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Ionic Conductivity and Dielectric Properties of CMC Doped NH₄SCN Solid Biopolymer Electrolytes

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Abstract. In this work, solid biopolymer electrolytes (SBE) containing carboxymethyl cellulose (CMC) doped with ammonium thiocyanate (NH₄SCN) were prepared via solution casting method. The ionic conductivity and dielectric properties of CMC-NH₄SCN system were investigated by electrical impedance spectroscopy in the temperature range of 303-353 K. The dc conductivity shows that the highest ionic conductivity of $6.48 \times 10^{-5} \text{ Scm}^{-1}$ at ambient temperature was obtained when 25 wt.% of NH₄SCN was incorporated. The temperature dependence of ionic conductivity revealed that CMC-NH₄SCN system was discovered to obey Arrhenius law where the regression value is almost unity ($R^2 \approx 1$). Activation energy of CMC-NH₄SCN system was found to decrease with the increment of NH₄SCN concentration. The dielectric behaviour of the CMC-NH₄SCN system have been analyzed using dielectric permittivity (ϵ^*) and electrical modulus (M^*) spectra. Results from dielectric studies showed a non-Debye behaviour of CMC-NH₄SCN system.

Introduction

The study of solid polymer electrolyte (SPE) was discovered by Wright and co-workers and was committed to the ionic nature for the conducting behaviour [1]. Since then, a great deal of research has been developed on polymer electrolyte due to their excellent performance and potential applications in various ionic devices, such as energy conversion units (batteries/fuel cells), electrochromic display devices/smart window, photochemical solar cells, supercapacitors and sensors [2]. In order to be industrialised, the SPE should exhibit high ionic mobility, ionic transport that is closely coupled to the high local flexibility and the segmental motion of the polymer chain. On the other hand, an understanding of interaction between the polymer host and dopant salt is important in order to achieve high ionic conductivity along with the requirements of chemical stability and mechanical strength [3].

One excellent candidate to act as polymer host for proton-conducting SBE is carboxymethyl cellulose (CMC) [4,5]. CMC is a natural polymer derived from cellulose, is generally prepared through the reaction of alkali cellulose with monochloroacetate or its sodium salt in organic medium. CMC possesses many desirable qualities, such as filming, emulsification, suspension, water maintaining, bind and inspissation. Therefore, it is used for various applications such as in medicine, food, textures, toilet, electrical elements, paper making, printing and dyeing [6]. In order to improve the conductivity and mechanical stability, SBE have been incorporated with various ammonium salts, which provide the ions for conduction such as NH₄I, NH₄SO₃CF₃ and NH₄NO₃ [7].

In this present paper, proton conducting SBE films based on CMC incorporating with NH₄SCN have been prepared via solution casting technique with various compositions. This work mainly focuses on studies of ionic conductivity and dielectric behaviours, with the aim of gaining understanding in ionic conduction of CMC incorporated with NH₄SCN SBE.

Experimental Details

In order to prepare the SBE films, CMC obtained from Acros Organic Co. was dissolved in distilled water and stirred until its completely dissolved. Next, the various concentration of NH_4SCN (wt.%) obtained from Sigma Aldrich were added into CMC solution and stirred continuously until mixture solutions became homogeneous with no phase separation. Then, the mixture solutions were poured into different glass petri dishes and left at room temperature for drying process until SBE films form. The SBE films were kept in desiccator for further drying to ensure there is no water content in the films.

The SBE films were characterized via electrical impedance spectroscopy (EIS) using HIOKI 3532-50 LCR Hi-Tester in order to investigate the ionic conductivity in the frequency between 50 Hz and 1 MHz at 303 K to 353 K. The SBE films were cut into small discs of 2 cm in diameter and sandwiched between two stainless steel electrodes under spring pressure for EIS measurement. The ionic conductivity of the SBE films were calculated by:

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

where t (cm) is the thickness of the SBE films, A (cm^2) is the electrode-electrolyte contact area of the SBE films and R_b is the bulk resistance obtained from the complex impedance plot (Cole-cole plot).

