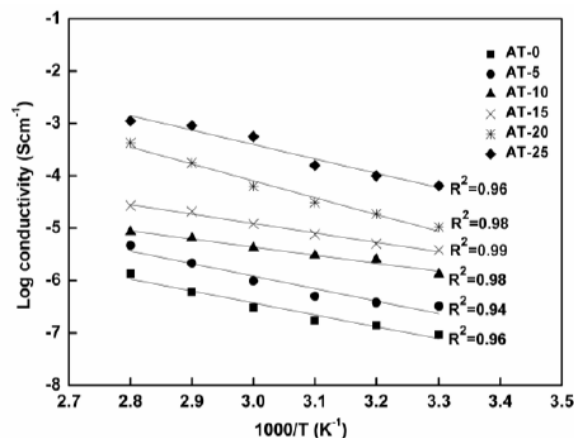


Fig. 2: Arrhenius plot of CMC-NH4SCN SBE system at temperature range 303 K to 353 K.

From the slope of the graph in Figure 3, the activation energy,  $E_a$  of CMC-NH4SCN SBE system can be calculated using Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \tag{2}$$

where  $\sigma_0$  is the pre exponential factor,  $k$  is the Boltzmann constant and  $T$  is the temperature. Activation energy is the energy required for an ion to initiate movement. When the ion has acquired sufficient energy, it is able to break away from the donor site and move to another donor site [18]. Figure 3 presents the activation energy versus NH4SCN concentration. It can be shown that the activation energy decreases with enhancement

NH4SCN concentration. According to the Anderson-Stuart model, the activation energy is the sum of the binding energy of the ion to its site and the kinetics energy for migration [19]. If the energy of the ion to its site and the kinetic energy for migration. If the energy of the ion is only sufficient to overcome the binding energy, then it will be dislocated from its site but will still be at the same location. Only if it has more energy than this binding energy will it be a free ion. It can be observed that  $E_a$  decreases as conductivity of sample increases implying that the ions in highly conducting samples require lower energy for migration.

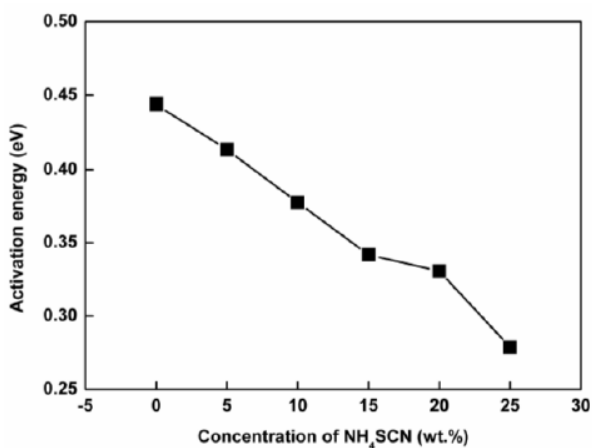


Fig. 3: Variation of activation energy,  $E_a$  as a function of concentration of NH4SCN.

4.2 FTIR analysis:

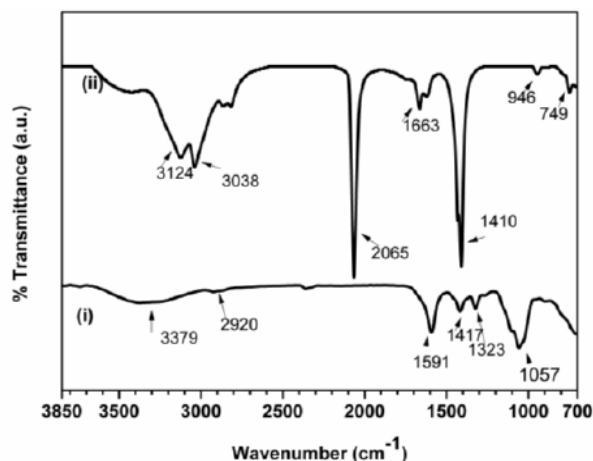
FTIR spectroscopy has been done to study the interactions between polymer and ionic dopant in CMC-NH4SCN SBE system. Figure 4 depicts the FTIR spectrum of CMC film and pure NH4SCN from 700 to 4000 cm<sup>-1</sup>. Figure 6 shows the FTIR spectra of the CMC film, CMC-NH4SCN doped with various salt concentrations and pure NH4SCN recorded from 700 to 3850 cm<sup>-1</sup> at room temperature.

From Figure 4, it can be observed that, in the CMC spectrum, the characteristic transmission band at 3379 cm<sup>-1</sup> show the hydrogen bonding OH stretching region of CMC. According to M.N. Chai et al., the small hump at 2920 cm<sup>-1</sup> was ascribed to C-H stretching associated with the ring methane hydrogen atoms. The sharp band observed at 1591 cm<sup>-1</sup> confirmed the presence of COO<sup>-</sup> and assigned to stretching of the carboxyl group. The band at 1417 cm<sup>-1</sup> and 1323 cm<sup>-1</sup> was assigned to OH stretching in-plane and C-H stretching in symmetric of CMC,

respectively. The FTIR spectrum of CMC polymer showed the bands at 1057 cm<sup>-1</sup> were characteristic of the C-O stretching on polysaccharide skeleton [20].

