Effect of Lithium Chloride Addition on the Electrical Conductivity of Polyvinyl Alcohol Films

Noor M. Jalal[1], Zainab A. Ali[1], Shrok A .Allami[1*], Salma M. Hassan[2], Mutaur R. Ali[1]

[1]*Ministry of Science and Technology. Iraq, Baghdad.*
[2]*Baghdad University, Iraq, baghdad*

ABSTRACT: *In this Study, PVA/ (0.2, 0.4, 0.6, 0.8, 1) wt. % LiCl films were prepared by a casting method. The electrical conductivity of the mixed solutions increased with the addition LiCl to pure PVA solution. To demonstrate the effect of LiCl addition on the PVA films chemical bonds, FTIR investigations were held. Polymeric films D.C electrical conductivity had been studies under different temperatures (273- 373) ̊K. Results showed that DC electrical conductivity increased with increasing LiCl concentration and temperature. It was found that LiCl concentration decreased activation energies of the PVA films.*
Keywords: *PVA, Electrical conductivity, D.C Electrical Properties*

I.   INTRODUCTION

During the past few decades, a great deal of attention has been received to conductive polymers due to their light weight and usage in important applications like rechargeable batteries, chemical and thermal sensors, super capacitors, light emitting diodes, organic solar cells [1,2] and many other applications like dental resin composite reinforcement [3]. Simply conductive polymers are polymers who conduct electricity. They are produced in many methods like chemical, electrochemical, hydrogels, composites and electrospinning processes [4].

Composite polymers are polymers prepared by adding additives to a homogeneous polymers matrix in order to improve or create new properties [5]. Composite materials are one of the modern materials which are widely used in engineering and technological fields [6]. Conventional polymers have many advantages such as easy synthesizing , preparation and fabrication [7] , greater workability, light weight, resistance to corrosion and chemical attack, low cost as well as their properties can be tailored to the required applications [8]. PVA are a conventional polymers well-known as good electrical insulators, in order to enhance the electrical conductivity of insulating polymers, conductive particles such as carbon black, carbon fibers, metals particles or inherently conductive polymers such as polyaniline [9]. This method is used to enhance not only electrical conductivity but also processability, mechanical and physical properties of polymers [10]. Electrical conductivity increased with additives increment. Ionic salts such as ($CaCl_2$, NaCl, AgCl,….etc.) are usually used to enhance the electrical conductivity of polymeric materials. The electrical conductivity as well as the charge density of polymeric solutions increased with increasing the salts concentration, which is responsible for increasing the number of ions in the produced solutions [11].

PVA (Polyvinyl alcohol) is soluble in highly polar and hydrophilic solvents, such as water, Dimethyl Sulfoxide (DMSO), Ethylene Glycol (EG), and N-Methyl Pyrrolidone (NMP) but water is the most important solvent for PVA [12].

(PVA) has exceptional properties such as biodegradability, biocompatibility, non-toxicity, and non-carcinogenetic that possesses the capability to form hydrogels by chemical or physical methods[13]. So PVA introduces into a wide range of industrial applications and high practical importance as viscosity enhancing agents, flocculating agents, as well as food additives [14], pharmaceuticals, paint, textiles, paper, constructions, adhesives, coatings and water treatment [15].

PVA has a hydroxyl group in its structure as shown in Fig. 1. The extent of hydrolysis and content of acetate groups in PVA affect the crystallizability and solubility of PVA [16].
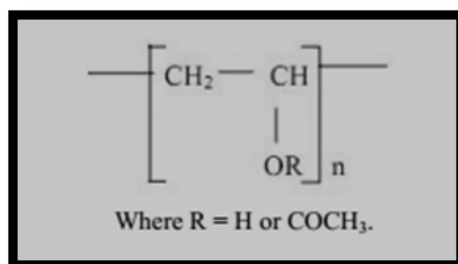
Figure 1: Structure of polyvinyl alcohol.

