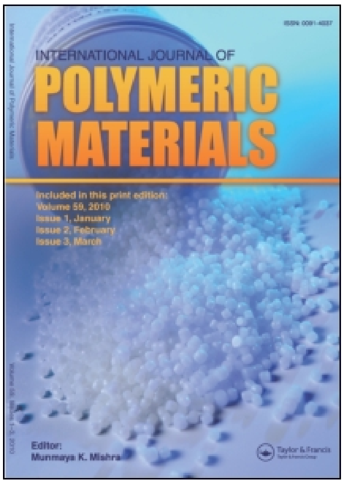

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Thermal and Aging Effects on the Ion-Selective Conduction of PVC/PEO Membrane

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The ion-selective conduction of the PVC/PEO blended membranes was investigated as a function of frequency, temperature and aging time through impedance spectroscopy. It was found that the dielectric behavior of the blended membrane is affected by these physical factors. Analysis of the impedance data showed that the AC conductivity increases with increasing temperature, frequency and aging time. It also was found that the calculated activation energy of the thermoelectrical process decreases with temperature due to enhancement of the ionic conduction in the membrane bulk. However, the enhanced ion-selective conduction suggests the suitability of the prepared blended membranes to be used in the ion selective electrode technology.

Keywords: Membrane; ac-impedance; aging; dielectric; conduction; activation energy

1. INTRODUCTION

Great interests in Polyethylene Oxide (PEO) polymer have been generated since the work of Wright [1]. Many researches have studied the blends of PEO with other polymers [2-4]. These studies showed that blending of noncrystalline polymers reduces the crystallinity of the PEO matrix and thus increasing the chain mobility leading to higher electrical conductivity [4-7].

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Ion-selective liquid membranes 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. A powerful method to study the electrical behavior of the ion-selective electrodes is the impedance spectroscopy. This technique has been used by few authors [5–7]. The ion-exchange membrane studies reported this technique. Abu-Samrah and Zihlif [5] investigated the aging effect on the impedance behavior of PVC ion-selective electrodes. Brand and Rechnitz [6] studied the time dependence for calcium ion-selective liquid membrane. Ghannam and Zihlif [7] studied the thermal behavior of Mica-PVC aged membrane ion-selective electrodes.

The present work deals with studying the aging and thermal effects on the ion-exchange process in a blend of PVC/PEO when used to work as liquid ion-selective electrode. This study may be of interest to electrochemical industry, medicine and commercial applications [8].

2. EXPERIMENTAL

2.1. Sample Preparation

The used (PEO) polymer has a molecular weight of 4,000,000. A blend of 50 wt.% PEO/PVC was prepared by casting method [7]. The PVC and PEO resins were mixed and dissolved in Tetrahydrofuran (THF) by stirring at 30°C for 6–8 hours. Thin films were obtained by casting the solution onto a stainless steel ring resting on a Teflon sheet. To ensure complete removal of the solvent the casted thin films were kept in an oven at 50°C and dried at atmospheric pressure for 48 hours.

2.2. Impedance Measurements

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) $FeCl_3$. The impedance of the film was measured using a Hewlet Packard 4192 A impedance analyser. Impedance measurements were carried out at room temperature for membrane of 50% wt.% PEO in a frequency range from 10 Hz to 13 MHz. The effect of aging on liquid membrane electrode was studied over a period of 30 days. The electrical characteristics of the membrane was tested in the temperature range 17 – 58°C aged for 30 days.

3. RESULTS AND DISCUSSION

The measured impedance data are plotted against frequency on a logarithmic scale in Figure 1. At frequency below 1 MHz, the measured impedance was found to be almost constant and then decreases as the frequency is increased. This behavior may be attributed to the drop in orientational polarization since, at high frequency, the dipoles no longer have enough time to orient themselves with the electric field [19]. A drop in impedance with aging time is also observed which may be attributed to the enhancement of the molecular and the ionic mobilities due to weeking of the physical bonding to the surface [10].