In the NH<sub>4</sub>SCN spectra shown in Figure 4, according to S. Selvasekarapandian et al., the bands at 3124 cm<sup>-1</sup> and 1410 cm<sup>-1</sup> are ascribed to NH stretching and NH deformation modes, respectively.

The strong and intense peak observed at 2065 cm<sup>-1</sup> is ascribed to thiocyanate (-S-C≡N) antisymmetric vibration of pure NH<sub>4</sub>SCN. The broad and intense peak at 1663 cm<sup>-1</sup> is ascribed to C≡N asymmetric vibrations of NH<sub>4</sub>SCN [21]. The broad and intense band observed at 946 cm<sup>-1</sup> and 749 cm<sup>-1</sup> are associated to SCN bending and C-S stretching respectively [22].



**Fig. 4:** FTIR spectra of (i) CMC film and (ii) pure NH<sub>4</sub>SCN.

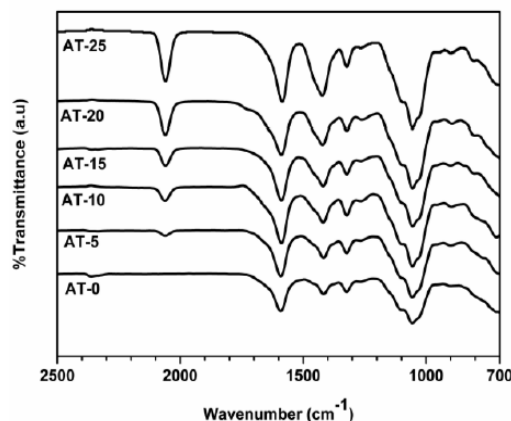
From Figure 5, it can be observed that the carboxyl group C=O at 1591 cm<sup>-1</sup> have shifted to a lower wavenumber upon enhancement of ionic dopant in CMC-NH<sub>4</sub>SCN SBE system. The changes of peaks are expected and is believed due to the coordination interaction of C=O moiety in CMC with H<sup>+</sup> of NH<sub>4</sub><sup>+</sup> substructure in NH<sub>4</sub>SCN which reflects the protonation between the cation H<sup>+</sup> and the carboxyl group of CMC. Moreover, with enhancement concentration of NH<sub>4</sub>SCN in CMC, so that concentration of H<sup>+</sup> are higher, thus, more electrons are withdrawn toward CMC via C=O to form hydrogen bonding which can be proven from the shifting of C=O stretching to the lower wavenumber and increasing of peak intensity. The shifts to lower wavenumber due to stretching vibration of C=O is expected as a result of electrons being introverted from the C=O moiety to form strong hydrogen bonding between CMC and concentration of NH<sub>4</sub>SCN [4]. Furthermore, the peak at 1057 cm<sup>-1</sup> for CMC film has shifted to a lower wavenumber with the enhancement of NH<sub>4</sub>SCN. However, the interaction that occurred due to C-O-mode is slightly which was projected by a small shifted comparable to C=O mode that was identified as a strong absorption mode in CMC as reported by [4]. So that, its supports the coordination interaction taking place at COO<sup>-</sup> moiety particularly at C=O and C-O<sup>-</sup>. In addition, it can be observed in Figure 5 that the strong peak of NH deformation (1410 cm<sup>-1</sup>) overlapped with CMC spectrum (1417 cm<sup>-1</sup>) via O-H and increase in relative intensity with the addition of incorporating ionic dopant concentration. These phenomena could be ascribed to the coordination of

NH<sub>4</sub><sup>+</sup> ion with the polar group of CMC via hydrogen bonds. According to literature (H.J. Woo et al., 2011), there are two possible charge carrier species in this polymer-salt system, i.e., cation and anion [23]. The transporting cation could be either H<sup>+</sup> and NH<sub>3</sub><sup>+</sup> or NH<sub>4</sub><sup>+</sup>. Srivastava et al. has conducted coulombmetric investigation on PEO-NH<sub>4</sub>SCN system and concluded that H<sup>+</sup> is the only cation contributing to the ionic transport. Similar results were obtained from other researchers. Hashim et al., Maurya et al. and Srivastava and Chandra reported protonic motion due to H<sup>+</sup> ion in different polymer-ammonium salt complexes, i.e., PEO-NH<sub>4</sub>ClO<sub>4</sub>, PEO-NH<sub>4</sub>I and PESC-NH<sub>4</sub>ClO<sub>4</sub>, respectively. Each NH<sub>4</sub><sup>+</sup> cation has a tetrahedral structure where one of the four hydrogen atom is most weakly bound. It can be easily dissociated upon an applied electric field. This H<sup>+</sup> ion can hop from one site to another leaving a vacancy which will filled by another H<sup>+</sup> ion from a neighboring site. Thus, the charge transport is carried out by structure diffusion or better known as Grotthus mechanism (the conduction occurs through proton exchange between CMC-NH<sub>4</sub>SCN complexed sites). Proton conduction by the Grotthus mechanism involves intermolecular proton jump creating a vacant site followed by reorientation to occupy the vacant site [19]. So that, protonic transport in CMC-NH<sub>4</sub>SCN SBE system is expected by Grotthus mechanism.