The solubility of PVA in water depends firstly on the degree of polymerization (DP), secondly on hydrolysis and thirdly on solution temperature. Any change in these three factors will affect the degree and character of hydrogen bonding in the aqueous solutions, and hence the solubility of PVA. It has been reported that PVA grades with high degrees of hydrolysis have low solubility in water [17]. The solubility, viscosity, and surface tension of polymeric solution depend on temperature, concentration, % hydrolysis and molecular weight of the polymer [18].

The DC conductivity in solid materials depends on the presence of free electrons and free positive holes. While the semiconductor materials electrical conductivity is dependent on the temperature because it needs thermal energy for electron excitation to the conduction band. So, for this reason, the electrical conductivity will be a function of temperature [19]. This means when the temperature increases, the movement of charge carriers along the polymer chain will increase too and so increasing in the electrical conductivity. The temperature dependence will give information about the inter-chain conduction in the polymer [20].

In this study, the electrical conductivity of PVA which is an insulating material will be increased by using Lithium Chloride (LiCl) and this will be confirmed by D.C test.

II. EXPERIMENTAL WORK

2.1 Solutions Preparations:

PVA was purchased from SIGMA-ALDRICH CHEMINE Gmbh , USA , PVA molecular weight is 80,000 (g/mol). PVA solution was prepared at concentration 20 % in distilled water at the temperature (203 - 213)°K by stirring for two hours. LiCl atomic weight is 42.39 gm. mol^{-1} was purchased from Scharlau, Spain. 10 wt. %Lithium Chloride solution was prepared by dissolving the salt in the distilled water. PVA with (0.2, 0.4, 0.6, 0.8, and 1) wt. % LiCl was prepared by adding LiCl solution to pure PVA solution, and the obtained solutions were continuously stirred for (3 hours) at room temperature to increase homogeneity.

2.2 Characterization of Prepared Solution, Electrical conductivity:

The electrical conductivity of prepared solutions was measured by electrical conductivity device type (C and 7110 inolab). The probe of the device was dipped in the polymeric solution to read conductivity values. The conductivity of solutions would be measured in mS /cm.

2.3 PVA Films Casting:

After cooling the polymeric solution for sufficient time, the solutions have to be cast in a Petri dish for three days, and then the films would be removed from the Petri dishes.

2.4 PVA Films Characterization.
2.4.1 Thickness Measurement:

Due to the big role of the films thickness in the electrical conductivity measurements as well as in the activation energy estimation, it would be a necessary test for the films. The thickness of PVA films was tested by (COATING THICKNESS METER CM 8829S). The device probe stands vertically over the device substrate and touches the films that put over the substrate slightly, the thickness measured in nm and μm units.

2.4.2 FT-IR

Infrared spectroscopy is considered to be one of the most important techniques for analytical chemists in laboratory and industry. It is a non-destructive technique used for yielding information about the chemical composition and molecule of present samples. Samples may be in the form of powders, liquids, gasses, and films. The advantage of this technique is the multi - component analyses capability, high sensitivity, simple calibration, and speed. FT-IR spectrum is a record for absorption of electromagnetic radiation of the sample in the range of wave number from (4000 - 400) cm -1 [18, 21].

Samples of the PVA films were prepared for FTIR spectrometer (BRUKER , TENSOR-27). FTIR results used to study the effect of additives on the structure and chemical bond on pure PVA and confirm doping taken place. This was done by distinguishing the FT-IR characterization of pure PVA and PVA /0.4 wt.% LiCl films .

