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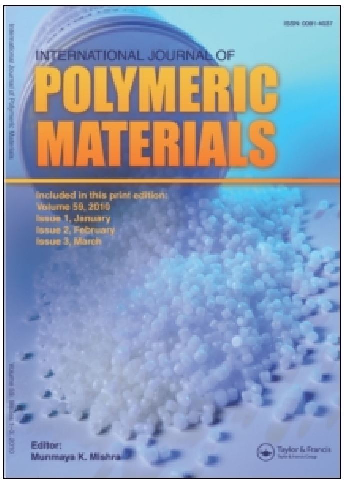

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Arwa Eid[a]; Yahya Ramadin[a]; Awwad Zihlif[a]
[a] Physics Department, The University of Jordan, Amman, Jordan

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Ion-selective Conduction in Poly(vinylchloride)/Poly(ethylene oxide) Blended Membrane*

ARWA EID, YAHYA RAMADIN and AWWAD ZIHLIF†

Physics Department, The University of Jordan, Amman, Jordan

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The dielectric properties and ion-selective conduction in polyvinylchloride/polyethylene oxide (PVC/PEO) blended membrane of different composition immersed in electrolyte have been studied under the influence of frequency and temperature. It was found that the dielectric constant of the prepared alloy increases with increasing the PEO concentration, the AC-conductivity increases with increasing the applied frequency, and the PEO content in the blended membrane. The thermal behavior was also investigated on a blend of 50 wt.% PEO. It was observed that the temperature increases the dielectric constant at lower frequencies and enhances the AC-conductivity. Furthermore, it was found that the activation energy and the ionic conduction increase with temperature. The present study suggests the suitability of PVC/PEO blended membrane to be used as ion-selective electrode.

Keywords: Impedance; ion-selective; membrane; dielectric; conductivity; electrode

1. INTRODUCTION

The PEO polymer has a wide range of applications including the use as pharmaceutical excipients, food additives and placticizers [1]. However, much progress has been made in studying the electrical conduction in polyethylene oxide (PEO) since the work of Wright [2]. Previous studies have been centered on enhancement of its ionic

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†Corresponding author.

conductivity with aim of developing the material to have promising electrical applications [2–4].

The blending of PEO with other polymers have been adopted as a strategy for enhancing the mechanical stability of PEO [2]. Ion-selective liquid membrane are examples of how polymeric systems are adjusted to serve as electrodes whose function is based on transport selectivity in a conduction process. Polymeric membranes with ion selective transport are of importance for phase separations and for biological applications [5–8]. The electrochemical industry has achieved good progress in the development of ion-selective electrodes by using blended and unblended polymeric membranes or barriers [9–11].

Impedance spectroscopy is a useful technique to characterize the electrical behavior of the ion-selective membrane electrodes [12, 13]. Brand and Rechnitz [13] observed the time dependence of ion-selective liquid membrane electrodes. Abu Samrah and Zihlif [14] investigated the aging effect on the impedance behavior of PVC ion-selective electrodes. Ghannam and Zihlif [17] studied the thermal and aging behavior of mica-PVC membrane as ion-selective electrode.

In the present study, the conduction process by ion-exchange in a liquid PVC/PEO membrane is investigated as a function of applied frequency and temperature. As far as we know, no studies have been performed to characterize the electrical behavior of PEO blended membrane as ion-selective electrode. We believe that this study is of great interest for some applications in the electrochemical industry using some blended polymeric membranes.

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2. EXPERIMENTAL

Appropriate amounts of PVC and PEO resins were mixed and dissolved in Tetrahydrofuran (THF) by stirring at 30°C for 6–8 hours. The solution was casted onto a stainless steel ring resting on a Teflon sheet. To ensure complete removal of the solvent, the thin films were kept in an oven and dried at atmospheric pressure at 50°C for 48 hours. Five different membranes were prepared by varying PEO content as: 0, 5, 40, 50, and 70 wt.%. Disk-shaped specimens of average thickness 60 μm were cemented to flat narrow end of a glass tube with PVC adhesive dissolved in THF. Silver wires serve as electrodes were immersed in an electrolytic solution consisting of 0.005 M (mol/dm^3) $FeCl_3$.

