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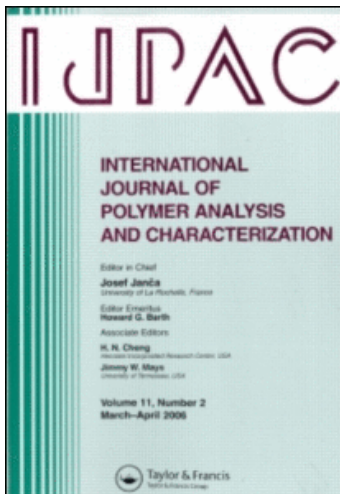## Solid Polymer Electrolytes Based on Methylcellulose: FT-IR and Ionic Conductivity Studies

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SOLID POLYMER ELECTROLYTES BASED ON METHYLCELLULOSE: FT-IR AND IONIC CONDUCTIVITY STUDIES

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Polymer electrolytes of methylcellulose (MC) as the polymer host and ammonium fluoride (NH₄F) as a dopant were prepared by the solution casting technique. Fourier Transform-infrared (FT-IR) spectroscopy and X-ray diffraction (XRD) were used to study the complexation between the salt and polymer. The highest ionic conductivity value was found to be 6.40×10^{-7} Scm^{-1} at room temperature (303 K) for sample AF-18. The conductivity-temperature plots were found to follow Arrhenius behavior with the highest conductivity that gives low activation energy.

INTRODUCTION

Since the initial reports on electrical conductivity in ionic polymers by Wright and coworkers,[1,2] this topic has attracted considerable interest by other researchers. In recent years, polymer proton conductors have been given much attention due to their possible applications in electrochemical devices such as batteries, fuel cells, humidity and gas sensors, capacitors, and electrochemical displays.[3,4] One class of proton-conducting polymer electrolytes is the polymer-ammonium complex, in which NH_4^+ is believed to be responsible for the ionic conduction. Within so many applications, polymer electrolytes with good properties such as thermal, chemical, and mechanical stability, as well as water absorption characteristics, are of great importance in obtaining good conductivity.

One of the main issues concerned in studies of polymer electrolytes is the question of what types of polymers might be useful. Natural polymers are particularly interesting due to their abundance in nature, very low cost, and, principally, biodegradation properties. For these reasons, different solid polymeric electrolytes (SPE) have been obtained using starch, chitosan, and rubber. In this research, the polymer that has been chosen is methylcellulose. Cellulose is an abundant and

naturally occurring polymer exhibiting good mechanical properties; moreover, it is renewable, biodegradable, and derivatizable.[5]

In the open literature, there were no studies reported incorporating MC as the host in anionic conducting polymer electrolytes. Therefore, the main interest of this study is to develop a natural, low-cost, and biodegradable and renewable polymer electrolyte based on MC. The potential of MC as an SPE will be investigated extensively by means of conductivity, electrical, optical, and ionic transport studies.

EXPERIMENTAL SECTION

Sample Preparation

MC was obtained from Sigma Aldrich. A 2 g quantity of MC powder was then dissolved in 100 mL distilled water. This solution was stirred for a few hours until the methylcellulose powder was completely dissolved. Then different weight percentages (wt.%) of NH_4F (99%, Sigma Aldrich) were added to the MC solution and stirred until they dissolved. The mixtures were then cast into plastic petri dishes and left to dry at room temperature. The films were then kept in desiccators (with silica gel desiccant) for further drying. The compositions of the MC and NH_4F used are shown in Table I.

Characterization of Samples

Fourier transform-infrared (FT-IR) spectroscopy. A Thermo Nicolet Avatar 380 FT-IR spectrometer was used to analyze the samples. The spectrometer was equipped with an attenuated total reflection (ATR) accessory with a germanium crystal. The sample was put on a germanium crystal and infrared light was passed through the sample with a frequency ranging from 4000 to 675 cm^{-1} with spectra resolution of 4 cm^{-1}.

X-ray diffraction (XRD). XRD patterns were recorded at room temperature on a MiniFlex II diffractometer equipped with an X'celerator, using Cu Kα radiation in the range of $2\theta = 5°$–$80°$.