2.4.3 Films Preparation for Electrical Conductivity Measurement:
The electrodes used in DC measurement were made by making two squares of Al electrodes by thermal evaporation device with the aid of mask foil [22]. After deposition of Al electrodes, the silver paste will be used to cover the Al electrodes and contact the thin copper wires with the polymeric substrate. Fig. 2 represents the foil template and the silver paste electrodes used in this research
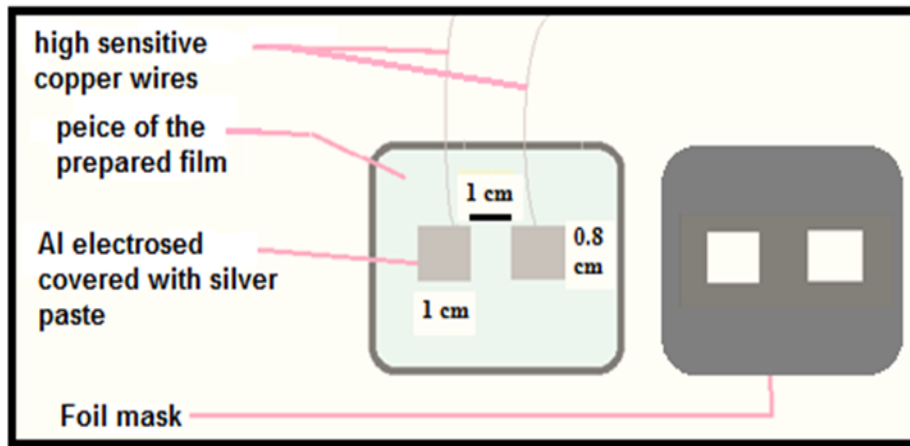

Figure 2: The electrodes connecting to the copper wires with the foil template

Silver paste is used as contact metallization in the microelectronic devices due to its low surface resistivity and thermal stability. Al is used to make ohmic contact between the polymer films and copper wires. Al will be vacuum deposited easily by thermal evaporation device as a result of low boiling point specialized to Al [23]. Silver has lower resistance than that of Aluminum while   Aluminum adheres with the polymeric surfaces better than the silver paste. In general, silver and Aluminum are used for making metallization contacts due to their desired properties like low specific resistivity, good thermal stability, low particle contamination , good adherence to substrate and Low manufacturing costs [24] .

2.4.4 Electrical conductivity of PVA films .
The electrical resistance of the polymeric films has been measured as a function of temperature in the range (20-100)°C. Two Al electrodes adhered by silver paste to the samples, these electrodes connected to a sensitive digital electrometer type KEITHLY 616 and electrical oven type memmert.
In general, we measured the changing in the electrical conductivity with temperature in most cases of semiconducting materials as given by the equation:
$$\sigma = \sigma_{\circ} \exp (Ea / K_B T) \text{ --------- (1)}$$
Ea = activation energy in eV (corresponding to Eg /2 for intrinsic conduction)
T = the absolute temperature in K0, KB = Boltzmann constant = 1.38 x10-23 J/K , and dividing by the electron charge, KB = 8.62 x10-5 eV.
σ o = the minimum electrical conductivity at 0oK [25] .
The resistance of the films can be calculated from the equation:
$$\rho = R. W.t / L \text{ -------------- (2)}$$
Where R is the resistance, w is the width of the electrode, L is the distance   between the electrodes and t is the thickness of the thin film. The conductivity (σ) of the film would be determined from the relationship:
$$\sigma = 1/\rho \text{ ----------- (3)}$$
Then by plotting the calculated conductivity ln (σ) as a function of reciprocal temperature, the activation energy can be calculated from the plot slope.

III.   RESULTS AND DISCUSSION
3.1 Solution Electrical Conductivity.
LiCl increased the electrical conductivity of PVA solution from (0.581 mS/cm) to (20.313 mS/cm) when 1% LiCl added to pure PVA. Adding   LiCl, which considered to be one of the ionic salts, cause the

