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# Poly (Methyl Methacrylate)-Salicylic Acid-Oleic Acid Plasticized Gel Electrolyte System: Electrical and Ionic Transport Study

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## ABSTRACT

The effect of temperature on electrical and ionic transport properties of PMMA-SA-OA Gel Polymer Electrolyte (GPE) system have been studied in this work. The GPEs have been prepared via solution casting technique and investigated in the temperature ranges from ambient to 368 K. Electrochemical Impedance Spectroscopy technique has been employed to determine the behaviors. The conductivity of the GPE is $8.65 \times 10^{-4}$ S cm$^{-1}$ at ambient temperature and increases to $1.93 \times 10^{-2}$ S cm$^{-1}$ at 368 K. The GPEs show non-Debye type of materials where the regression value obtained from the log conductivity versus reciprocal temperature is close to unity ($R^2 \sim 1$). The complex permittivity, electrical modulus and tangent loss study shows the plurality of relaxation process, thus confirm the Grouttus' mechanism process occurred in the GPE system. The activation energy calculated decreases with temperature. The conductivity shows significant influenced of the ionic transport properties i.e. number of ions (n), mobility of ions ($\mu$) and diffusion coefficient of ions (D).

Key words: Electrical study, ionic transport, PMMA, gel electrolytes

## INTRODUCTION

The usage of polymeric electrolytes has been primer work due to the wide range of possible applications. Proton conducting polymeric electrolytes is used in application such as batteries, capacitors, sensors, electrochromic displays, photo-electrochemical solar cells and fuel cells (Wieczorek and Stevens, 1997). In order to enhance the transport properties of Polymer Electrolytes (PE) to make it more viable for various applications, various researches has been done and reported in the past years. Through extensive and laborious investigations, it can be concluded that the polymer can be group into two major classes, i.e. Solid Polymer Electrolytes (SPEs) and Gel Polymer Electrolytes (GPEs). Advantages in space and mass, structural stability and low volatility are some of the reminiscent of polymer electrolytes comparable to the other types of solid state electrolytes. The GPEs are reported as suitable electrolytes for their optimized properties (Kreuer, 1997; Gary, 1997). For instance, cheap and easily produced electrolytes are needed for large-scale fuel cell applications.

In this study, the conductivity, dielectric behavior and ionic transport parameter was investigated at ambient and elevated temperature of 293-323 K. The activation energy and the relaxation energy for the polymer gel electrolyte also calculated in order to prove the hopping mechanism of the contributing ions.

## MATERIALS AND METHODS

**Sample preparation:** The solvents (EC-PC) were mix at room temperature. Then the salicylic acid was added and dissolved. Later the oleic acid was added and stirred until homogenous solutions obtained. Finally, poly methyl methacrylate (PMMA) (MW = 60,000 g mol$^{-1}$) was added and the whole mixture was heated to 70°C to promote gel formation. Finally the mixture was caste into petri dishes and let dry at room temperature for 24 h before further drying in the desiccators.

**Electrical impedance spectroscopy (EIS) study:** The sample was sandwich between two stainless steel electrodes for impedance spectroscopy analysis. The EIS was measured using a computer-interfaced HIOKI 3531-01 LCR bridge with frequency ranging from 42 Hz to 1 MHz. The EIS was measured at room and elevated temperatures (298-353 K). The electrical conductivity was obtained by inserting the bulk resistance ($R_b$), thickness (t) and area of contact between the gel and the electrode (A) into the Eq. 1:

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

The bulk resistance $R_b$ was obtained from the intercept at the x-axis of the complex impedance plot, $-Z_i$ vs. $Z_r$ as shown in Fig. 1.