Electrochemical impedance. Conductivities of (MC-NH_4F) were measured using a Hioki 3532-50 LCR Hi-Tester, interfaced to a computer, in the frequency range 50 Hz to 1 MHz. When the films were formed they were cut into a suitable size and placed between the blocking stainless steel electrodes of a sample holder,

Table I. Composition of the electrolytes

Sample	Methylcellulose (g)	Salt (wt.%)	Salt (g)
AF-8	2	8	0.177
AF-11	2	11	0.250
AF-14	2	14	0.333
AF-18	2	18	0.429
AF-21	2	21	0.539
AF-25	2	25	0.667

which are connected to a computer. Negative imaginary impendance ($-Z_i$) versus real impedance (Z_r) values were obtained from the plot; in order to get bulk resistance, R_b, the horizontal and vertical axes must be in the same scale. According to Majid and Arof,[6] the conductivity can be calculated as follows:

$$\sigma = \frac{t}{R_b A} \tag{1}$$

where t is the thickness of the sample and A is the electrode-electrolyte contact area.

RESULTS AND DISCUSSION

FT-IR Analysis

The hydroxyl band of pure MC can be assigned in the wave number region between 3447 and 3458 cm^{-1}, whereas the ether band appears at 1066 cm^{-1} and 1110 cm^{-1}. The asymmetric and symmetric band vibration for NH_4^+ in pure NH_4F is in the range of 1850–1500 cm^{-1}, and according to Zhao et al.,[7] the band vibration for NH_4^+ was found at ~1470 cm^{-1}. The important and influential functional group to prove the proton donor in the present electrolyte is NH_4^+. In the present polymer salt system, the NH_4^+ ions of NH_4F are coordinated to the O atom of the ether and to the hydroxyl group in methylcellulose. These interactions will prove that protonation occurs in the present electrolytes. It is visible in the shifting of hydroxyl, ether, and NH_4^+ band.

Figure 1 shows that the peak of NH_4^+ ion in pure NH_4F at 1470 cm^{-1} is shifted to 1464 cm^{-1}. The peak intensity increases when the concentration of NH_4F increases. The above-mentioned shifts in wave numbers observed in salts-doped systems compared to pure MC, according to Hema et al.,[8] are due to the specific interactions between the proton from NH_4F with the polar groups of the pure polymer, MC.

Figure 2 shows that the FT-IR spectra with wave numbers in the range between 900 and 2300 cm^{-1}. The peak at ~1066 cm^{-1} is due to the ether group of pure MC, as mentioned before. The peaks are slight or sharp due to the increment of wt.% of NH_4F. For AF-25 it is also shifted to the higher wavelength, due to the interaction between NH_4F with C$-$O$-$C. Based on Figures 1 and 2, it is suggested that protonation occurred in the present samples and the interactions between MC and NH_4F existed.

XRD Study

The X-ray diffraction patterns of pure MC and samples AF-8, AF-18, and AF-21 at room temperature from $2\theta = 5°$ to $80°$ are shown in Figure 3. The graph for pure MC shows two peaks, at $2\theta = 9°$ and $20°$. The presence of the peak at ~9° is evidence of cellulose modification,[9] and the peak at ~20° is due to the strongest cellulose peak.[10] From the figure, it can be observed that the relative intensity of the broad peak at $2\theta = 20°$ decreased and the peak at $2\theta = 9°$ disappears after the addition of NH_4F. This change of intensity and the broad nature of the peaks in the polymer electrolytes suggests the amorphous nature of the polymer electrolytes.[11]
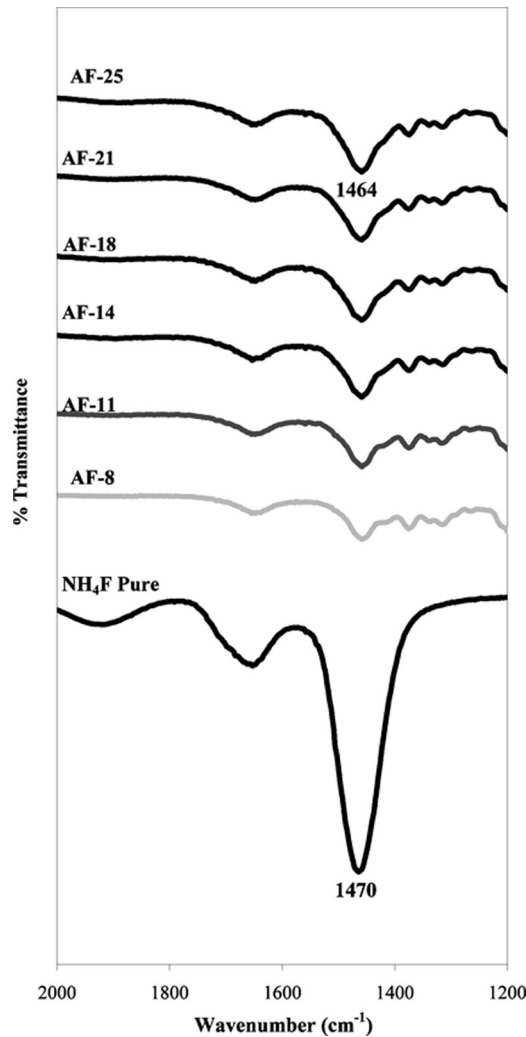
Figure 1. FT-IR spectrum of the sample in the region between 1200 and 2000 cm^{-1}.