The impedance is given by $Z = Zr + Zc$, where Zr and Zc represent the real and imaginary parts of Z, respectively. Impedance components Zc and Zr are calculated from the relations $Zr = Z\cos\varphi$ and $Zc =$

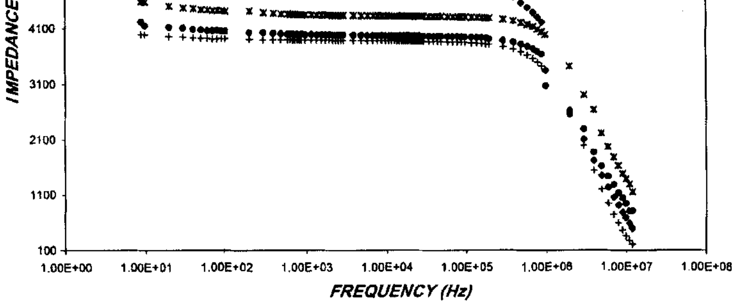

FIGURE 1 The variation of the impedance Z with the frequency f at different aging time.

$Z \sin\varphi$, where φ is the phase angle. A Cole–Cole plot of *Zr versus Zc* for different aging times is shown in Figure 2. The geometrical shape of the complex plane plot suggests that the membrane is equivalent to parallel RC network connected in series. Similar behavior was observed previously and reported elsewhere [6, 7, 10, 11].

The complex impedance plots looks like a semicircle at high frequency with the appearance of an other arc at low frequencies. These approximate distorted two semi-circles can be interpreted as two series circuits. The high frequency parallel combination is due to the bulk effect. They are composed of bulk resistance and geometric capacitance of both electrolytic space charge regions at outer surfaces of the membrane. The bulk effect creates an excess of mobile charged particles, which enhances the electrical transport through the bulk. The inclined area appears at lower frequencies is attributed to Warburg-diffusion process occurring at the membrane surface [10, 13]. The ion diffusion process blocks the charge transport and as a consequence reduces electrical conduction and enhances the bulk resistance. The observed drop in resistance with aging time indicates that the bulk effect seems to be a dominant factor in increasing the ion- exchange, and as a result enhancing electrical conduction as reported recently [10].

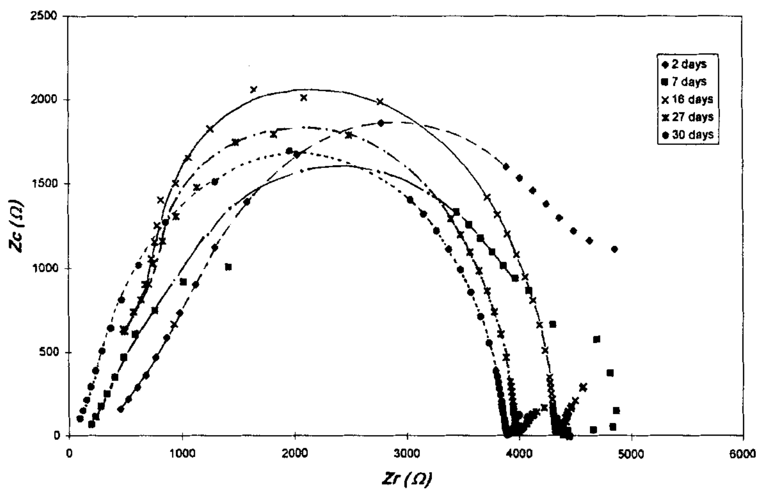

FIGURE 2 Complex impedance plots at different aging time.

The complex dielectric constant is given by

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \tag{1}$$

Where (ε') and (ε'') are the real and the imaginary components of the dielectric constant, respectively, and are given by

$$\varepsilon' = \frac{Z_c}{2\pi f C_o Z^2} \tag{2}$$

And

$$\varepsilon'' = \frac{Z_r}{2\pi f C_o Z^2} \tag{3}$$

Where, C_o is the capacitance of the electrodes and f is the frequency. The variation of the dielectric constant with frequency is shown in Figure 3. The frequency dispersion at low frequency indicates that the blended membrane is polar [14], it also indicates that the polar molecules in the membrane can rotate with the direction of the electric field at low frequency while at high frequencies their rotation is blocked. The low-frequency dispersion arises from the localized charge carrier

