The Effect of Addition 0.1 % by Weight Sodium Iodide on Activation Energy of Polyethylene Oxide Films

Husam Miqdad [*], **Ibrahim Abdel-Rahman**[**]**, Ayssar Nahlé**[**]

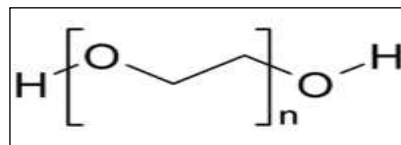[*] Department of Basic Science, Applied Science Private University

[**] Chemistry Department, College of Sciences, University of Sharjah, P.O. Box: 27272, UAE.

Abstract

The activation energy of thin films polymers made of pure polyethylene oxide (PEO) and PEO doped with sodium iodide (0.1 % wt.) was investigated. The observed physical constants of the casted thin films such as the activation energy (Ea) were determined. The films were prepared by casting method using electricity. The present study investigated the variation of the activation energy of thin films of pure (PEO) and PEO doped with sodium iodide (0.1 % wt.) with the variation in frequency in the range of (200-800) kHz and in the temperature range between (30 -55) °C. The results proved that there is a significant change in the values of the activation energy (Ea) for both studied thin films with the variation in frequency. It was found that the values of the (Ea) of the prepared thin films are decreased by doping PEO with sodium iodide (0.1 % wt.). The values of (Ea) for both studied thin films decrease with the increase in frequency.

Keywords: PEO, sodium iodide, activation energy, frequency, temperature.

I. INTRODUCTION

Polymer composites and polymer electrolytes are the most widely used materials in the past few decades, which have a wide range of applications in the automotive, aerospace, and construction industries. Most polymeric materials are poor conductors of electricity because of the unavailability of large number of free electrons or ions to participate in the conduction process, so a great attention was focused on enhancing their electrical conduction and improving their properties. So, to promote optical and electrical properties of polymeric materials, many different materials were added as conductors to produce polymers electrolytes and polymer composites [1].

Because of their desired qualities that made them preferable to other commercial materials, conductive polymer composites (CPC) have sparked a lot of interest in various industrial applications. The change from insulating to conductive behavior, achieved by adding various conducting elements such as metallic particles, carbon or steel fibers, aluminum flakes, and sodium iodide. The addition of sodium iodide is an important aspect of these qualities. Thermoplastic polyethylene is a good insulator in general. Polymers containing conductive fillers are sometimes referred to as conductive polymer composites. These fillers provide the composite its conducting qualities [2]. The study of (CPC) for numerous industrial applications have sparked a lot of interest. The term CPC refer to the process of combining conductive particles with insulating polymers to change their electrical characteristics [3].

Polyethylene Oxide (PEO) is a nonionic homopolymer of ethylene oxide, represented by the formula $(-CH_2CH_2O-)n$, in which n represents the average number of oxyethylene group in the polymer and its chemical structure is represented in the below formula:

Polyethylene oxide (PEO) is a synthetic polyether that is readily available in a range of molecular weights (M. wt.). Polymers with (M. wt.) <100,000 g/mol are usually called polyethylene glycol (PEG), while polymers with higher than that value are classified as PEO.

Polyethylene oxide is a well-known thermoplastic polymer that can be classified as either crystalline or non-crystalline (amorphous). PEO is a synthetic polyether with the ability to create molecular complexes that improve electrical conductivity [4]. It is widely available in a variety of molecular weights. PEO refers to polymers with a molecular weight greater than 200,000 g/mol, and depending on their molecular weights, they behave as liquids or solids with low melting points [5].

Polyethylene oxide is a familiar example of the thermoplastic polymers, which can be further sub-divided into amorphous and crystalline polymers as represented in Table 1.

Table 1.
Physical properties of Polyethylene oxide (PEO)

Appearance	White Powder
Melting Point (Molecular Weight > 200, 000)	65 °C
Refractive index	1.456
Dielectric constant	4.5
Glass Transition Temperatures (Tg)	- 65 °C

Sodium iodide is known to form polymer complexes when doped into polymers. The addition of sodium iodide to polymers affects their electrical and dielectric properties, conductivity, charge storage capacity, dielectric loss, dipole moment and relaxation time [6]. Sodium iodide, when doped in polymers, may reside at various sites. It may go substitutionally into the polymer chains, or reside at the amorphous/crystalline and diffuse preferentially through the amorphous region forming charge transfer complex (CTC), or may exist in the form of molecular aggregates between the polymer chains [7].