Results and Discussion

The evolution of the ionic conductivity of CMC- NH_4SCN system at room temperature as a function of the NH_4SCN concentration is shown in Fig. 1. The dependence of conductivity toward salt concentration provides certain information on the complexation between dopant salts and polymer matrix. The behavior of conductivity-dopant salts variations can be explained in terms of weak electrolytes theory. The weak electrolytes theory states that $\sigma = \eta q \mu$, where η is the number of mobile charge carrier which in motion under the action of an electric field, q is the electronic charge and μ is the mobility of ionic species. From Fig. 1, it can be clearly observed that the ionic conductivity increases drastically with the enhancement of NH_4SCN concentration and reaches the optimum ionic conductivity of $6.48 \times 10^{-5} \text{ Scm}^{-1}$ at 25 wt.% of NH_4SCN -doped CMC. The increase in ionic conductivity with increment in NH_4SCN addition is due to the increment in number of mobile ions or charge carrier (η). As the concentration of dopant salts increases, more protons (H^+) are supplied due to the dissociation of NH_4SCN [8].

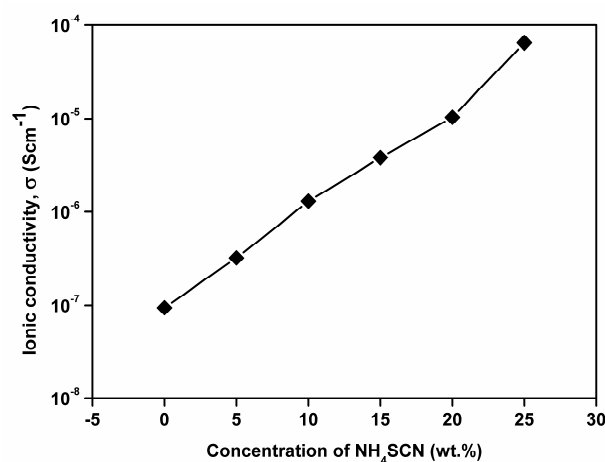


Fig. 1. Effect of NH_4SCN concentration on the conductivity of CMC- NH_4SCN system measured at room temperature

The temperature dependence of ionic conductivity was carried out to investigate the effect of temperature on the behaviour of the ionic conductivity in CMC-NH₄SCN SBE system. The plots of log conductivity versus 1000/T for all samples at the temperature range from 303 K to 353 K are illustrated in Fig. 2 which shows that the ionic conductivity increases with the increasing temperature for all samples. This is due to the expansion of polymer matrix [9]. The polymer matrix expands with the increase in temperature resulted in the formation of free volume and empty spaces for the migration of ions. This assists the mobility of ions and minimizes the effect of ion clouds at the electrode and electrolyte interface. The vibrational mode of polymer segments also increases with the increase in temperature. As a result, the polymer segments have sufficient energy to overcome the hydrostatic pressure which is imposed by its surrounding atoms. This results in the formation of voids and facilitates the segmental transportation of charge carriers. Hence, there is an increase in ionic conductivity. The regression values of all samples are close to unity ($R^2 \approx 1$), indicating that the temperature-dependence ionic conductivity of CMC-NH₄SCN system obeys Arrhenius law, hence indicating that the conductivity mechanism is thermally assisted [10]. According to Arrhenius behaviour, the nature of cation transport can be deduced to be similar to that in ionic crystals, where ions jump into neighbouring vacant sites [11].

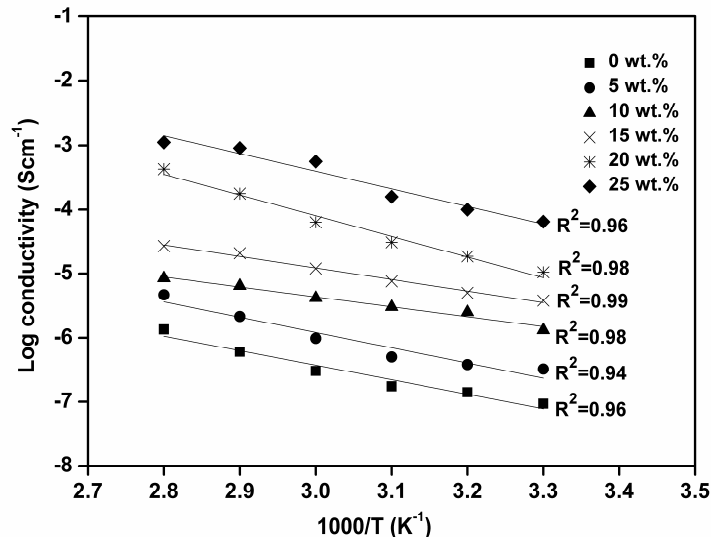


Fig. 2. Arrhenius plots for the conductivity of CMC-NH₄SCN system

From the plot of log conductivity vs. 1000/T graph, the activation energy, E_a was calculated using the Arrhenius equation.