Thus, the XRD analysis reveals the complex formation in the polymer matrices and shows that the sample is amorphous.

Conductivity Study

Electrical conductivity values were obtained from complex impedance plots. The electrical conductivity of the samples was in the range of 10^{-11} to 10^{-7} Scm^{-1} at room temperature (303 K), as shown in Figure 4. The highest conductivity obtained for MC-NH$_4$F system at room temperature (303 K) was 6.40×10^{-7} Scm^{-1}, for sample AF-18. According to Vieira et al.,[12] the dependence of ionic conductivity on the salt concentration provides information on the specific interaction
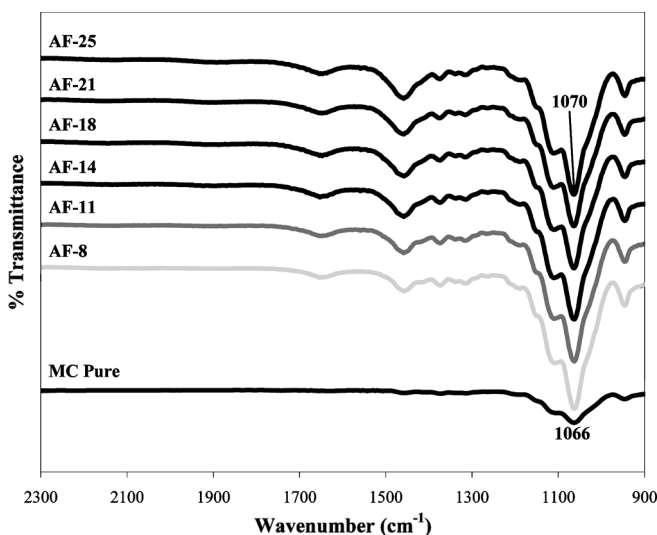
Figure 2. FT-IR spectrum of the sample in the region between 900 and 2300 cm^{-1}.

between the salt and the polymer matrix. In the present FT-IR study, those interactions occurred.