In this work, sodium iodide was used as a filler. Sodium iodide is a white, crystalline salt with chemical formula NaI. It is a kind of scintillation crystal with good properties. It has a very high luminescence efficiency with melting point 661°C. It is used in radiation detection, treatment of iodine deficiency, nuclear medicine and in many other applications, such as x-ray detectors with high spectrometric quality. Sodium iodide crystallizes in the FCC space group, with four sodium and four iodide atoms per unit cell. Sodium iodide is known to form polymer halogen complexes when doped into polymers, and to affect their electrical and dielectric properties, conductivity, charge storage capacity, dielectric loss, dipole moment and relaxation time [8].

In this study the activation energy values of pure PEO and PEO doped with sodium iodide (0.1 % wt.) thin films were determined. The results were reported and discussed. The activation energy of pure PEO and PEO doped with sodium iodide (0.1 % wt.) thin films was studied as a function of frequency.

II. EXPERIMENTAL WORK

In this study, pure PEO thin films and PEO doped with sodium iodide thin films were prepared and examined. The activation energy of both films was determined at various frequencies and various temperatures.

A. Preparation of PEO Thin Films

PEO and sodium iodide powders were blended in methanol as a convenient solvent. The mixture was mixed for two days using a rotary magnet to get a homogeneous mixture. The mixture was put on a glass mold and directly casted to delicate films. The films kept at room temperature for two days to remove methanol. Finally, all samples were dried in the oven at a temperature of 40 °C for another two days to remove methanol completely.

B. Measurements of Electrical Properties

Hewlett Packard (HP) 4192A impedance analyzer was used to measure impedance and phase angle values by varying the applied frequency from (5 - 13) MHz's. The specimen was placed firmly between two copper electrodes in a sample holder as shown in Figure 1. These electrodes are connected through cables to the impedance analyzer. Impedance measurements were performed in a frequency range of (200-1000) kHz and a temperature range of (30 – 55) °C with steps of 5 °C. Since the melting point (Tm) for PEO is about 60 °C, no higher temperature measurements were conducted. Temperature readings were taken in a steady state condition.
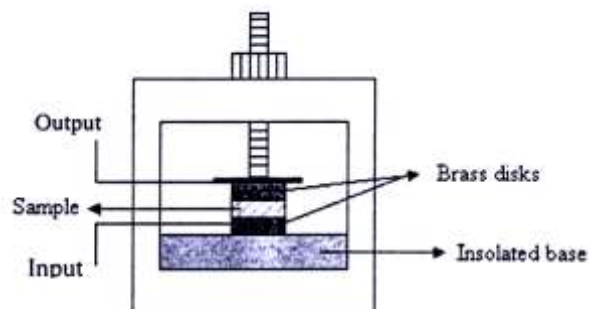

Figure 1. The sample holder diagram impedance analyzer

Dielectric materials are a special class of substances that, under almost all conditions, are insulators. They have the interesting and useful property that their electrons, ions, or molecules may be polarized under the influence of an external electric field. When such materials are placed between charged plates as in capacitors, they increase the total capacity of these devices. This application constitutes one of the important applications of these materials [9].

Connecting a capacitor (C) to a resistor (R) in parallel, the impedance (Z), the real component of the impedance (Z') and the imaginary component of the impedance (Z") of the circuit are represented in the following equations:

$$Z = \frac{R\,(1 - i\omega\,C\,R)}{1 + (\omega\,C\,R)^2} \tag{1}$$

$$Z' = \frac{R}{1 + (\omega\,C\,R)^2} \tag{2}$$

$$Z'' = \frac{\omega\,CR^2}{1 + (\omega\,CR\,)^2} \tag{3}$$

The dielectric constant (ε') which is related to the stored energy within the medium, and the dielectric loss (ε") which is related to the loss of energy within the medium in form of heat generated by an electric field are determined from the following relations [10]:

$$\varepsilon' = \frac{Z''}{2\pi f C_o Z^2} \tag{4}$$

$$\varepsilon'' = \frac{Z'}{2\pi f C_o Z^2} \tag{5}$$

Where, C_0 is the capacitance without the thin film, and f is the frequency (AC) of the electric field.