Impedance measurements were carried out using HP 4192A impedance analyzer. The real and imaginary parts of the complex dielectric constant were calculated from:

$$\varepsilon' = \frac{Z_i}{2\pi f C_0 Z^2} \tag{1}$$

$$\varepsilon'' = \frac{Z_r}{2\pi f C_0 Z^2} \tag{2}$$

where, $C_0 = (\varepsilon_0 A/d)$ the capacitance of the electrodes, A the area of the electrode, ε_0 the permitivity of the free space, and d the thickness of the membrane. The impedance Z is given by $(Z = Z_r - jZ_i)$, where Z_r, Z_i are the real and the imaginary parts of the impedance, respectively.

The AC conductivity is calculated from the equation:

$$\sigma_{AC} = 2\pi f \varepsilon_0 \varepsilon''. \tag{3}$$

3. RESULTS AND DISCUSSION

Impedance measurements have been performed on blended membranes of different PEO concentration in a frequency range from about 10 Hz up to 400 kHz and temperature range 25°C–65°C. It was observed that the phase angle is always negative indicating that the material is capacetive and can be represented by parallel RC networks.

Figure 1 represents the dependence of impedance on frequency at room temperature for blended membranes of different PEO content. At lower frequency (< 200 Hz) the impedance has high values and is nearly independent of frequency; with increasing the frequency the impedance is decreased. The observed decrease in impedance values with increasing PEO wt.% is due to protonic migration transported through the ethereal oxygens of PEO. Thus, protonic migration in PEO and the ion exchange of Cl^- ion in PVC may lead to high electrical conduction in the blended membrane [10, 14, 19, 23]. Figure 2 shows the Cole–Cole plot for the real part (Z_r) and the imaginary

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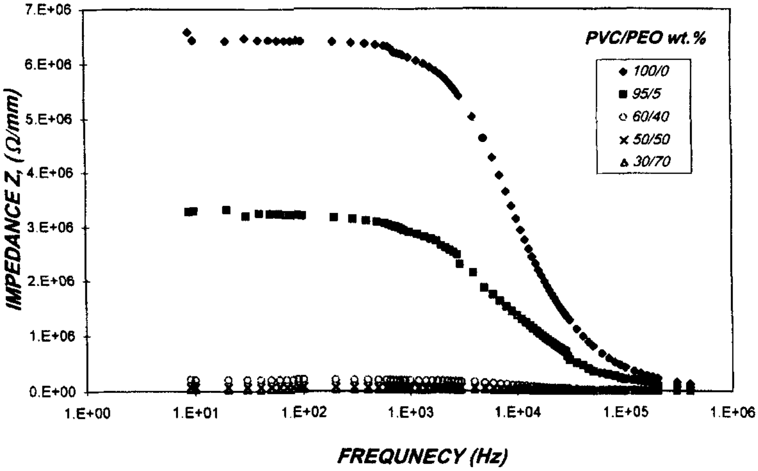

FIGURE 1 The variation of the impedance with the frequency at room temperature. (Membrane is immersed in electrolyte $FeCl_3$ in all cases).

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part (Z_i) of impedance for different PVC/PEO blended membranes. The Cole–Cole construction yields slightly inclined and distorted semicircles. The geometrical shape of the complex impedance plane plots indicates that the membrane cell is electrically equivalent to RC networks which reduces to a pure resistance at both high and low frequencies. Also it can be seen from the intercept of these circles with the real axis of the impedance values (Z_r) that bulk ohmic resistance is reduced as the PEO concentration is increased, which corresponds to increasing the electrical conductivity. It is observed that the behavior of the impedance plane diagram favors the bulk process and not the Warburg diffusion process. The bulk effect creates excess in moveable charged particles, which enhances the electrical transport through the bulk. It seems that the bulk effect is a dominant factor in increasing the electrical ion-exchange and thus electrical conduction is enhanced.

The variation of the calculated dielectric constant (ε') with frequency for membranes of different PEO content is shown in Figure 3. It is can be seen that (ε') decreases with increasing the frequency, verifying the fact that for polar materials as PVC and PEO the initial value of (ε') is high, but as the frequency is increased, the dielectric constant is dropped [19, 22]. As the PEO concentration increases, the low-frequency dielectric dispersion becomes stronger due to ions