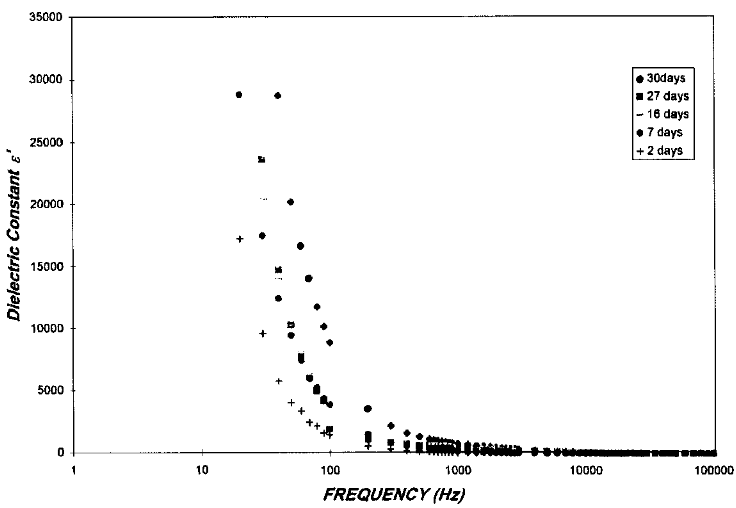

FIGURE 3 The dependence of the dielectric constant on frequency for different aging time.

conduction, which is characterized by a diffusive ion transport mechanism in PEO [15]. The dielectric loss increases with increasing the aging time as shown in Figure 4. The interaction between the membrane and the electrolyte medium may occurs through diffusion and absorption, which may lead, to large losses and thus increasing ionic mobility.

The Cole–Cole plots for different temperatures are shown in Figure 5 and show distorted semi-circles. The impedance real component was found to decrease with increasing temperature indicating that ionic conductivity increases with temperature. Figure 6 represents the variation of (ε') with temperature at constant frequency and for 30 days aging. The variation ε' indicates that when temperature rises the orientation of dipoles is facilitated and hence increases the dielectric constant (ε').

The tanloss for different frequencies and different temperatures is shown in Figure 7. This plot indicates that the membrane is polar. The shape of the tanloss is determined mainly by polarization and electrical conduction losses.

Figure 8 shows the AC conductivity (σ) obtained for different temperatures. The AC conductivity was calculated using the relation-

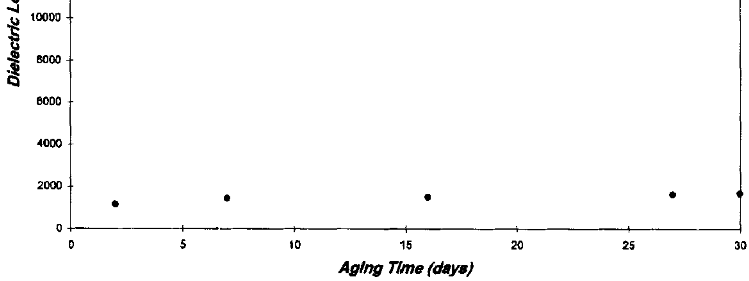

FIGURE 4 The variation of the dielectric loss with aging time.

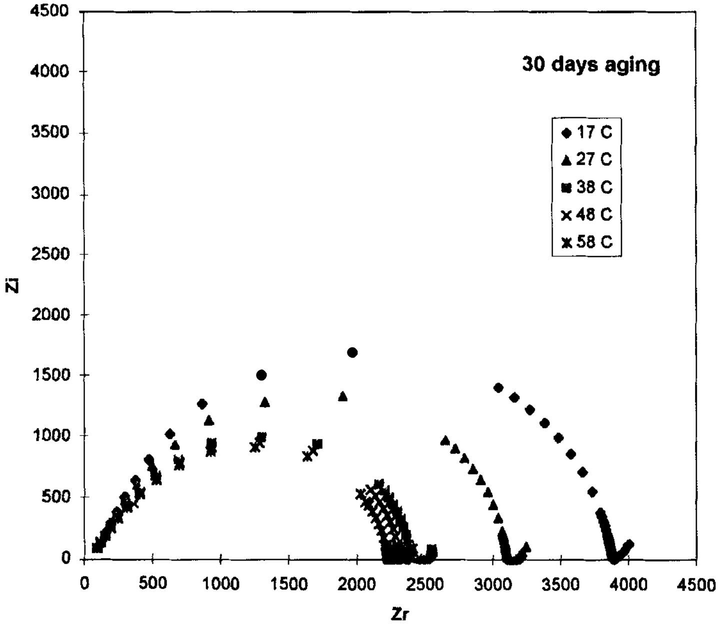

FIGURE 5 The Cole–Cole plot at different temperatures.