The AC conductivity (σ_{AC}) of the thin film is given by the following relation:

$$\sigma_{AC} = 2\pi\,f\,\varepsilon_o\,\varepsilon'' \tag{6}$$

Using Arrhenius equation, the activation energy (Ea) of the conduction process is determined, by [11]:

$$\sigma = \sigma_0 \exp\left[- Ea / k_B\,T\right] \tag{7}$$

Where, k_B is the Boltzmann constant, T is the temperature in Kelvin, σ_0 is the material conductivity constant and σ is the electrical conductivity [12].

III.   RESULTS AND DISCUSSION

A dopant sodium iodide appended to the matrix of polyethylene oxide (PEO) to compose solid electrolyte thin films. The role of doping sodium iodide in the process of the activation energy and how it affected by the electric field was studied. The objective of this study is to realize the type and nature of the charge transmission in conducting materials [13].

A.   Activation Energy Determination

The minimum amount of thermal energy that is required to activate ions, atoms, and molecules to do conduction, in which they can undergo physical transition, is known as activation energy (Ea). The values of activation energy were determined from the slopes of the straight lines obtained by drawing the natural logarithm of the conductivity (Ln σ_{AC}) versus (1000/T) for all thin films at the frequencies (200, 400, 600 and 800) kHz as shown in Figures (2 and 3).

By using Arrhenius Equation, the activation energy values were calculated and tabulated in Tables (2 and 3). It was observed that, the activation energy decreases with increasing frequency for all tested composites. The decrease in activation energy reflects an increase in ionic mobility, electrical charge (ionic) and electrical conduction in the membranes of thin composite films [14].

Table 2.
The activation energy values for pure PEO thin films

Frequency (kHz)	Activation Energy $\times 10^2$ (eV)
200	39
400	33
600	31
800	29

Table 3.
The activation energy values for PEO with sodium iodide (0.1 % wt.) composites thin films

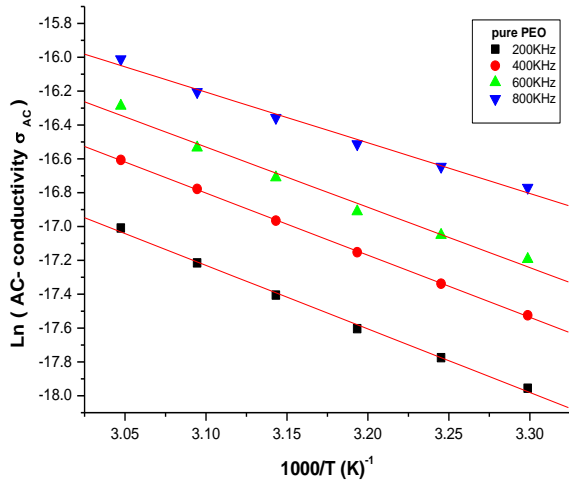| Frequency (kHz)	Activation Energy $\times 10^2$ (eV)
200	25
400	23
600	22
800	19

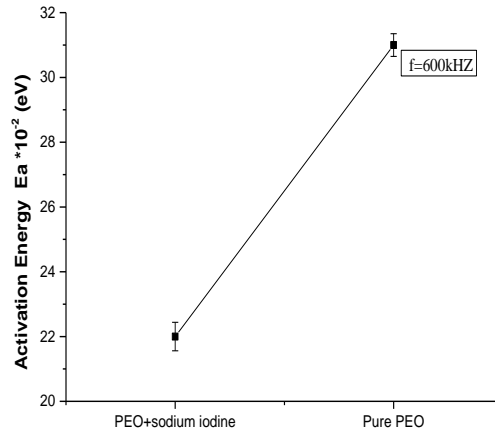Figure 2. Ln (AC-conductivity) versus (1000/T) for PEO/ sodium iodide (0.1 % wt.) thin films

Figure 4. Variation of (Ea) values of pure PEO and PEO/sodium iodide (0.1 % wt.) thin films at 600 kHz
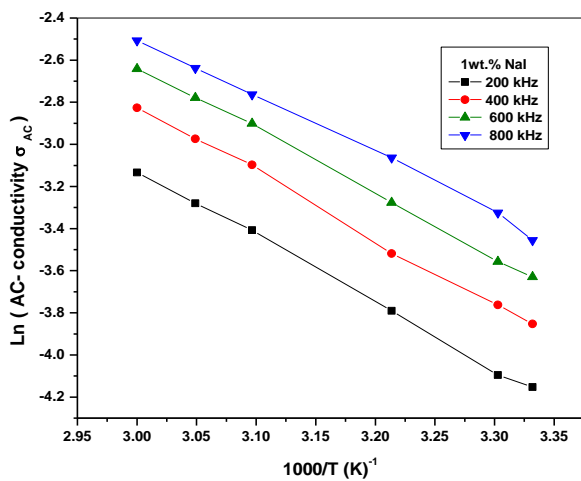