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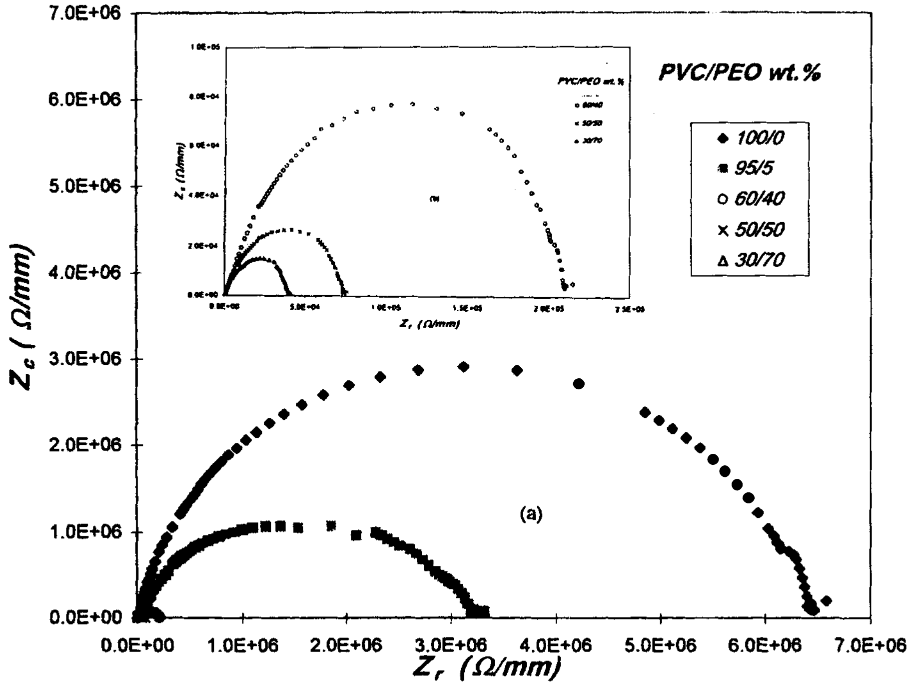

FIGURE 2 Complex impedance plots at different PEO content.

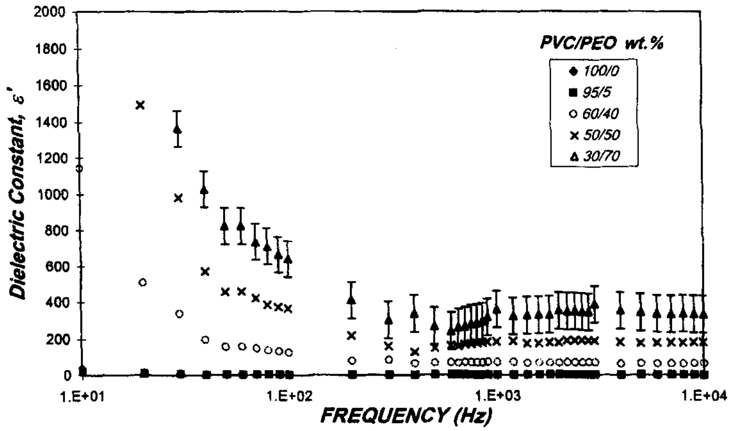

FIGURE 3 The dependence of the dielectric constant on frequency.

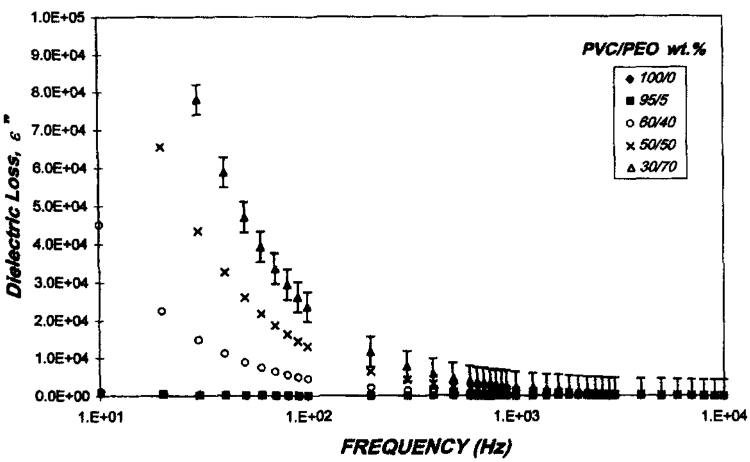

FIGURE 4 The variation of the dielectric loss as a function of the frequency.

diffusion in the membrane bulk. This observed dispersion is a dominant mechanism caused by conductivity enhancement due to increasing the PEO content [19]. The dielectric loss (ε'') is plotted against the frequency in Figure 4. At low frequencies (ε'') has a high value and then it starts to decrease at higher frequencies. The low-frequency dispersion in ε'' is attributed charge carriers which lead to large losses at low frequencies. Also it can be seen that both (ε') and (ε'') increase