## RESULTS AND DISCUSSION

From the complex impedance plot of Fig. 1, it can be observed that the bulk resistance ($R_L$) of the samples decreases as temperature increases. From the inset of Fig. 1, it can be observed that the depressed circle corresponds to the parallel combination of bulk resistance and Constant Phase Elements (CPE), in series with another CPE from the inclined straight line assigned to the double layer capacitance for the gel electrolyte. From Eq. 1, the value of conductivity was calculated for temperature between 298 and 353 K and depicted in Fig. 2.
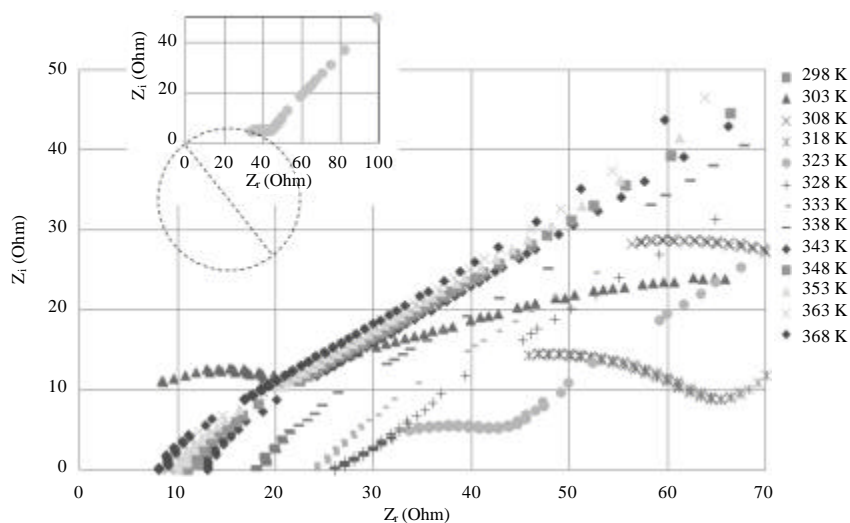


Fig. 1: The complex impedance plot, $-Z_i$ vs. $Z_r$ for sample PMMA-SA-OA at room and elevated temperature (inset: depressed circle of sample at 323 K)
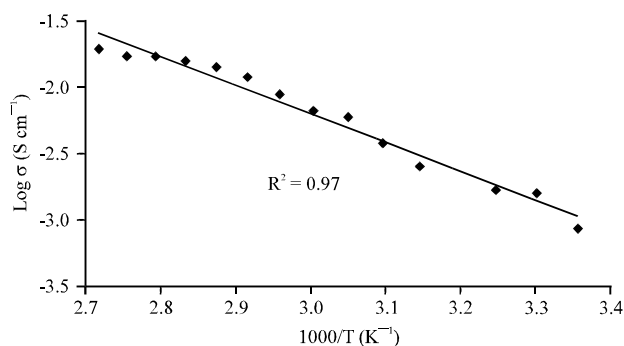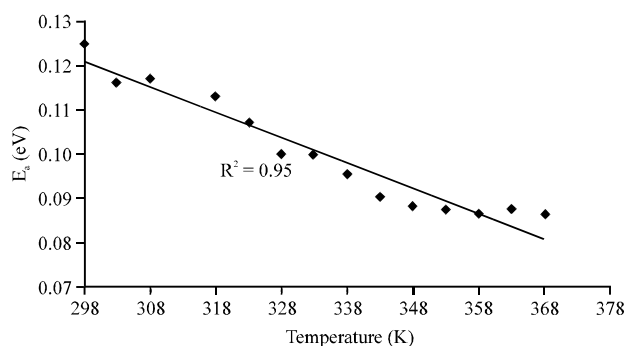
Fig. 2: Log conductivity (σ) vs. 1000/T plot



Fig. 3: The values of $E_a$ at various temperatures

From the temperature dependence of conductivity plot, the linear relationship is observed which confirms that the variation in ionic conductivity with temperature obeys the Arrhenius type thermally activated process. This indicates that there is no phase transition occurring in the polymer matrix or that domains are formed by the addition of acid (Idris *et al.*, 2009). Therefore, no dynamic conformational change in the polymer matrix and $H^+$ ions might migrate through the conduction path formed by the lattice structure of the polymer chains (Hema *et al.*, 2009).

From the plot of log σ versus 1000/T, the activation energy was calculated using the Arrhenius equation:

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

where, $\sigma_o$ is the pre-exponential factor; $E_a$ is the activation energy; T is the absolute temperature and k is the Boltzmann's constant. The $E_a$ was calculated for every temperature and depicted in Fig. 3.

