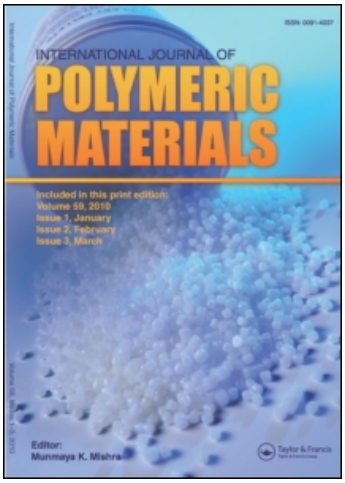

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Temperature dependence of the electrical properties of Poly(ethylene oxide)/salt complex composite

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TEMPERATURE DEPENDENCE OF THE ELECTRICAL PROPERTIES OF POLY(ETHYLENE OXIDE)/SALT COMPLEX COMPOSITE

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The electrical properties of Poly(ethylene)/Salt complex membrane containing 50 wt.% natural salts evaporated from the Dead Sea water were studied as a function of temperature in the range 25–55°C through the impedance technique. It was found that the impedance decreases and the AC ionic conductivity increases with increasing temperature. The variation in the dielectric constants, relaxation time and activation energy with temperature are discussed. It was found that the observed relaxation peak is shifted to higher frequency as the temperature is increased. Thus, it was seen that addition of the Dead Sea salt complex can improve the electrical conduction behavior of the prepared composite.

Keywords: electrical properties, salt complex membrane, temperature, ionic conductivity, frequency, relaxation, activation, energy

1. INTRODUCTION

Recent years have witnessed a growing interest in studying solid polymer electrolytes which are solvent-free ion conducting and provide new and attractive applications in solid batteries, smart windows,

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S. Saq'an is on a sabbatical leave from Jordan University of Science and Technology.

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components in signal sensors and electrical transistors [1–3]. For example, the poly(ethylene oxide) polymer (PEO) has a wide range of applications including the use as pharmaceutical excipients, food additives and placitizers [4]. Much progress has been made in studying the electrical conduction in the PEO polymer since the work of Wright [5] and Armond [6].

A strong interest has appeared to focus research on developing new polymeric electrolytes as blends and composites to be used in promising electrical applications. The blending of PEO with other polymers has been adopted as a strategy for enhancing its mechanical stability [5]. Polymeric membranes with ion selective transport are of importance for many electrochemistry applications [6–8]. Fanggao *et al.* [9] carried out impedance measurements in the frequency range [5 Hz–10 MHz] on pure PEO and observed a large increase in the dielectric constants when temperature approaches the melting point of the polymer Wanchart *et al.* [10] found that the electrical conductivity mixtures of consisting of PEO and KSCN takes a low value at certain ratio, while at other ratios the conductivity is high. Keld *et al.* [11] reported the conductance temperature dependence of PEO/$Hg(ClO_4)$ system at different ratio of ethylene oxide units. Wright [5] determined a wide range of activation energies in PEO/$LiClO_4$ system. He found that the thermal activation energies decreases as the salts complex content decreases in the electrolyte polymer. Tzong *et al.* [12] studied the effect of PVF polymer on the ionic conductivity of PEO/salt electrolytes.

Recently, a series of studies has been carried out in our "Physics of Materials Laboratory". Ramadin *et al.* [13] studied the optical properties (in the UV-visible region) of PEO matrix containing up to 50 wt.% Dead Sea salt and found the optical energy gap depends on the salt content. Al-Jamali [14] studied the electrical characterization of PEO/Dead Sea salt system as a function of applied electric field frequency and salt concentration using the powerful impedance technique. His study covers the AC conductivity, dielectric constants and activation energy. Eid *et al.* [15] studied the dielectric properties and the ion-selective conduction in PVC/PEO blended membrane of different composition immersed in electrolyte. Al-Khouli *et al.* [16] studied the effect of the molecular weight of PEO, frequency and temperature on the AC conductivity and dielectric properties of PVC/PEO blended membrane. It was found that increasing temperature and frequency enhances the AC conductivity of the membrane; and lowering the molecular weight gives higher conductivity due to lower viscosity and higher content of polar hydroxyl groups. Ahmad *et al.* [17] studied the optoelectrical properties of PEO/Alum

composite and presented a reasonable correlation between the observed optical energy gaps and the AC conductivity. They attributed the enhancement in the electrical quantities to impurity and ionic interaction that takes place in the bulk of the double electrolyte solid solution.