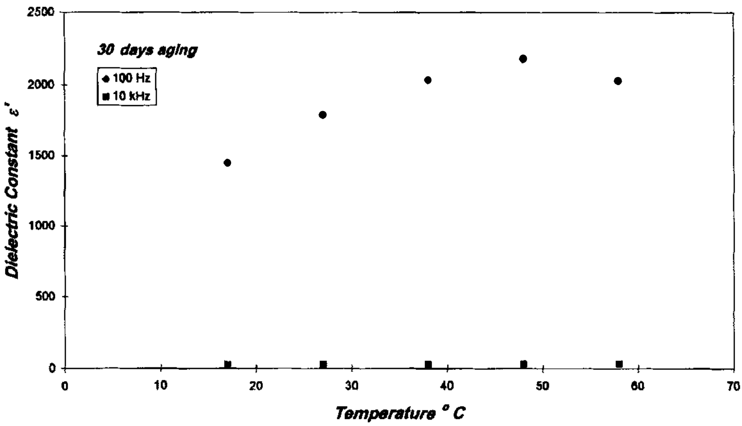

FIGURE 6 The variation of dielectric constant with temperature at constant frequencies.

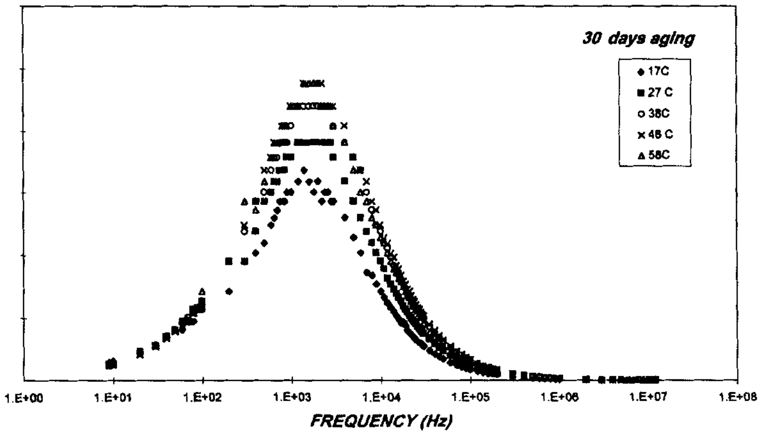

FIGURE 7 The temperature dependence of the tanloss at different frequencies.

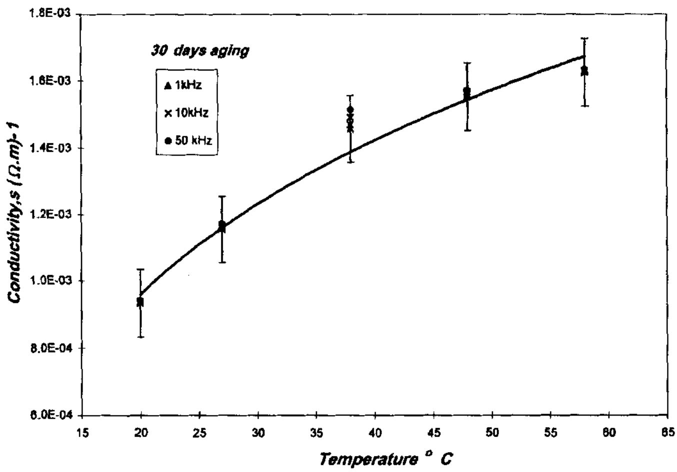

FIGURE 8 The AC-conductivity as a function of temperature for different frequencies.

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$$\sigma_{AC} = 2\pi f \varepsilon_o \varepsilon'' \quad (4)$$

It can be seen from the plot that the conductivity increases almost linearly with temperature. The activation energy listed in Table I was

TABLE I The values of activation energy for 50 wt.% PVC/PEO at temperatures range from 17°C to 58°C

Frequency	*Activation energy* (*eV*)
100 Hz	~0.19
1 KHz	~0.18
10 KHz	~0.15
25 KHz	~0.12
50 KHz	~0.10

calculated using Arhenuis equation [17].

$$\sigma = \sigma_o \exp(-E_a/kT). \tag{5}$$

The decreased values of activation energy with increasing frequency, reflect higher conductivity of the blended membrane.

4. CONCLUSIONS

The electrical behavior of the PVC/PEO blended membranes was investigated as a function of frequency, temperatures and aging time. From the obtained results the following conclusions may be drawn:

1. Temperature, frequency and aging time affect the dielectric behavior of the blended membrane and enhance the ionic conduction process.
2. The AC conductivity increases with temperature, frequency and aging time.
3. The activation energy of the thermal process decreases with temperature due to enhancement of the ionic conduction in the membrane bulk.
4. The enhanced ionic conduction suggests the suitability of the prepared blended membranes to be used in the ion-selective electrode technology.

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