

EFFECT OF DIMETHYL CARBONATE PLASTICIZER ON IONIC CONDUCTIVITY OF METHYL CELLULOSE-BASED POLYMER ELECTROLYTES

(Pengaruh Pemplastik Dimetil Karbonat ke atas Kekonduksian Ionik Elektrolit Polimer Berasaskan Metil Selulos)

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Abstract

Influences of dimethyl carbonate (DMC) plasticizer on ionic conductivity, dielectric permittivity and electrical modulus formalism of methyl cellulose (MC)-based polymer electrolytes have been studied. The room temperature electrical conductivity as measured by impedance spectroscopy shows that a methyl cellulose film has a conductivity of $\sim 10^{-10}$ S cm⁻¹. In this study, other than KOH ionic dopant, DMC plasticizer is also added to the polymer with the aim of enhancing the electrical conductivity of the polymer. The highest room temperature conductivity of the plasticized sample is $\sim 10^{-5}$ S cm⁻¹. The plot of $\log \sigma$ versus $10^3/T$ for the highest conducting sample obeys Arrhenius rule indicating that the conductivity occurs by thermally activated mechanism.

Keywords: methylcellulose, ionic conductivity, dimethyl carbonate, Arrhenius rule

Abstrak

Pengaruh karbonat plasticizer dimetil (DMC) pada kekonduksian ionik, ketelusan dielektrik dan formalisme modulus elektrik metilselulosa (MC) berasaskan elektrolit polimer telah dikaji. Suhu bilik kekonduksian elektrik seperti yang diukur oleh spektroskopi impedans menunjukkan bahawa sebuah filem MC mempunyai kekonduksian $\sim 10^{-10}$ Scm⁻¹. Dalam kajian ini, selain daripada penambahan ionik KOH, plasticizer DMC juga ditambah ke dalam polimer dengan tujuan untuk meningkatkan kekonduksian elektrik polimer. Sampel yang ditambah plasticizer DMC menunjukkan bacaan konduktiviti yang tertinggi pada suhu bilik $\sim 10^{-5}$ Scm⁻¹. Di dapati, plot $\log \sigma$ berbanding $10^3/T$ untuk sampel dengan bacaan konduktiviti tertinggi mematuhi peraturan Arrhenius menunjukkan bahawa kekonduksian berlaku melalui mekanisme haba aktif.

Kata kunci: metilselulosa, kekonduksi anionik, karbonat dimetil, peraturan Arrhenius

Introduction

In order to improve the potential applications in electrochemical devices, solid polymer electrolyte (SPE) have attracted much attention from researchers [1]. Due to its dimensional stability, processability, flexibility, electrochemical stability, safety and long life, SPE is expected to replace the conventional sol-gel electrolyte in the future. Polymer electrolyte has played important roles by forming thin film which can be fabricated with a large surface area and gives high power, it also can provide a better connection between electrode and electrolyte and have high ionic conductivity. An amorphous polymer of methyl cellulose (MC), is used in this study because methyl cellulose is easily available, low cost and easy to process. Due to the presence of lone pair electrons on the oxygen atom as shown in Fig.1 allow MC to act as a host for ionic conduction. By dissolving a salt in a polymer host, it will form polymer electrolytes with improved ionic conductivity. Shuhaimi et.al [2] has investigated the transport studies of methyl cellulose doped with NH₄NO₃ electrolyte. It has been reported that the highest conductivity of

ammonium salt doped methyl cellulose is around 10^{-6} Scm^{-1} at room temperature. Therefore, one of the possible method to enhance the ionic conductivity of the polymer is by plasticizing the polymer electrolyte with small organic molecules such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), which have high dielectric constant and low vapor pressure. DMC is expected to increase the amorphosity of the sample and thus increasing the ionic conductivity of the sample. In this work, the aim is to study the effect of DMC as a plasticizer on the conductivity of potassium hydroxide-doped methyl cellulose.