Conductivity varies with a wide range factors, such as cation and anion types, salts concentration, temperature, etc.[13] As observed in Figure 4, ionic conductivity increases with the increase in the NH$_4$F concentration up to 18 wt.%. Enhancement in the ionic conductivity with increasing salt concentration up to 18 wt.% can be related to the increase in the number of mobile charge carriers[14] and also to
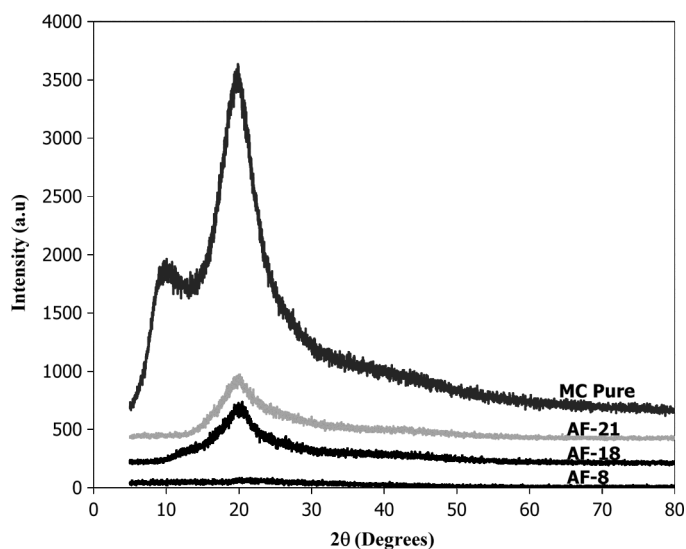
Figure 3. XRD patterns for pure MC and different samples of MC-AF.
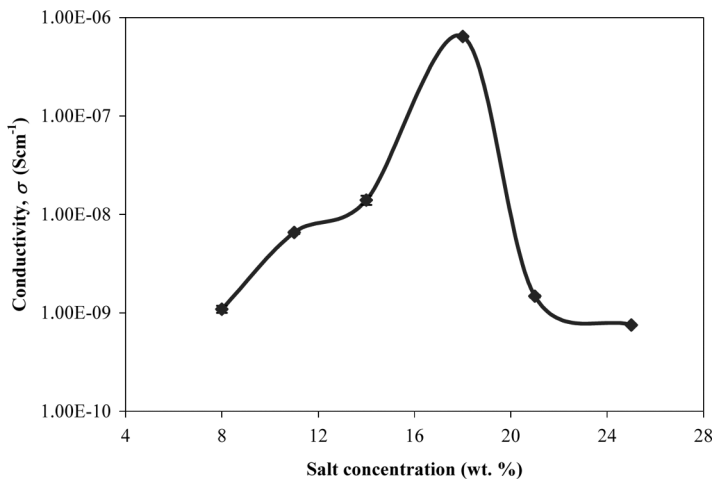
Figure 4. Plot of conductivity, σ, Scm^{-1} vs. wt.% of NH_4F.

the interaction between NH_4^+ ion with hydroxyl and ether group, which brings high dispersion of H^+ that increases the conductivity of the electrolyte.

Conductivity starts to decrease after 18 wt.% of salts concentration. The decrease in conductivity value at higher salt concentrations can be explained by the aggregation of the ion cluster, thus decreasing the number of mobile charge carriers and hence the mobility.[15]

Figure 5 shows the temperature-dependent ionic conductivity measurements that were carried out to analyze the mechanism of ionic conduction in the polymer electrolytes. The ionic conductivity of the electrolytes increases with increasing

Figure 5. Temperature dependence for conductivity of MC-AF electrolyte.

temperature for all compositions, indicating an Arrhenius-type thermally activated process[16] given by the relation

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

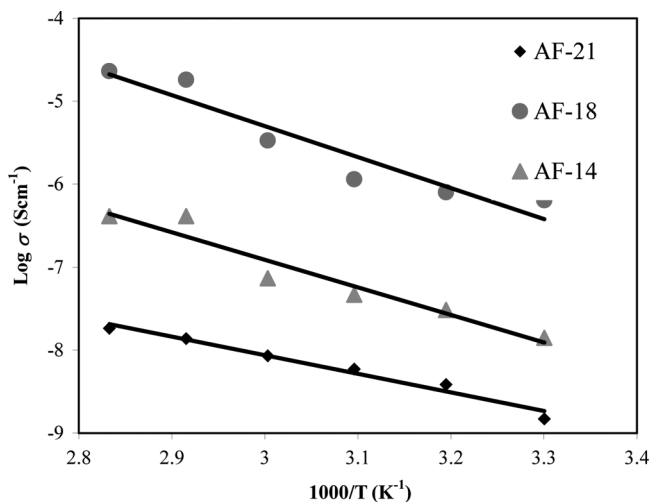where σ_o is the pre-exponential factor, E_a is activation energy, k is the Boltzmann constant, and T is the absolute temperature.[17] E_a can be obtained from the slope and the pre-exponential factor can be obtained from the intercept at the vertical axis from the plot of log σ versus $1000/T$.[18]

Figure 6 shows the activation energy at different wt.% of salt, and the results reveal that E_a is a complex function of conductivity. The number density of the mobile ions, n, can be calculated as follows:

$$n = \frac{3\sigma kTm}{2e^2 E_a \tau \exp(-E_a/kT)} \tag{3}$$

where m is the mass of proton, E_a is the activation energy, and T is the relaxation time.