In the present study, the thermal electrical behavior of Poly-(ethylene oxide)/salt complex membrane containing 50 wt.% salts evaporated from the Dead Sea is investigated as a function of temperature using the impedance spectroscopy technique reported in previous publications of our research work [17–19].

2. EXPERIMENTAL

2.1. Materials and Membrane Preparation

The filler dispersed in the PEO matrix are salt complexes evaporated from the Dead Sea (located in Jordan) water which approximately contains: NaCl : 7.81%; KCl : 1.22%; $MgCl_2$: 14.48%; $MgBr_2$: 0.48%; $CaCl_2$: 3.78%; H_2O : 72.24% in weight and other minor complex elements [20]. The Poly(ethylene oxide) resin of 5 millions molecular weight was obtained from the CNR (Napoli) of Italy. The seawater was evaporated and the remaining salts were ground to fine powder. Equal weights of PEO resin and salts were dissolved separately in methanol at 30°C. The two solutions were mixed and stirred by a magnetic stirrer for one hour. The final solution was cast into thin films of (0.1–0.34 mm) thickness. The solvent (methanol) was carefully evaporated for a long time at different temperatures. The films were successively weighted to constant weight.

2.2. Impedance Measurements

The phase angle and the AC-impedance of the given composite were measured by HB gain-phase meter. This instrument is capable of measuring directly the ratio of the input to the output signals in dB and the phase angle in degrees as a function of frequency. The real component (ε') and the imaginary component (ε'') of the complex dielectric constant (ε^*) are related to impedance (Z) and phase angle as:

$$\varepsilon' = Z_c/2\pi f C_0 Z^2 \tag{1}$$

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

where f is the frequency, $C_0 = \varepsilon_0 A/d$ is the electrodes capacitance, d the specimen thickness, ε_0 the permitivity of free space, A the area of the

disk, Z_c and Z_r are the imaginary and real components of the complex impedance ($Z = Z_r - jZ_c$), respectively [20, 21]. The AC electrical conductivity (σ) was calculated from the relationship:

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

3. RESULTS AND DISCUSSION

Studying the electrical and dielectric behavior by the powerful impedance spectroscopy is a promising technique to characterize the material properties to be utilized in advanced technologies. Impedance measurements were carried out in temperature range from 25°C to 55°C and frequency range 10 Hz–10 MHz. Since the added Salt complexes are mainly chlorides the prepared membranes consist of double electrolyte substances (chlorides plus PEO polymer).

Figure 1 shows the variation of the phase angle with the applied field frequency at different temperatures. It can be noticed that the values of the phase angle are negative indicating that the bulk material for the filled PEO films can be represented by equivalent RC network in parallel [23]. The figure also shows that the phase angle takes higher negative value with increasing temperature, but the membrane is still capacitive even at salt filler of amount 50 wt.%. The decrease in impedance values with temperature as shown in Figure 2 indicates enhancement of ionic conduction in the bulk of the prepared membranes.

The real (Z_r) and imaginary (Z_c) components of the AC complex impedance ($Z^* = Z_r - jZ_c$) were calculated from the (Z^*) and phase angle [18]. A plot of (Z_c) *versus* (Z_r) at different temperatures is shown in Figure 3, which yields Cole–Cole plots (distorted semicircles) with intercepts on the (Z_r) axis decreasing with increasing temperature. This decrease in the resistive part (Z_r) of filled (PEO) membrane is due to the decrease of the bulk resistance, *i.e.*, increase in the ionic mobility. From the distorted Cole–Cole plots one can approximately calculate the relaxation time and the activation energy of the thermal conduction process. Assuming undistorted semicircles, the maximum values of (Z_c) were obtained from the Cole–Cole plots of Figure 3, and the corresponding maximum frequency (ω_{max}) values using the relation ($\omega_{max}\tau = 1$) which gives the relaxation time (τ). Figure 4 shows a decrease in the relaxation time of the conduction process as a function of temperature. Also this is an indication that the ions transport in the filled polymer is increasing and thus the ionic conduction is enhanced by raising the temperature. Assuming the temperature dependence of the relaxation time (τ) follows an Arrhenius law, then:

$$\tau = \tau_0 e^{-E_a/RT} \tag{4}$$

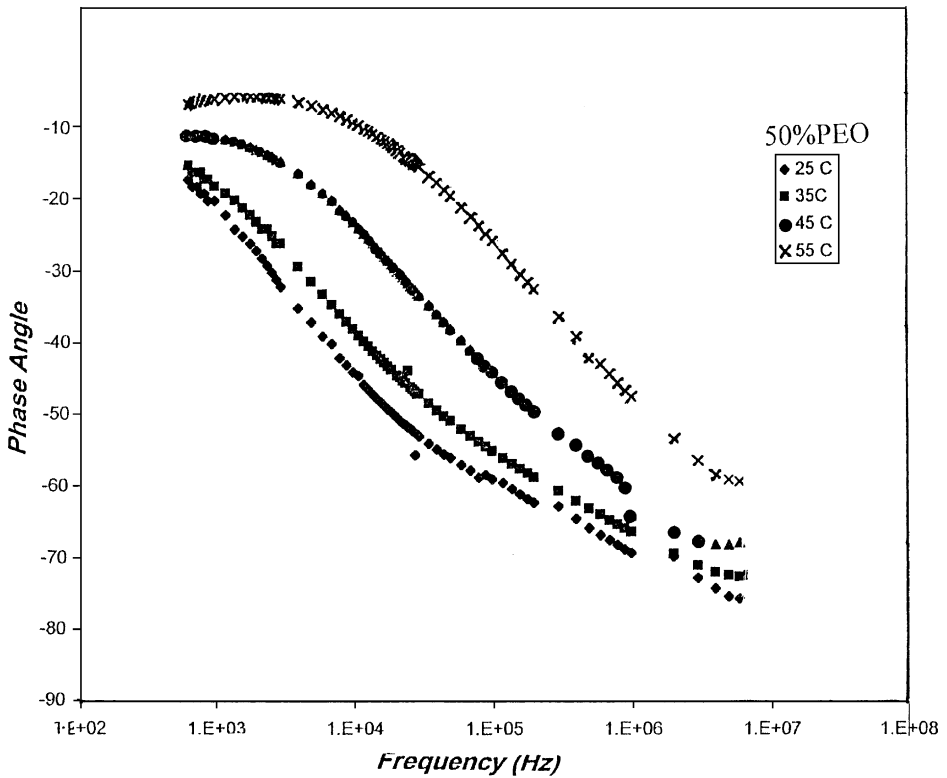

FIGURE 1 Phase angle *vs.* frequency at different temperatures for 50 wt.% Salt complex/PEO composite.

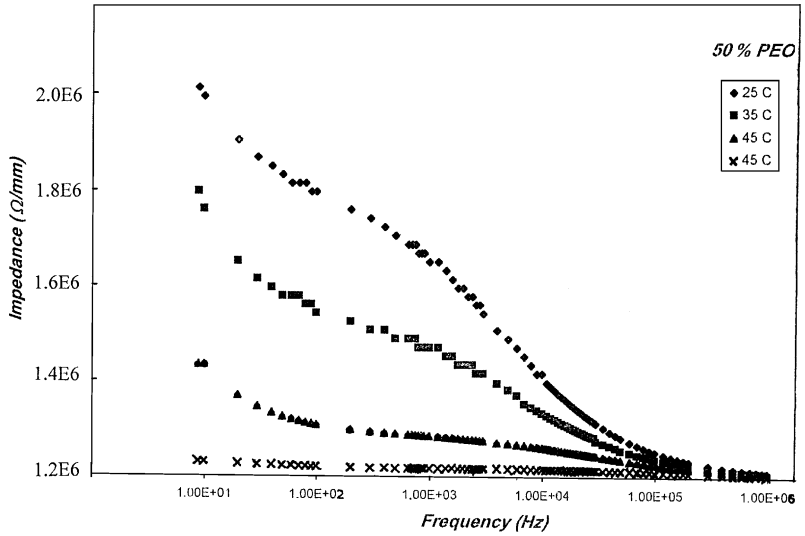

FIGURE 2 Impedance dependence on frequency at different temperatures.