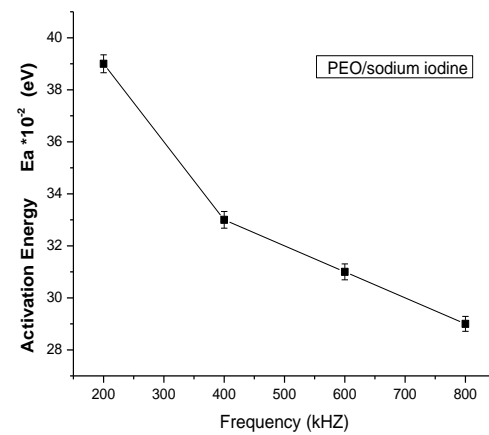Figure 3. Ln (AC-conductivity) versus (1000/T) for pure PEO thin films

Figure 5. Variation of (Ea) values with frequency for PEO/ sodium iodide (0.1 % wt.) thin films

Figure 4 shows that, the activation energy value of pure PEO films at 600 kHz decreases from 31×10^{-2} eV to 22×10^{-2} eV of PEO doped with sodium iodide (0.1 % wt.). This noticed reduction in activation energy value means that the polyethylene oxide/sodium iodide thin films energy levels become narrower to each other than in pure PEO films.

Figure 5 shows that the activation energy (Ea) decreases with increasing the frequency, because at higher field, more charges are moved, causing more participation of activated charges to the conduction band. It can be clearly noticed that the (Ea) decreases with the increase in frequency and with the addition of sodium iodine to PEO films.

This observed decreases in Ea value implies that the energy of the prepared polyethylene oxide / sodium iodide thin films becomes narrower due to creation of localized energy states by heating which enhances the ion mobility and ability of the electron to tunnel or hop easily from the valence band to conduction energy band. Similar observations were reported by Mohan et. al. on a study of the DC conductivity of PEO complexes with Fluorides, and attributed the increases in the conductivity to some structural transitions from crystalline phase of the polymer to amorphous phase. These events increase the amorphous region in the polymer PEO and produce more active segmental motion which stimulates the electron hopping mechanism and thus the conductivity becomes high. In this study, the observed increase in conductivity and decrease in the activation energy values with the addition of NaI or with the increase in temperature can be dominated by the mobility in the localized states bridged by the doped NaI molecules in the amorphous regions existing in the solid polymer electrolyte.

The low activation energy for sodium ion transport is due to the completely amorphous nature of polymer electrolyte that facilitates the fast Na+ ions motions in the polymer network [15,16].

In Fig 6, the conductivity of thin films increases with increasing frequency, which can be attributed to the increase in the ability of the electron to tunnel or jump from the valence shell to the conduction energy band and increases ion mobility. These transitions increase the amorphous region in the polymer PEO and produce more active segmental motions which stimulate the electron hopping mechanism and thus the conductivity becomes higher. In this study, the noticed increase in conductivity and reduction in the (Ea) values with increasing frequency or the doping of sodium iodide with PEO could be controlled by the mobility in the localized positions bridged by the particles of sodium iodide in the amorphous regions present in the polymer electrolyte. The low (Ea) for charges in the sodium iodide transition refers to the amorphous nature of polymer which simplifies the rapid electrons movements in the polymer complex [17,18].
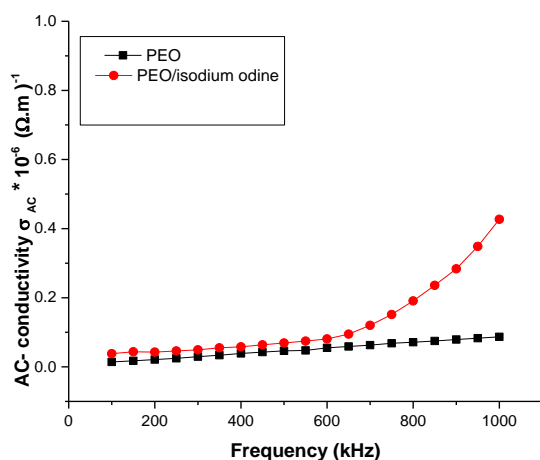

Figure 6. Dependence of AC conductivity for pure PEO and PEO/sodium iodide thin films as a function of frequency

IV. CONCLUSIONS

The activation energy (Ea) values of the thin films of pure PEO and PEO doped with (o.1 % wt.) sodium iodine were determined. From the results, the following can be concluded:

- The activation energy of PEO doped with sodium iodine films is lower than pure PEO films.