Figure 3 shows that the activation energy decreases with the temperature. The sample with highest conductivity has the lowest activation energy. The decrease in activation energy is due to the density of ions in the polymer electrolyte increase with increasing temperature; hence, the energy barrier to the proton transport decreases which would lead to a decrease in the $E_a$ (Filho *et al.*, 2007). Rice and Roth (1972) hypothesized that energy gap, ε, exists in the ionic conductor which ions of mass (M) belonging to the conducting species can be thermally excited

from localized ionic states to free ion-like states in which an ion propagates throughout the solid with a velocity (υ). The velocity is given by $υ = (2E/M)^{1/2}$. Such an excited free-ion-like state is supposed to have a finite lifetime (t). The mean free path or distance from one complexed site to another (ℓ) is given by $ℓ = υt$ (Zhao *et al.*, 2007).

The Rice and Roth model (Rice and Roth, 1972) was employed in this study in order to determine the transport parameters for the samples. The Rice and Roth model expresses the conductivity as:

$$\sigma = \frac{3e^2}{2kTM} nE_a \tau \left[ \exp\left( -E_a / kT \right) \right] \tag{3}$$

The exponential term tends to unity. Hence τ calculated from the Rice and Roth conductivity is of the order $10^{-14}$ s. Using the value of τ and the $E_a$ from the log σ versus 1000/T plot, the number density of mobile ions, n, can be calculated at every temperature. Using the Nernst-Einstein equation and the values of n obtained from earlier, mobility of mobile ions (μ) and diffusion coefficient of the mobile ions (D) were calculated. The ionic mobility is defined as:

$$\mu = \frac{\sigma}{nq} \tag{4}$$

and diffusion coefficient is given by Nernst-Einstein equation:

$$D = \left( \frac{kT\sigma}{ne^2} \right) \tag{5}$$

Table 1 lists the estimated values of n, μ and D for the OA-plasticized gel electrolyte of the present work at varied temperature studied.

From Table 1, the increase in conductivity with temperature is observed to be influenced by the n and μ, since the D of the ions remains constant throughout the temperature range in the present investigation. n increases with temperature while μ decreases with temperature. The decrease in μ with temperature is attributed to the blocking effect due to 'ion overcrowding', thereby making the ions less mobile. Hence, temperature helps to dissociate the acid into ions thereby leading to an increase in conductivity.

The value of n and D calculated from the Rice and Roth equation is in reasonable agreement with that obtained by Wieczorek and Stevens (1997), Kreuer (1997), Gary (1997) if τ takes the value of $\sim 10^{-14}$ sec. The mobility is of the order $10^{-6}$ cm$^2$ V$^{-1}$ sec$^{-1}$ and is the same for the samples studied by other workers.

Table 1: The estimated values of n, μ and D for the OA-plasticized gel electrolytes at ambient and elevated temperature

| T (K) | σ (S cm$^{-1}$) | n (cm$^{-3}$) | μ (cm$^2$ V$^{-1}$ sec$^{-1}$) | D (cm$^2$ sec$^{-1}$) |
|---|---|---|---|---|
| 293 | $8.65 \times 10^{-4}$ | $3.18 \times 10^{+20}$ | $3.01 \times 10^{-6}$ | $7.60 \times 10^{-8}$ |
| 303 | $1.58 \times 10^{-3}$ | $3.70 \times 10^{+20}$ | $2.91 \times 10^{-6}$ | $7.60 \times 10^{-8}$ |
| 313 | $1.70 \times 10^{-3}$ | $4.17 \times 10^{+20}$ | $2.82 \times 10^{-6}$ | $7.60 \times 10^{-8}$ |
| 323 | $2.52 \times 10^{-3}$ | $4.58 \times 10^{+20}$ | $2.73 \times 10^{-6}$ | $7.60 \times 10^{-8}$ |
| 333 | $3.79 \times 10^{-3}$ | $6.33 \times 10^{+20}$ | $2.65 \times 10^{-6}$ | $7.60 \times 10^{-8}$ |
| 343 | $5.92 \times 10^{-3}$ | $7.69 \times 10^{+20}$ | $2.57 \times 10^{-6}$ | $7.60 \times 10^{-8}$ |