where τ_0 is the relaxation time at infinite temperature, E_a the activation energy, T is the absolute temperature, and R is the universal gas constant. Taking ($\tau = 1/\omega_{max}$) at which the (Z_c) exhibits maxima, and plotting (ln ω_{max}) against (1/T) as shown in Figure 5 a linear Arrhenius plot gives (E_a) value of about 0.96 eV for 50 wt.% filled PEO polymer. The error in this estimated value of (E_a) is about ± 0.02 eV.

Figure 6 shows the frequency dependence of the dielectric constant (ε') on frequency at different temperatures, 25,35,45 and 55°C. It can be seen that the (ε') values are high at low frequency (<100 H_z) due to the electrode polarization effect; and the (ε') is higher at higher temperature due to the thermal behavior of ions transport process in the filled (treated) PEO membrane. Figure 7 shows the tan loss dependence on frequency at different temperatures. The relaxation peaks shift with increasing frequency, and the (ω_{max}) or the intensity of relaxation peaks increases as the temperature increases due to facilitating the dipoles rotation under the thermal effect. Also, a plot of (ω_{max}) of the relaxation peaks against the reciprocal of temperature results in a straight line whose slope gives (E_a) a value of about 0.94 eV which is consistent with that reported value [23]. The calculated value of the activation energy of the observed relaxation process is near the activation energy of the β process in polar polymers, which is attributed to rotation of the side polar groups around the chain axes [24, 25].

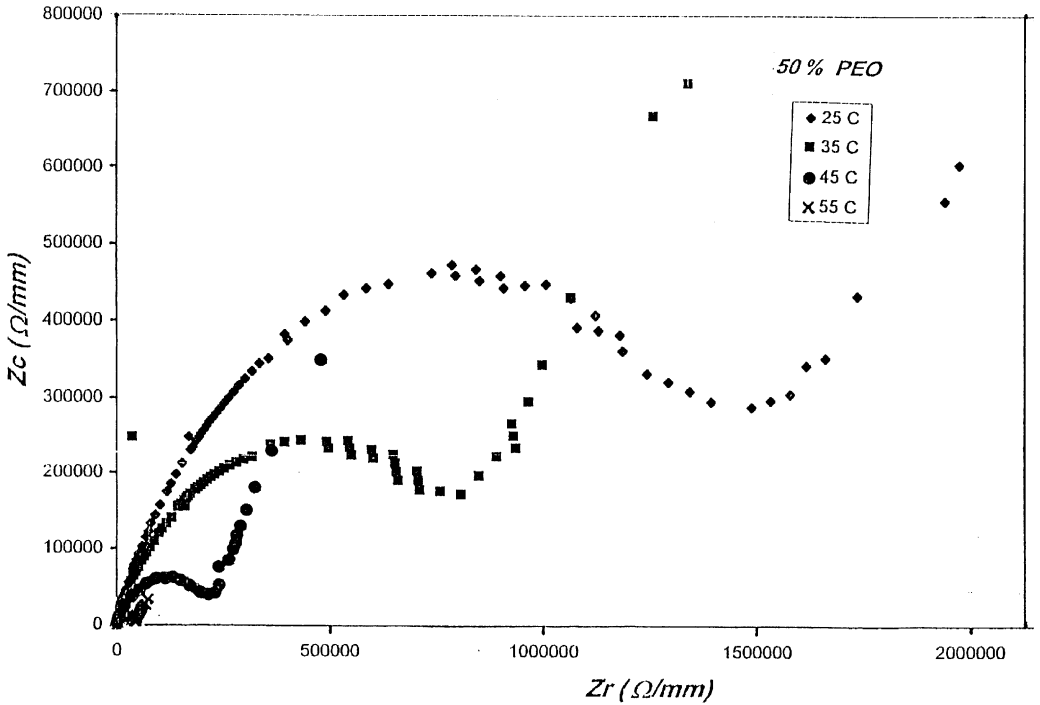

FIGURE 3 Z_c (imaginary component) *vs.* Z_r (real component) of the complex impedance (Z) at different temperatures.