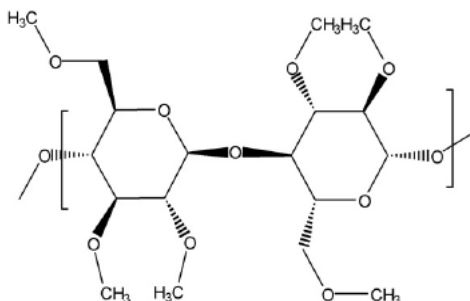


Fig 1. Methyl cellulose structure

Materials and Methods

By using solvent casting method, the MC based polymer electrolytes were prepared. MC, purchased from Sigma-Aldrich was used as the polymer host while potassium hydroxide (KOH) was used to provide protons. 0.5g of MC was dissolved in 25ml distilled water. Then, the desired amount of potassium hydroxide is added into the solution and stirred until it become homogenous. The solutions were poured into different petri dishes and left to dry at room temperature for 3-4 days until a thin film is formed.

To determine the impedance of the polymer electrolyte film, electrochemical impedance spectroscopy (EIS) using the HIOKI 3531-01 LCR Bridge was employed. The frequency range is from 50 Hz to 1MHz. The conductivity, σ of the sample can be calculated using the equation below:

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

t is the thickness of the sample, R_b is the bulk resistance of the sample determined from the EIS spectra and A is the area of the samples.

The optimum composition of MC-KOH that provided the highest conductivity sample was again prepared with addition of different wt% of DMC as a plasticizer. The impedance of the samples was studied using impedance spectroscopy (EIS) in the frequency range from 50 Hz to 1 MHz.

Results and Discussion

Impedance spectroscopy analysis

Table 1 shows the results of variation ionic conductivities of MC doped with different KOH salt concentration at room temperature.

Table 1. Room temperature ionic conductivity of MC doped with KOH salt

wt% KOH	Conductivity, σ (Scm^{-1})
0	2.60E-10
10	1.62E-09
20	2.87E-06
30	7.23E-06
40	6.04E-06
50	3.69E-08

The room temperature conductivity for pure MC is $2.6 \times 10^{-10} \text{ Scm}^{-1}$. Shuhaimiet.al [2] reported that the conductivity of pure MC at room temperature is $3.08 \times 10^{-11} \text{ Scm}^{-1}$. As the wt% KOH increases the conductivity also increases until it reaches a maximum at 30 wt% with the conductivity value of $7.23 \times 10^{-6} \text{ Scm}^{-1}$. The increased in the ionic conductivity upon the addition of the salts can be contribute to the increase of the ions dissociation of the salt, thus the number of the free ions are increases. However, at 50% of the salt concentrations, the salt tends to associate more ions thus increasing the viscosity of the sample which lowering the ionic mobility and hence decrease the conductivity. In order to enhance ionic conductivity of the samples, DMC was then added into the MC-KOH solution from the first stage.