Permittivity is a measure of the degree to which a medium can resist the flow of charge. Since ac conductivity is known to increase with frequency, permittivity must decrease with frequency so that the flow of charge will not encounter much resistance in the high frequency regime. Information on relaxing dipole in a medium may be obtained from an analysis of complex permittivity. The relaxation frequency and strength are characteristics of the relaxing dipoles. In order to detect any relaxation peak in the high frequency region, the modulus formalism is adopted. If the modulus formalism did not show any relaxation peaks, loss tangent which can be calculated from the ratio of imaginary modulus and real modulus will be adopted. The permittivity was calculated from the equations below:

$$\text{Dielectric}\left(\varepsilon^{*}\right) = \frac{Z_I}{\omega C_O \left(Z_R{}^2 + Z_I{}^2\right)} + \frac{jZ_R}{\omega C_O \left(Z_R{}^2 + Z_I{}^2\right)} \tag{6}$$

$$\text{Electrical}\left(M^{*}\right) = \frac{Z_i}{\omega C_O \left(Z_r{}^2 + Z_i{}^2\right)} + \frac{jZ_r}{\omega C_O \left(Z_r{}^2 + Z_i{}^2\right)} \tag{7}$$

$$\text{oss}\tan\text{gent}\left(\tan\delta\right) = \frac{M_i}{M_r} = \frac{\varepsilon_i}{\varepsilon_r} \tag{8}$$

$\varepsilon_r$ versus frequency, f, is as shown in Fig. 4. $\varepsilon_r$ shows an increasing trend with decrease in frequency. The plots exhibit frequency dispersion at all temperatures investigated. The decrease in $\varepsilon_r$ arises from the fact that polarization does not occur instantaneously with the application of the electric field due to inertia (Damay and Klein, 2003). The delay in response toward the applied electric field leads to the lost and decline in $\varepsilon_r$. This implies plurality of relaxation times (Murugaraj and Govindaraj, 2005) as indicated by the tilt in the circle of the Cole-Cole plot.

At low frequencies, all types of polarization contribute. As frequency is increased, the mobile charge (or ions) with large relaxation times cease to respond leading to a decrease in $\varepsilon_r$. At low frequencies, contribution from space charge polarization is high. This reduces with increase in
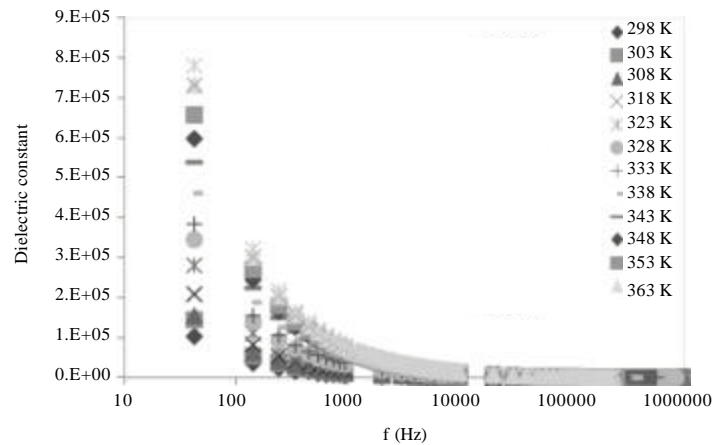