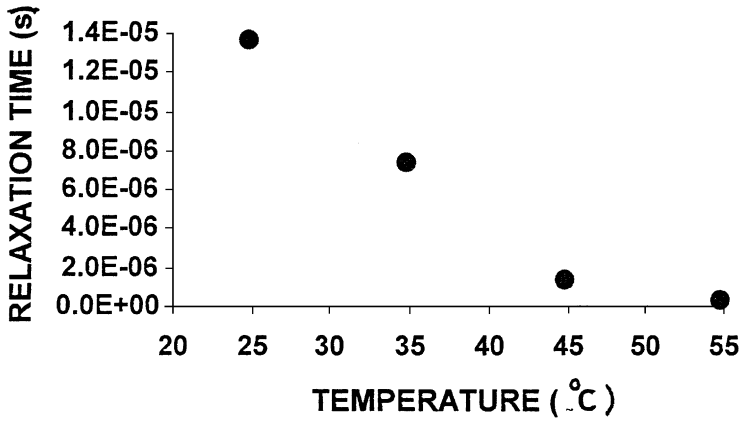

FIGURE 4 Dependence of the relaxation time on temperature.

Figure 8 shows the AC conductivity dependence on frequency at different temperatures for the 50 wt.% PEO/salt membrane. The AC conductivity (σ_{AC}) was calculated from the known equation for the ionic conduction:

$$\sigma_{AC} = 2\pi f \varepsilon_0 \varepsilon'' \tag{5}$$

where (ε_0) is the permitivity of space and (ε'') is the dielectric loss calculated from the (Z_c) and (Z_r) data [16–18] . The (σ_{AC}) increases with the applied field frequency and enhances with temperature. The (σ_{AC}) increases rapidly at high frequencies ($>10^4$ Hz) and this is expected since at higher applied field more ions and charges move, resulting in enhancement of the ion conduction process. The variation of (σ_{AC}) with temperature at different frequencies is shown in Figure 9. The dominant ionic (σ_{AC}) increases rapidly with temperature. Using the Arhenius type equation:

$$\sigma = \sigma_0 e^{-E_a/kT} \tag{6}$$

where k is the Boltzman constant, σ_0 is the material constant, T the absolute temperature. The activation energy (E_a) was calculated from the approximated slope of the straight line of ln σ_{AC} *versus* (1000/T). The dependence of the (E_a) on frequency for thermally activated ionic conduction process is shown in Figure 10. The decrease in the activation energy values reflects higher ionic conduction and protonic migration transported through the ethereal oxygens of PEO in the PEO/salt membrane. Finally, it seems that addition of the Dead Sea salt complexes can improve the electrical behavior of the prepared membranes. It is expected that the protonic migration in the PEO