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with increasing the PEO content due to enhancement of the ionic conductivity in the liquid membrane. Figure 5 shows the Cole–Cole plots for the 50 wt.% PEO membrane at different temperatures. The plots are also distorted semicircles exhibiting different electrical conduction processes with relaxation time spectrum. The relaxation time (τ) was determined by approximating these Cole–Cole plots to semicircles using the relation $\omega_{max}\tau = 1$, where ω_{max} is the angular frequency at maximum values of Z_i observed on the constructed plots. The figure shows that the impedance real component (Z_r) decreases with increasing the temperature, *i.e.*, the membrane becomes less resistive or more conductive. These semicircles can be attributed to the Warburg ionic diffusion takes place in the membrane bulk [16]. Figure 6 shows that the calculated relaxation time (τ) decreases with increasing temperature. This may be attributed to ionic mobility which increases as temperature increases [16]. Figure 7 shows the temperature dependence of the dielectric constant (ε'), where it increases temperature. This increase in (ε') value is more pronounced at lower frequencies, and may be due to the increase of the total polarization in polar dielectrics [20]. The variation of dielectric loss (ε'') with temperature at different frequencies is shown in Figure 8. The

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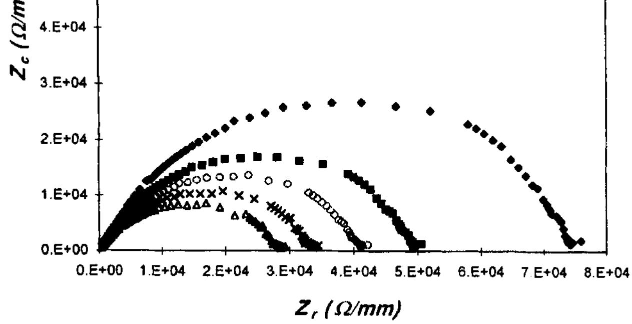

FIGURE 5 The Cole–Cole plot at different temperatures.

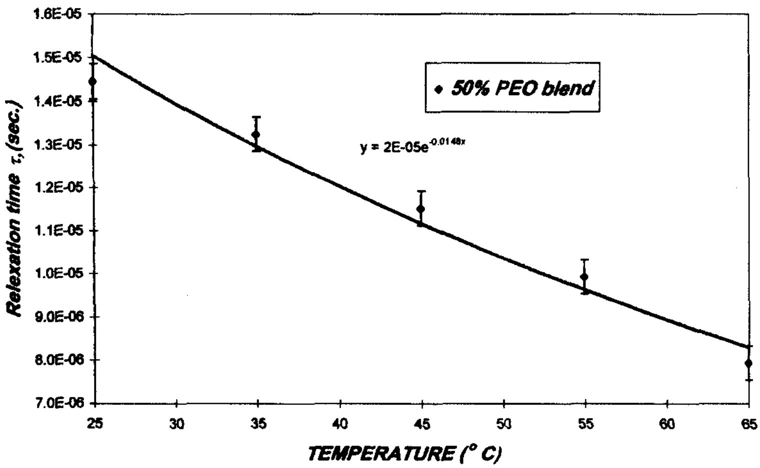

FIGURE 6 The relaxation time as a function of temperature.

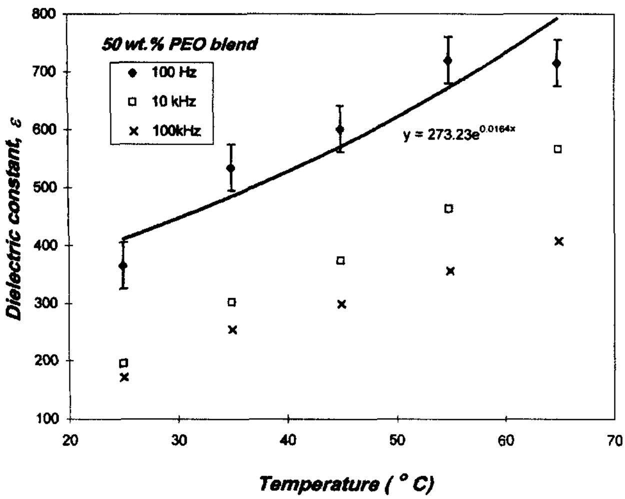

FIGURE 7 The temperature dependence of the dielectric constant.

dielectric loss increases with increasing temperature, especially at lower frequencies. The observed increase in (ε'') is due to the enhancement of the ionic conductivity with increasing temperture and (PEO) addition.