Once the value of n was calculated the value of transport parameters such as ionic mobility μ and diffusion coefficient D can be obtained; they are listed in Table II. They are closely correlated by the Einstein-Smoulchowsky relation:

$$\mu = \frac{eD}{kT} \tag{4}$$

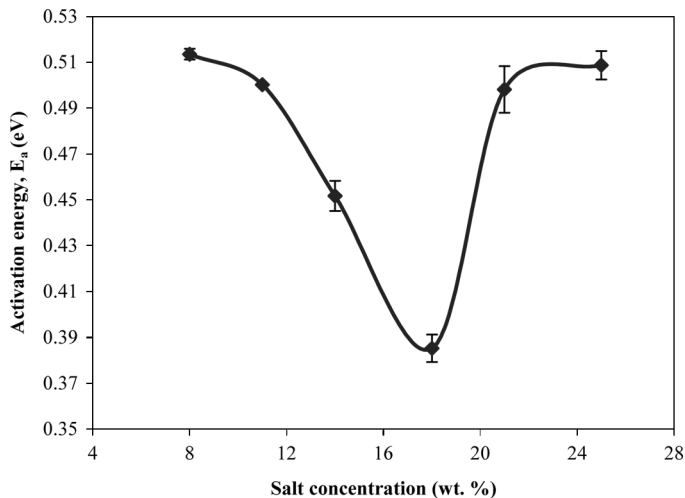The ionic mobility is defined as:

$$\mu = \frac{\sigma}{ne} \tag{5}$$

Figure 6. Plot of activation energy, E_a, vs. wt.% of NH_4F.

Table II. Transport parameters for the MC-AF electrolyte at room temperature

Sample	σ_{RT} (Scm^{-1})	n (cm^{-3})	D (cm^{2}s^{-1})	μ (cm^{2}V^{-1}s^{-1})
AF-8	1.09×10^{-09}	$1.29 \times 10^{+21}$	1.35×10^{-13}	5.25×10^{-12}
AF-11	6.55×10^{-09}	$4.71 \times 10^{+21}$	2.24×10^{-13}	8.70×10^{-12}
AF-14	1.40×10^{-08}	$1.60 \times 10^{+21}$	1.41×10^{-12}	5.47×10^{-11}
AF-18	6.40×10^{-07}	$5.93 \times 10^{+21}$	1.73×10^{-11}	6.74×10^{-10}
AF-21	1.48×10^{-09}	$9.84 \times 10^{+20}$	2.42×10^{-13}	9.41×10^{-12}
AF-25	7.52×10^{-10}	$7.46 \times 10^{+20}$	1.62×10^{-13}	6.30×10^{-12}

where μ is the mobility of ions, n is the number of free ions, e is the charge of electron (1.6×10^{-19}), and the diffusion coefficient D is given by:

$$D = \left(\frac{kT\sigma}{ne^2} \right) \qquad (6)$$

where k is the Boltzmann constant, T is the temperature in Kelvin, and σ is the conductivity.

Rice and Roth[19] proposed the hypothesis that in an ionic conductor there is an energy gap E_a above which conducting ions of mass, m, can be thermally excited from localized ionic states to free ion–like states in which the ion propagates throughout the solid with velocity, v. Such an excited free ion–like state has a finite life time, t. The velocity, v, is given by:

$$v = \sqrt{\frac{E_a}{m}} \qquad (7)$$

The "mean free path" or distance from one complexed site to another, l, is given by:

$$l = v\tau \qquad (8)$$

where τ is a finite lifetime and v is the velocity.

CONCLUSION

The highest conductivity obtained was 6.4×10^{-7} Scm^{-1}, for sample AF-18. The conductivity is still low compared to the current conductivity based on polymer, but studies in the literature indicate that it can be enhanced with the addition of plasticizer or filler. The polymer electrolyte obeys Arrhenius behavior from the plot $\log \sigma$ versus $1000/T$. The number of mobile ions has been calculated using the Rice and Roth model. Conductivity enhancement in the MC-NH$_4$F polymer electrolyte is caused not only by the increase in the concentration of free ions but also by the increase in mobility and diffusion coefficient of ions.

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