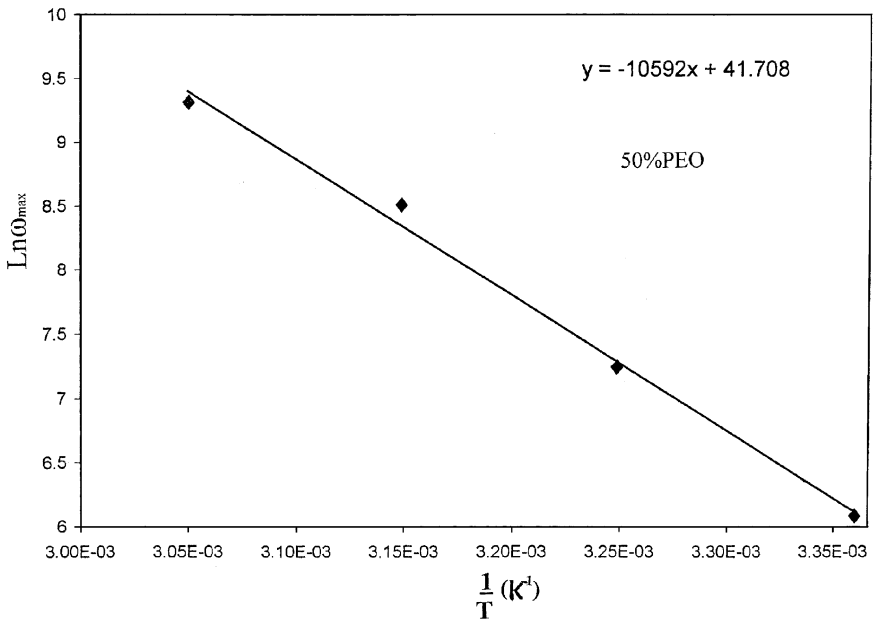

FIGURE 5 Ln ω_{max} *vs.* (1/T).

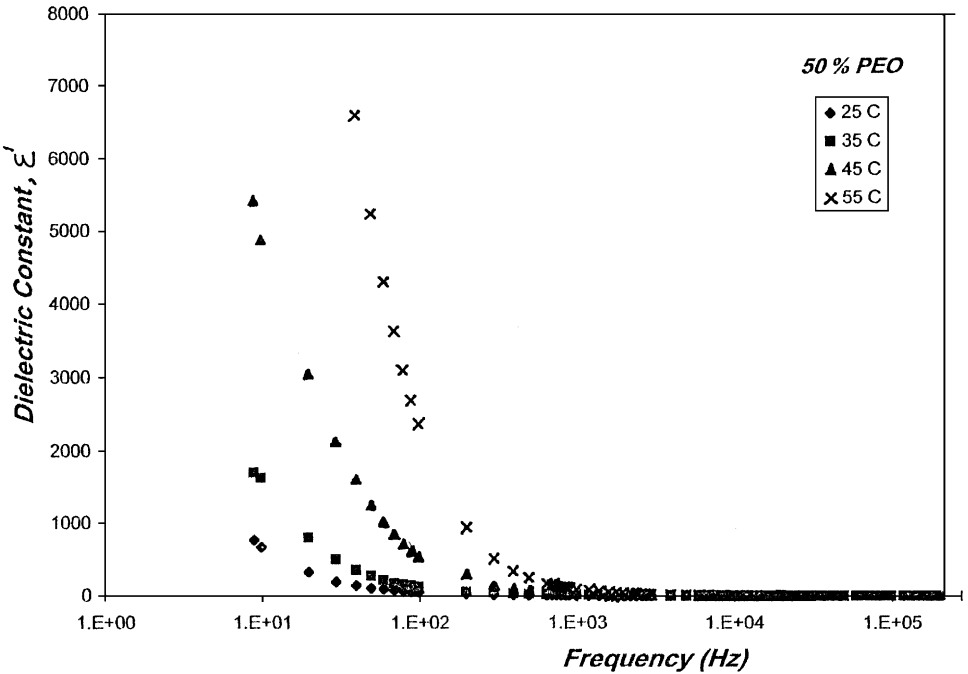

FIGURE 6 Variation of the dielectric constant with frequency at different temperatures.