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

where σ_0 is the pre-exponential factor, E_a is activation energy, k is Boltzmann constant and T is absolute temperature. Activation energy is a combination of the energy of defect formation and the energy for migration of ions [12]. E_a was calculated and depicted Fig. 3. as a function of NH₄SCN concentration. In addition, E_a was assumed to be the energy required to move the ion, presupposing that the structure remains unchanged, plus the energy required to deform the structure enough to allow the ion to pass. When the ion has sufficient energy, it is able to move away from the donor site to another one, which resulted in the conduction of charge and the energy required for conduction is known as activation energy [13]. It can be observed that E_a for conduction decreases gradually with increment in ionic conductivity for the CMC-NH₄SCN system, implying that the ions (in this work it is the proton) in highly conducting samples require lower energy for migration. The decreasing E_a with increasing ionic conductivity indicates that the ions in higher conducting electrolyte require less energy to migrate.

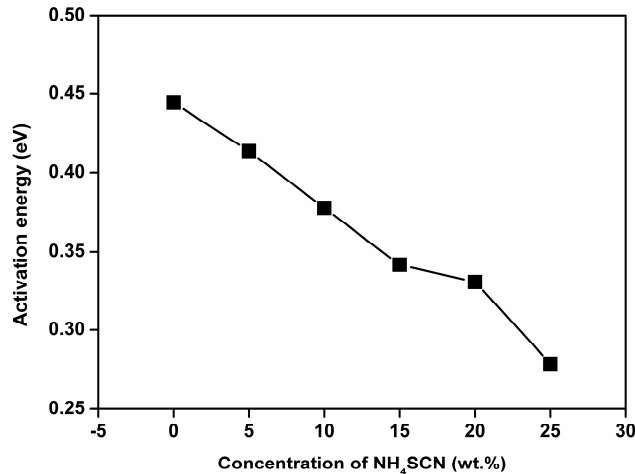


Fig. 3. Activation energy as a function of salt concentration at room temperature of CMC-NH₄SCN system

The dielectric relaxation behavior of the SPE brings significant insights into the ionic transport phenomenon. The measured impedance data are used to calculate the real and imaginary parts of the complex permittivity using the relation,

$$\varepsilon^* = \varepsilon_r + j\varepsilon_i = \varepsilon_r + j(\sigma_r/\omega\varepsilon_0) = 1/j\omega CZ^* \quad (3)$$

where real (ε_r) and imaginary (ε_i) components are the storage and loss of energy in each cycle of the applied electric field [14]. The frequency dependence of ε_r and ε_i at different temperatures for sample 25 wt.% NH₄SCN-doped CMC are shown in Figs 4 (a) and (b), respectively. It is clearly show in Figure 4, there are no appreciable relaxation peaks observed in the frequency range employed in this study. It can be observed, at low frequencies, both ε_r and ε_i rise sharply indicate that electrode polarization and space charge effects have occurred [15]. Hence, this study confirms non-Debye dependence [16]. Besides that, at high frequencies region, both ε_r and ε_i decreases rapidly and becoming frequency independence. This is because due to periodic reversal of the electric field occurs so fast so that, there is no excess ion diffusion in the direction of the field. Futhermore, the decrease in ε_r and ε_i due to polarization due to charge accumulation decreases [17]. The ε_r and ε_i increase due to the higher charge carrier density can be observed at higher temperatures. Since temperature increases, the degree of salt dissociation and redissociation of ion aggregates also increase ensuing in the increase in number of free ions or charge carrier density [14].