- The activation energy decreases with increasing frequency for both studied films.

- The activation energy decreases with increasing temperature for both studied films.

- The conductivity increases with increasing temperature for both studied films.

References

[1] Al-Faleh , R. S. and Zihlif, A. M. (2011), A study on optical absorption and constants of doped poly(ethylene oxide). Physica B , 406, 1919-1925.

[2] Myers, H. P., Introductory Solid State Physics 1990; Taylor and Francis, London.

[3] Romas, M. Al-Juma ily, A. and Puli, V. , Conductive Polymer-Composite Sensor for Gas Detection. 1st International Conference on Sensing Technology 2005;November 21-23.

[4] Fanggao, C. Saunders, G. Lanbson, E. Hampton, R. ,Temperature and Frequency Dependence of the Complex Dielectric Constant of Poly (Ethylene Oxide) Under Hydrostatic Pressure, Journal of Polymer Science 1996; 34:425-433.

[5] Epifanov, G.I., Solid State Physics 1979; 1st edition. Mir Publisher Moscow.

[6] (www.rotaperiod.com, Abdul Ghafor,2000, Lewis and Taylor, 1972).Abdul Ghafor, W.A.S. (2000), Hussain, W.A. Electrical properties of (Poly 8-hydroxy.quinoline 5,7diyl methylene) Thin Films. J.Polymer Science part B Polymer Physics 38: 2507-2514.

[7] Mehendru, P.C and Suresh Chand.(1983), Effect of sodiumiodine on depola rization behavior ofpolyvnyl fluoride (PVF) films. J. Phys. D: Appl. Phys.,1 6: 185-188.

[8] Neyertz, S., Brown, D., Thomas, J.(1995). Molecular dynamics simulation of the crystalline phase of Poly (ethylene oxide)- Sodium iodide, PEO3 NaI, Electrochemica Acta,Vol. 40.

[9] Pollock, D., (1993). Physical Properties of Materials for Engineers. (2nd ed.)CRC Press, Inc.

[10] Rapra Technology LTD, (1996). Polymeric Materials for Electrostatic Applications. UK.

[11] R. H. Crossman, (2004). Conductive Polymer Composites Polym. Journal of Engineering Science, 25 :507-513.

[12] Elimat, Z. M., (2006). Electrical and Thermal Conductivity of Poly(methyl methacrylate)/ Sodium iodineComposites. Mu'tah Lil- Buhuth wad-Dirasat, 21(2):169-182.

[13] Jastrzebski, Z. D., The nature and properties of engineering materials 1977; (2nd ed.), New York: John Wiley and Sons.

[14] Hummel, R. E., (1993). Electronic Properties of Materials, (2nd ed.), Springer-Verlag, NewYork.

[15] Agrawal, R. C. , Pandey, G. P. , (2008). Solid polymer electrolytes: materials designing and all-solid-state battery applications: an overview, Journal of Application Physics. 41 - 223001 (18pp).

[16] Ahmad, M.S, Haj Abdallah, M., Zihlif, A.M., Abdelazeez, M.K., (1991). Electrical Properties of Oilshale Rocks. Journal of Materials Science. 26: 203-207.

[17] Bhargav, P. Mohan, V., Sharma,. and Rao,A. (2006) , Structural , Electrical and optical characterization of PVA Polymer electrolyte films, Inter. J. polym. Mater. , 56 579.

[18] Miqdad, H., Abdel-Rahman,I., (2022) , The Activation Energy of Pure Polyethylene Oxide and Polyethylene Oxide Dispersed with Iodine JOURNAL OF SOUTHWEST JIAOTONG UNIVERSITY. 57(6):615-619.

Authors

- **First Author** – Husam Miqdad, Professor (Associate),Applied Science Private University,

- **Second Author** – Ibrahim Abdel-Rahman, Lecturer, University of Sharjah,

- **Third Author** – Ayssar Nahlé, Professor (Associate), University of Sharjah,