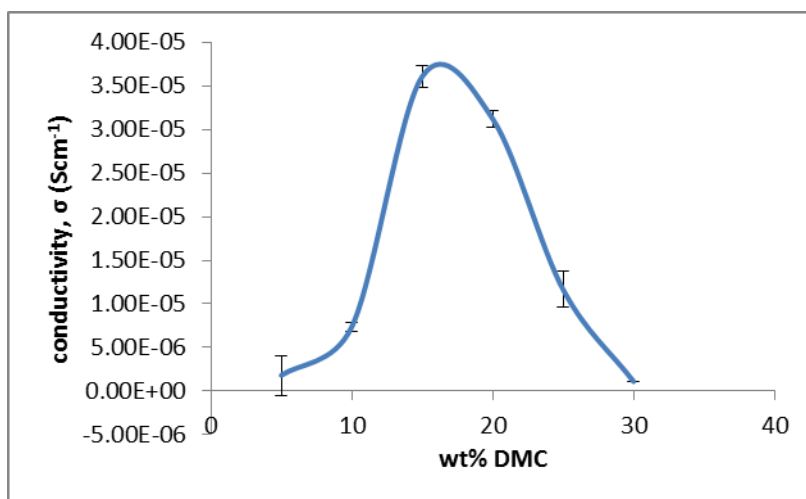


Fig 2. Graph of conductivity versus weight percent of DMC

From the conductivity plots of Figure 2, the values are observed to achieve a maximum at 15 wt% ($3.61 \times 10^{-5} \text{ Scm}^{-1}$). By increasing plasticizer content it is possible to construct a local effective pathway in the presence of a large number of liquid-filled micropores for ionic conduction [3]. The presence of mobile ions also increases the amorphous structure of the polymer through favorable free volume and therefore the ion migration takes place easily [4]. However, when more weight percentage of plasticizer added, the conductivity value has decreased due to the high viscosity which minimizes the movement of each ion.

Temperature dependence analysis

Fig. 3 depicts the Arrhenius plot for the plasticized samples. It can be noted that the conductivity increase as temperature increase in the temperature range from 303 K to 373 K. Regression values are close to unity suggesting that all the points line on a straight line. This can be inferred that conductivity is thermally assisted [5] and implies that when the sample was exposed to heat, more ions were created indicates the plasticizer has help salt to dissociate more ions. The relationship between conductivity and temperature is given in Arrhenius equation which is shown below:

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

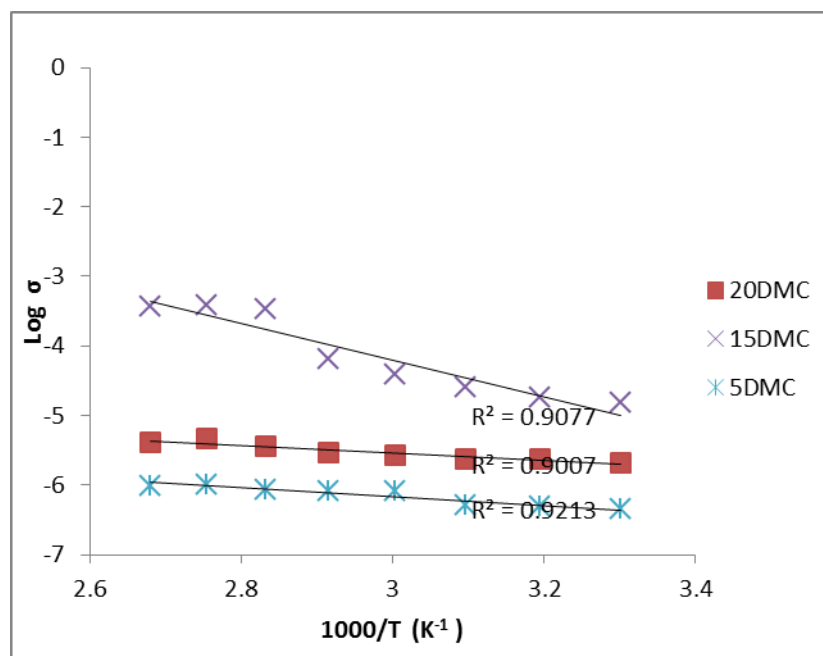


Fig 3. Temperature dependence of ionic conductivity for samples of MC doped with 30 wt% KOH and various concentrations of DMC

As there is no sudden change in the value of conductivity with the temperature it may be inferred that these complexes do not undergo any phase transitions within the temperature range investigated.

Dielectric analysis

Fig. 4 (a) and (b) represent the frequency dependence of dielectric constant, ϵ' (ω) and dielectric loss, $\epsilon''(\omega)$ for systems of MC doped with KOH in addition of DMC as plasticizer at 303K respectively. It can be observed that ϵ' and ϵ'' decreases with frequency and the saturations appear at the higher frequency.