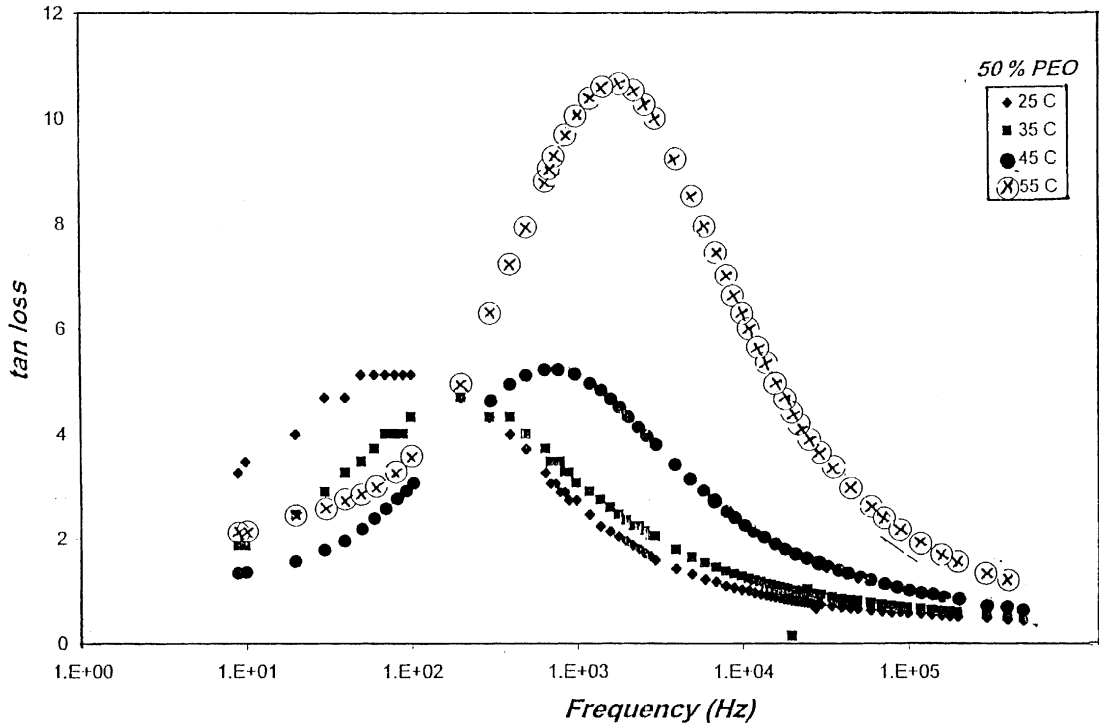

FIGURE 7 Variation of the tanloss with frequency at different temperatures.

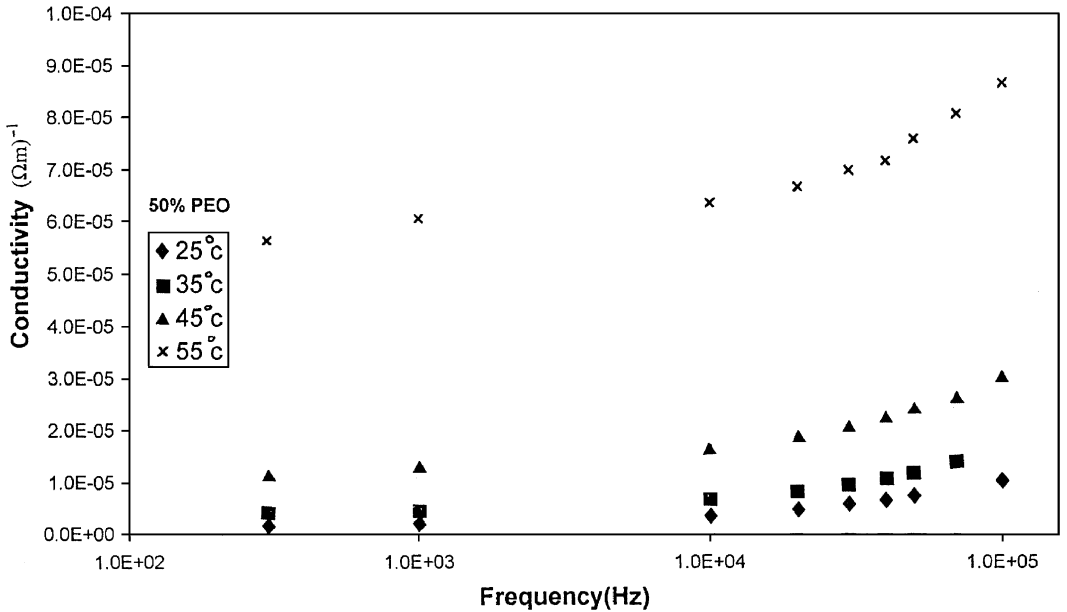

FIGURE 8 Dependence of the AC conductivity on frequency.