Moreover, the vibrational band ascribed to NH<sub>4</sub>SCN (1663cm<sup>-1</sup>) are found absent in polymer complexes which again shows the interaction between CMC and NH<sub>4</sub>SCN. It has been observed that the bands related to C≡N stretching modes and

CH bending vibrations of salt doped system broaden as the salt concentration increases. Two small peak observed at 946  $\text{cm}^{-1}$  and 749  $\text{cm}^{-1}$  are associated to SCN bending and C-S stretching respectively. Both peaks disappear in the polymer salt system with enhancement of salt confirmed that the salt has been dissolved by the polymer and incorporated into the

polymer matrix. From the above analysis, it can be inferred that the H atom of the  $\text{NH}_4^+$  from the salt is believed to hydrogen bonding with polymer matrix. Thus, from the FTIR spectroscopy analysis, the interaction between CMC and  $\text{NH}_4\text{SCN}$  has been occurred in the present CMC- $\text{NH}_4\text{SCN}$  system.

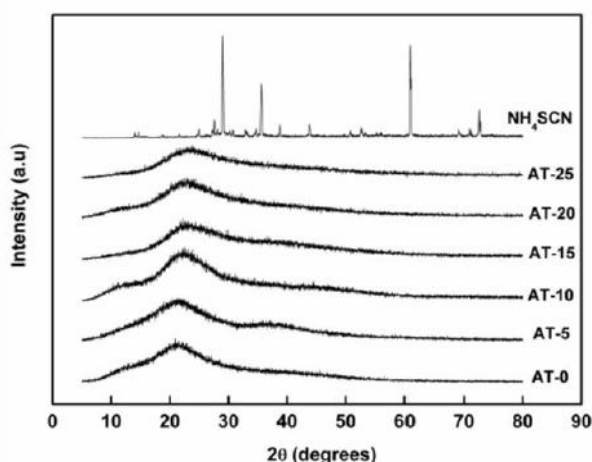


**Fig. 5:** FTIR spectrum of the sample (i) AT-0 (ii) AT-5 (iii) AT-10 (iv) AT-15 (v) AT-20 (vi) AT-25 for the region between 700 to 2400  $\text{cm}^{-1}$ .

#### 4.3. XRD Analysis:

X-ray diffraction studies was conducted to observe the occurrence of complex formation between the polymer and the salt and the degree of crystallinity of the polymer complex. The XRD patterns of CMC film, pure  $\text{NH}_4\text{SCN}$  and CMC- $\text{NH}_4\text{SCN}$  systems are shown in Figure 6 from  $2\theta = 5^\circ$  to  $80^\circ$ . The XRD pattern of  $\text{NH}_4\text{SCN}$  shows clear sharp peaks at  $2\theta = 30^\circ, 35^\circ, 60^\circ$  and  $75^\circ$ , which specify the crystalline nature of the salt. For CMC film, there is no such clear peaks were observed, instead a broad peak was observed at  $2\theta$  region of  $15-25^\circ$  which can be related with the amorphous nature of pure CMC. According to A.S. Samsudin et al., the broad peak is well-known as the amorphous hump and is characteristic of amorphous materials.

From Figure 6, it can be observed that the samples containing 25 wt.% salt exhibits highest amorphous nature which is revealed by the decrease of intensity and the increase of broadness of the diffraction peak of CMC compared to other electrolytes. This result is interpreted in terms of the Hodge et, al [24] criterion which establishes a correlation between the intensity of the peak and the degree of crystallinity. This change of intensity and broad nature of peaks in the polymer electrolyte suggests the amorphous nature of the polymer electrolytes [25]. No peaks observed corresponding to pure  $\text{NH}_4\text{SCN}$  were observed in complexed polymers which indicate the complete dissociation of the salt in the polymer matrix [26,27].



**Fig. 6:** XRD patterns for (i) AT-0 (ii) AT-5 (iii) AT-10 (iv) AT-15 (v) AT-20 (vi) AT-25 (vii) pure  $\text{NH}_4\text{SCN}$ .

### 5. Conclusion:

The development of new solid biopolymer electrolytes film based on CMC complexed with NH<sub>4</sub>SCN have been successfully prepared by the solution casting technique. The highest ionic conductivity at room temperature is  $6.48 \times 10^{-5}$  Scm<sup>-1</sup> for 25 wt.% NH<sub>4</sub>SCN. FTIR spectroscopy shows that the possible coordination interaction between CMC and NH<sub>4</sub>SCN which expected via Grotthuss mechanism. XRD measurements revealed that the CMC-NH<sub>4</sub>SCN SBE system predominantly amorphous in nature from the reduction in intensity and broad nature of CMC-NH<sub>4</sub>SCN SBE system.

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