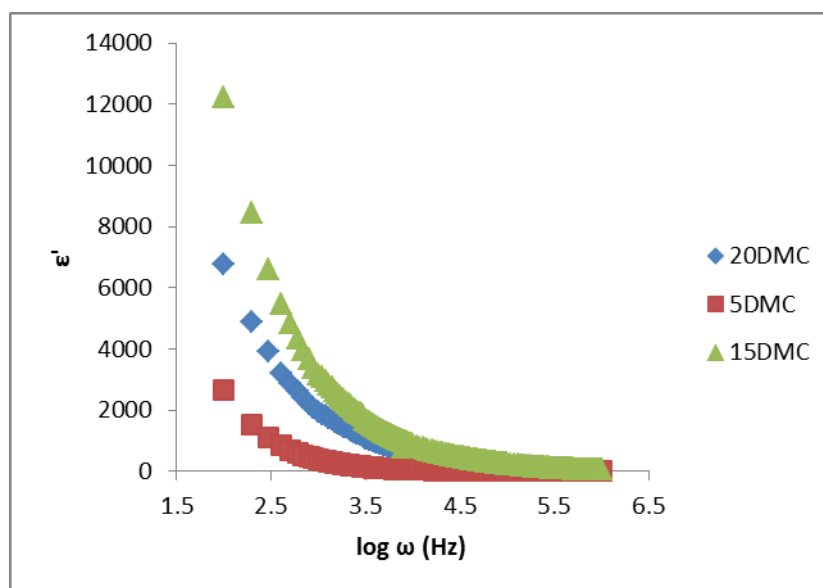


Fig 4(a). Frequency dependence of real part ϵ' (ω) of dielectric permittivity for the systems of MC-KOH-DMC

In the low frequency region, a strong frequency dispersion of permittivity is observed this can be attributed to the contribution of the electrode polarization effects [6, 7]. While a nearly frequency independent behavior is observed above 4.5 Hz. The decrease of ϵ' with increase in frequency may be due to the electrical relaxation process. Charge accumulation decreases will bring toward polarization which leads towards the decrease in dielectric constant and dielectric loss. The material electrode interface polarization superimposed with other relaxation processes at low frequencies [8]. It is seen that, in the lower frequency region the addition of 15 wt% DMC contribute to the highest value of ϵ . This attributed that the addition of 15 wt% plasticizer results in more localization of charge carriers and increasing ions mobility causing higher ionic conductivity. The graph also implies that in addition of higher wt% of plasticizer, the value of ϵ decrease due to large number of ions associates thus lower the mobility of ions.

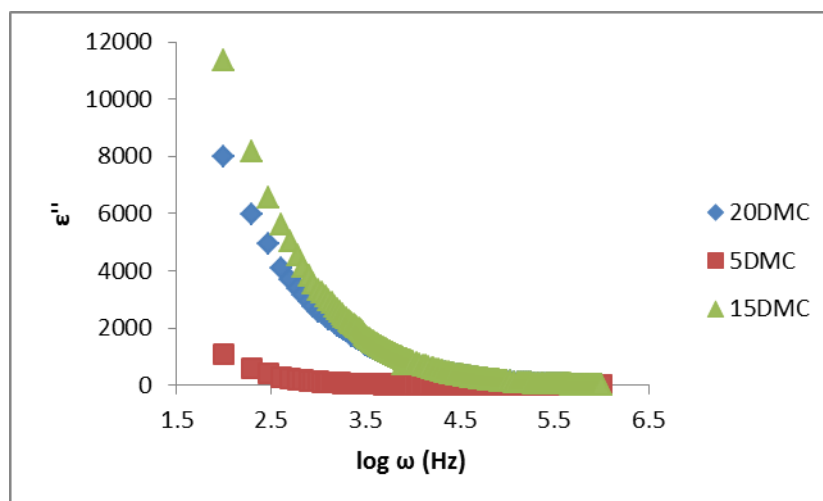


Fig 4(b). Frequency dependence of imaginary part ϵ'' (ω) of dielectric permittivity for the systems of MC-KOH-DMC

Modulus spectra analysis

The frequency dependence of the real part, M' (ω) and the imaginary part, M'' (ω) of electrical modulus formalism is depicted in Fig.5 (a) and (b) respectively.