Fig. 4: Dielectric constant vs. frequency at different temperature for OA-plasticized sample
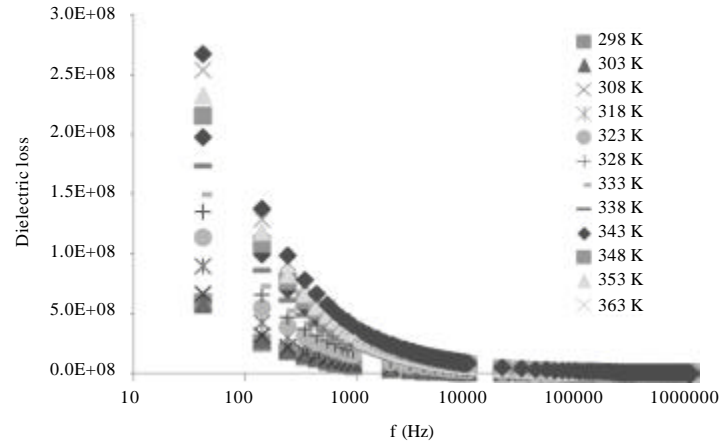
Fig. 5: Dielectric loss vs. frequency at different temperature for OA-plasticized sample

frequency. Space charge arises from ion accumulation at the electrode-electrolyte interface. Since these dipoles do not respond at higher frequencies, $\varepsilon_r$ drops. The $\varepsilon_r$ represents the fractional increase in the stored energy per unit voltage. This means that $\varepsilon_r$ represents the fractional increase in charge. The charge must come from the protons of the gel electrolytes. Hence a fractional increase in charge implies an increase in the number of ions. Since $\varepsilon_r$ for the gel increases with temperature as can be easily observed at low frequencies the number of ions also increases. As a rule, the conductivity, $\sigma$ is given by $\sigma = n\,q\,\mu$ where n is the number of charged species, q the electron charge and $\mu$ the mobility of the charged species. The frequency dependent conductivity of the gel increases with increasing temperature. This is consistent with the decrease in $\varepsilon_r$ with frequency of mobile ions although $\mu$ decreases with increasing temperature.

The $\varepsilon_i$ versus frequency, f, plot is shown in Fig. 5. The dielectric loss, $\varepsilon_i$, probes a wide variety of phenomena along with any relaxation time which may be present in the material. The relaxation time is a characteristic time that determines the sluggishness of the dipole segment to an applied ac field (Aziz *et al.*, 2010a). It is the mean time for the dipole to lose its alignment with the field due to its random interactions with other molecules.

Dipole relaxation occurs when the frequency of the applied ac field is such that there is a maximum energy transfer from the ac voltage source to heat in the dielectric through the molecular collisions and lattice vibrations. The peak occurs when the angular frequency of the ac field is the reciprocal relaxation time. By the above argument it is sufficient to say that at high temperatures the gel contains more ions, as the dielectric loss is higher at high gel temperature. This is because the higher number of ions will result in more random interactions which will finally lead to a longer relaxation time.

The real part of complex electrical modulus $M_r$ versus frequency, f, plot is shown in Fig. 6. It can be observed that there is a long tail exhibited beginning from $10^4$ Hz to lower frequencies. This long tail feature is characteristic of a highly capacitive material. At high frequencies ($>10^4$ Hz), $M_r$ continues to increase in the frequency range studied.

Imaginary electrical modulus, $M_i$ versus frequency, f, plot is shown in Fig. 7. $M_i$ increases with increasing frequency. The value of $M_i$ is lower as the temperature increases in the $M_i$ spectrum. This implies that the relaxation time for the protons at high temperature is shorter than that at low
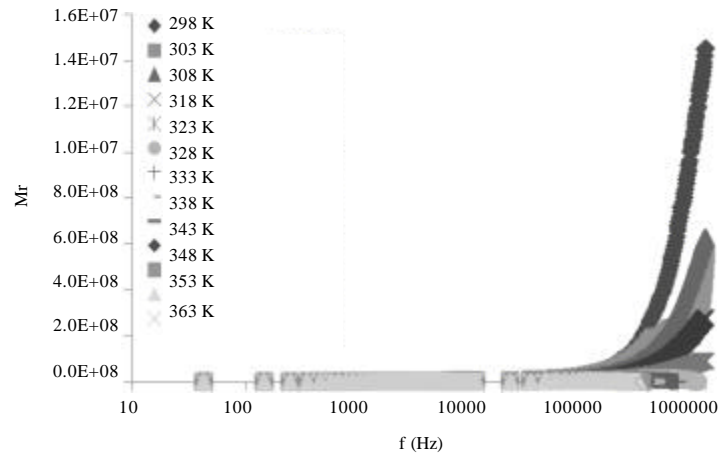
Fig. 6: Real part of dielectric modulus vs. frequency at different temperatures for OA-plasticized sample
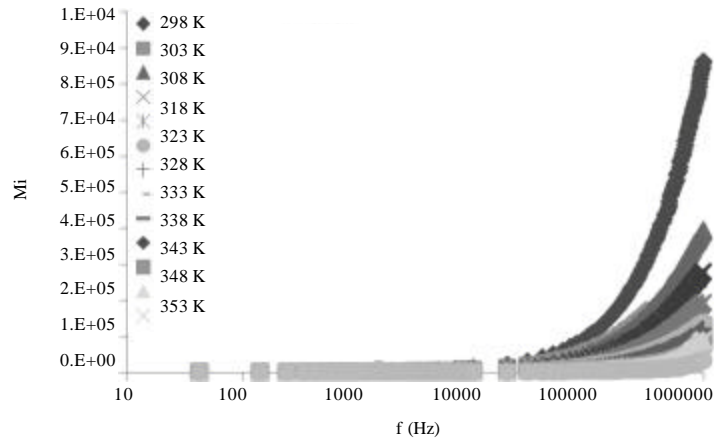