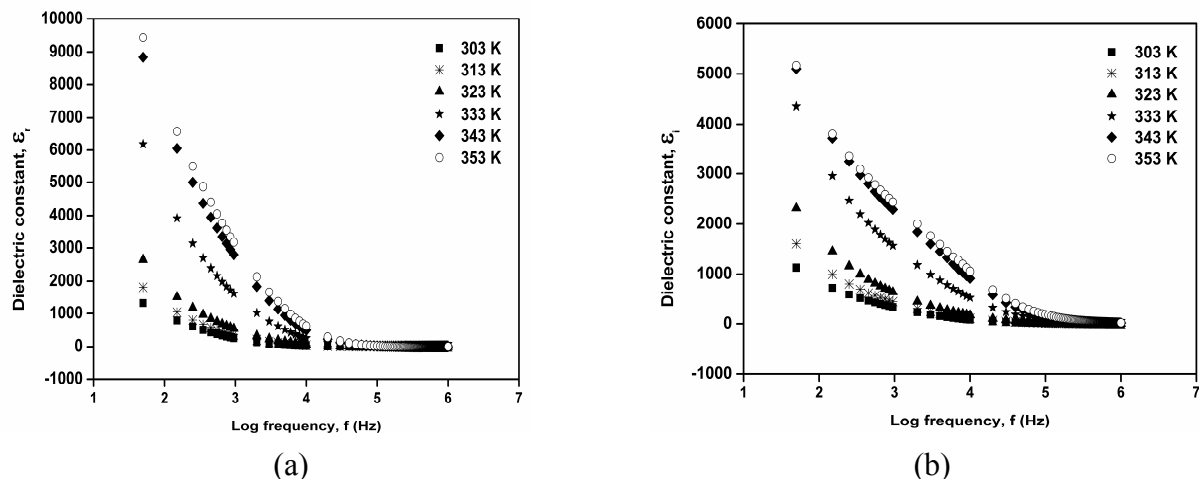


Fig. 4. Frequency dependence of (a) dielectric constant (b) dielectric loss for 25wt.% NH₄SCN-doped CMC at different temperatures

Fig. 5 illustrates the variation in real (M_r) and imaginary (M_i) parts of electrical modulus, respectively, as a function of frequency for 25wt.% NH_4SCN -doped CMC at various temperature. The value of M_r and M_i increase at the high frequency end due to the electrode polarization phenomena [18]. In addition, the possible presence of peaks in the modulus formalism at higher frequencies for all the polymer system and temperature indicates that the polymer electrolyte films are ionic conductors [19]. It can be seen in Fig. 5, both M_r and M_i approaches to zero at low frequency confirms the large capacitance effect associated to the electrode polarization. The plots show long tail at lower frequency confirms non-Debye behaviour in the CMC- NH_4SCN system [20].

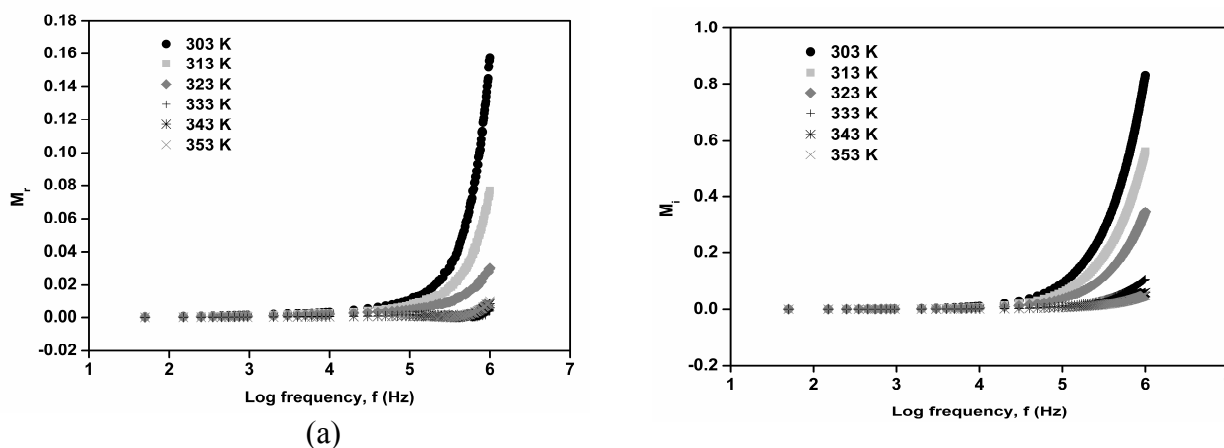


Fig. 5. Frequency dependence of electrical modulus (a) real part (b) imaginary part for 25wt.% NH_4SCN -doped CMC at different temperatures

Conclusion

New transparent SBE films based on CMC incorporating with NH_4SCN at various salt concentration has been successfully prepared using solution casting technique. The ionic conductivity of CMC- NH_4SCN system at room temperature was found to increase with the addition of NH_4SCN concentration. The highest ionic conductivity of $6.48 \times 10^{-5} \text{ Scm}^{-1}$ was observed for SBE film incorporating with 25wt.% of NH_4SCN -doped CMC. The temperature dependence of CMC- NH_4SCN system obeys Arrhenius law where $R^2 \approx 1$. The activation energy was revealed to be inversely proportional to ionic conductivity. The dielectric studies confirmed of the highest conductivity sample shows non-Debye behaviour of ionic conduction in CMC- NH_4SCN system.

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