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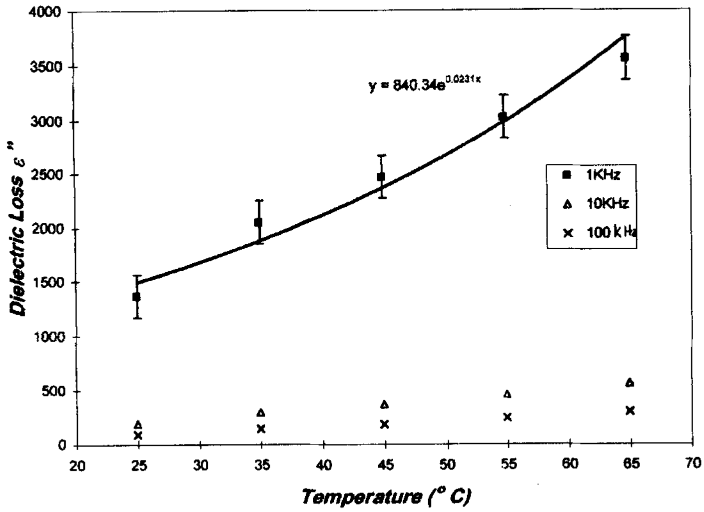

FIGURE 8 The dielectric loss as a function of temperature.

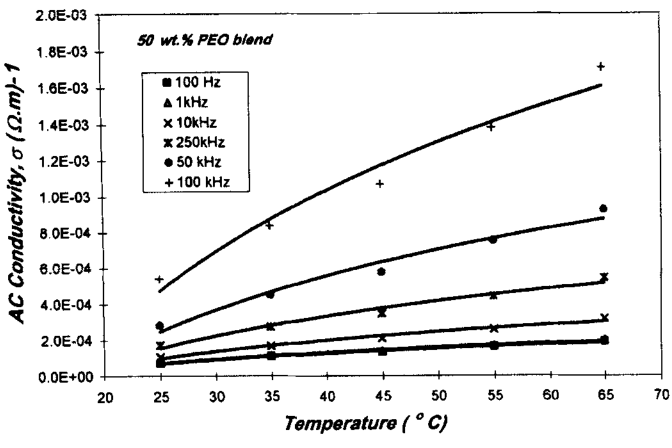

FIGURE 9 The AC-conductivity as a function of temperature for different frequencies.

The variation of the calculated AC conductivity (σ_{AC}) with temperature is shown in Figure 9 at different frequencies. It was found that (σ_{AC}) increases with temperature due to the flow of electrons or charged ions, established between the electrodes and thus leading to higher conduction [19]. The proposed equation by

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TABLE I 50 wt.% PEO membrane

Frequency (Hz)	*Activation energy (eV) (VTF)*
100	0.29
1000	0.24
10000	0.23
25000	0.20
50000	0.13
100000	0.12

Vogel-Tammann-Fulcher was used to calculate the activation energies shown in Table I.

$$\sigma = A\sqrt{T}\exp\left[\frac{-Ea}{k(T-T_0)}\right] \tag{4}$$

where, k is the Boltzman constant, A is proportional to the number of charge carriers, the T_0 is the ideal transition temperature and Ea is the activation energy [25]. The decrease in the activation energy values reflects higher ionic conduction in the PVC/PEO blended membranes when they are tested as ion-selective liquid electrodes. The values obtained from Eq. (5) show a similar decrease in the activation energy.

Finally, it seems that some factors can improve the electrical behavior of the blended membrane such as the structural modification and enhancement of the interaction between the ionic electrolyte-solution and the polymer bulk.

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4. CONCLUSION

The electrical behavior of the PVC/PEO blended membranes immersed in electrolyte was investigated at different frequency, temperature and (PEO) concentration. From the analysis of impedance results, one can conclude the following:

1. Temperature, frequency and PEO content affect the dielectrical behavior of the blended membranes.
2. The AC conductivity increases with increasing temperature, frequency and PEO content.

3. Temperature enhances the ionic conduction takes place under the applied electric field of varying frequency.
4. The ion-selective conduction exhibits electrical mechanism with relaxation time spectrum.
5. The activation energy of the thermally process conduction process decreases with temperature.

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