Fig. 7: Imaginary part of dielectric modulus vs. frequency at different temperatures for OA-plasticized sample

gel temperature. This also explains why the conductivity of the gel is higher at higher temperatures. Since no relaxation peaks are observed, the loss tangent formalism will be adopted (Aziz *et al.*, 2010b).

For the sake of clarity in presentation, some loss tangent versus frequency plots are presented. The plot of loss tangent versus frequency is shown in Fig. 8. It can be observed that the loss tangent curve increases with the frequency, passes through a loss peak and decreases with further increase in frequency. The peak shifts to higher frequencies as temperature increases, again supporting the fact that conductivity increases with temperature. It can be observed in the figure, the peak of the plot shifts towards higher temperatures as the frequency increased. This is because temperature facilitates dipole orientation (Khaled and Vafai, 2003). This in turn reduces the relaxation time and increases conductivity as temperature increases.
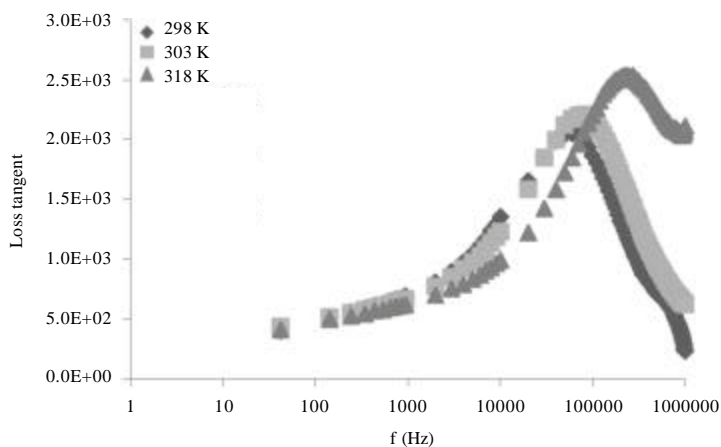
Fig. 8: Loss tangent vs. frequency at selected temperatures for OA-plasticized sample

## CONCLUSIONS

- The highest ionic conductivity at room temperature is $8.65 \times 10^{-4}$ S cm$^{-1}$ and the conductivity increases to $1.93 \times 10^{-2}$ S cm$^{-1}$ at 368 K
- The ionic mobility and diffusion coefficient values calculated using the $\sigma = nq\mu$ and the Nernst-Einstein equations are in reasonable agreement with the results evaluated from experiments to further strengthen that protons are the dominant charge carriers
- The number density of mobile ions was obtained from the Rice and Roth model
- The conductivity shows significant influenced of the ionic transport properties i.e. Number of ions, n, mobility of ions, $\mu$ and diffusion coefficient of ions (D)
- The dielectric study supports the transport study, where the conductivity is significantly influence by the temperature

## ACKNOWLEDGMENTS

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