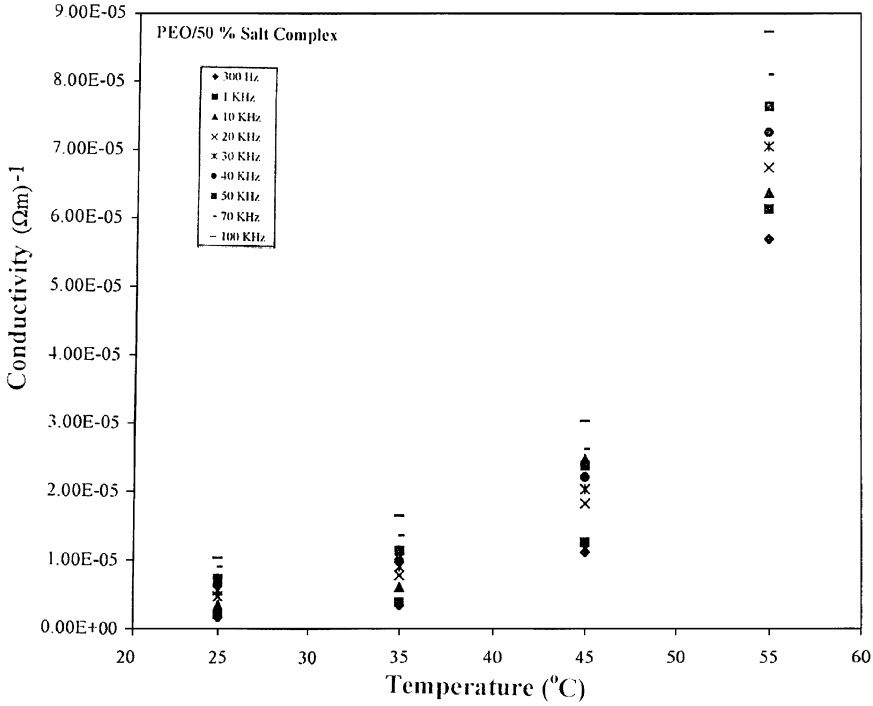

FIGURE 9 Dependence of the AC conductivity on temperature.

polymer and the ion exchanges in chlorides are accelerated under the effect of higher temperature [26, 27].

4. CONCLUSIONS

The research work presented in this paper deals with the effect of temperature on the electrical properties of poly(ethylene Oxide)/Salt complex membrane containing 50 wt.% salt evaporated from the Dead Sea water. The AC conductivity and the dielectric behavior were studied as a function of temperature and in the applied electric field frequency (10 Hz-10^6 Hz). From the obtained results the following conclusions are drawn:

(1) Temperature, frequency and salt content affect the electrical behavior of the PEO membrane.
(2) Temperature enhances the AC ionic conductivity measured at different frequencies, it creates an excess of moveable ions and other charged impurities.

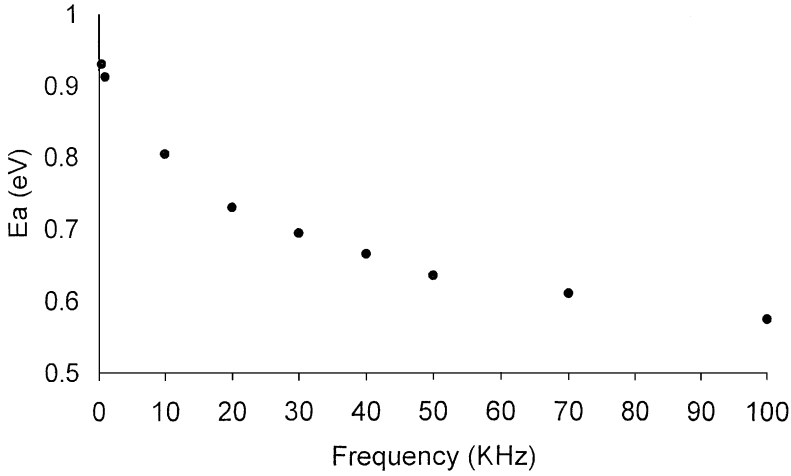

FIGURE 10 Variation of the activation energy with frequency under different temperatures.

(3) The tan loss relaxation peak shifts to higher frequency as the temperature is increased, and the relaxation time decreases with temperature.
(4) The intensity of the relaxation peak is higher at higher temperature indicating that the mobility of the polymer chains increases.
(5) The activation energy of the conduction mechanism showed temperature and frequency dependence.

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