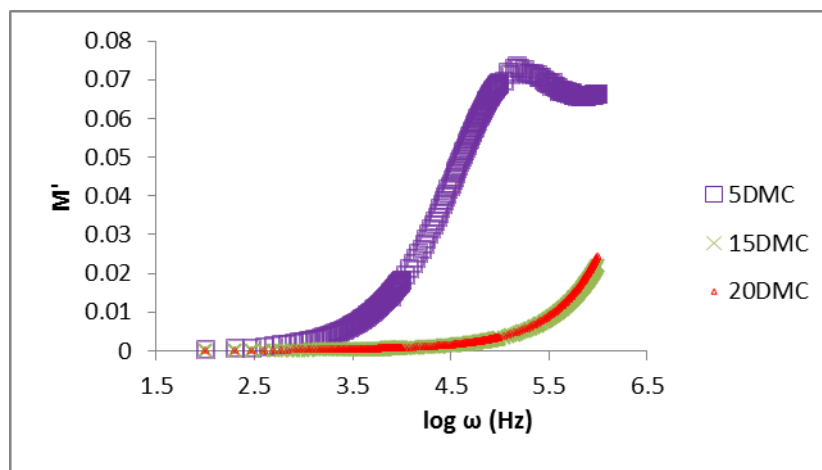


Fig 5(a). Frequency dependence of real part M' (ω) of dielectric modulus for the systems of MC-KOH-DMC at 303 K

The long tail (Fig.4 (a) and (b)) at the lower frequency region may be attributed to the large capacitance associates with the electrode. The presence of the peaks in the modulus formalism at higher frequencies for all the polymer complexes implies that the polymer electrolyte films are ionic conductor. A small M' peak is observed at the higher frequency region, which is from the addition of 5 wt% DMC. This may due to the heterogeneity in the texture of the polymer composites [9] and may be caused by bulk effect [10].

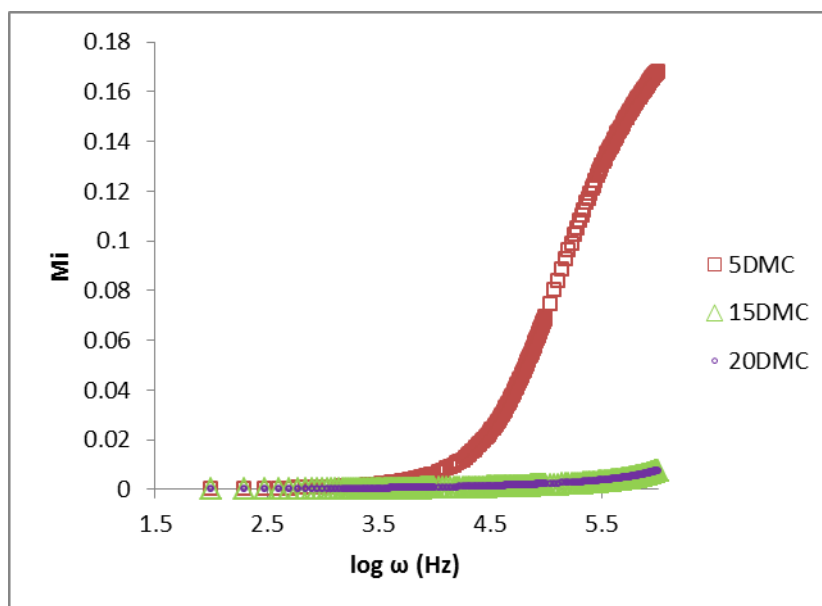


Fig 5(b). Frequency dependence of imaginary part M'' (ω) of dielectric modulus systems of MC-KOH-DMC at 303 K

Conclusion

The effects of DMC on ionic conductivity, dielectric permittivity and electrical modulus formalism have been studied. It has been found that the highest conductivity value after the addition of DMC is $3.61 \times 10^{-5} \text{ Scm}^{-1}$. The conductivity increases as temperature increase showing that the conductivity is thermally assisted and obeys Arrhenius rule. At low frequency, variation of dielectric constant indicates the presence of material electrode interface polarization.

Acknowledgement

Author would like to thank to University Technology Mara (UiTM) for the sponsorship and support from the members of Ionic Material and Devices Research Laboratory (*i-made*) of University Technology Mara.

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