formation of additional energy levels between the valance band and conduction band and thus these energy levels will decrease the band gab of the material and thus, the electrical conductivity will be increased [26]. Increasing charge carriers concentration in the solution would also increase electrical conductivity. The effect of LiCl on the polymeric solution conductivity represented in Fig.3
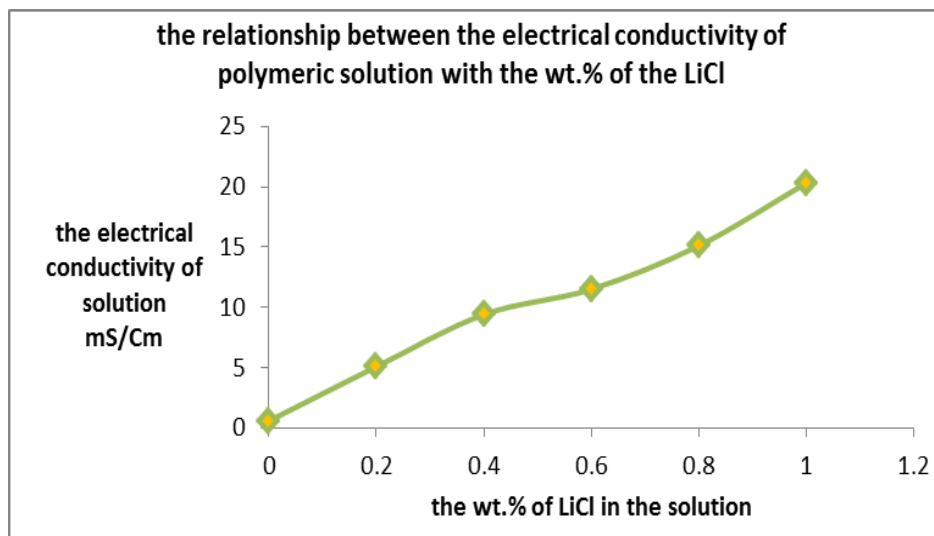

Figure 3: Relationship between electrical conductivity of polymeric solution and LiCl wt. %

3.2 Thickness Measurements

There are many conditions affecting casting process like volume of pouring solution in the petri dish, type of petri dish used, casting temperature, casting time .etc. With fixed conditions increasing the LiCl percentage in solution added to PVA solution cause the thickness of the produced films to be reduce gradually. This may be explains in related to the low density of the additive solution relative to PVA solution. Increasing LiCl solution will cause lower PVA percentage in the polymeric solution thus the produced films will have less density and thickness. The relationship between films thickness and the LiCl percentage in the produced films shown in Fig.4. The film containing 1% LiCl (the max amount of LiCl) removed difficultly from the Petri dish because it is very thin.
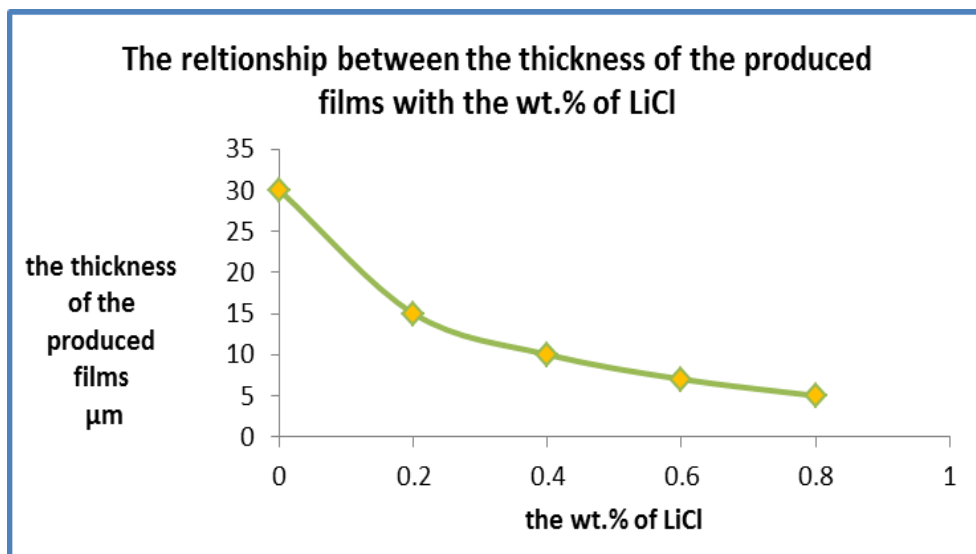

Figure 4: the relationship between the thickness of the produced films with the wt. % of LiCl .

3.3 FT-IR Results:

The chemical compositions of PVA and PVA/0.4wt.% LiCl films were characterized by using FT- IR technique as in Fig.5 and Fig. 6 that represents the observed peaks for the pure PVA and PVA / 0.4%wt. % LiCl film respectively.
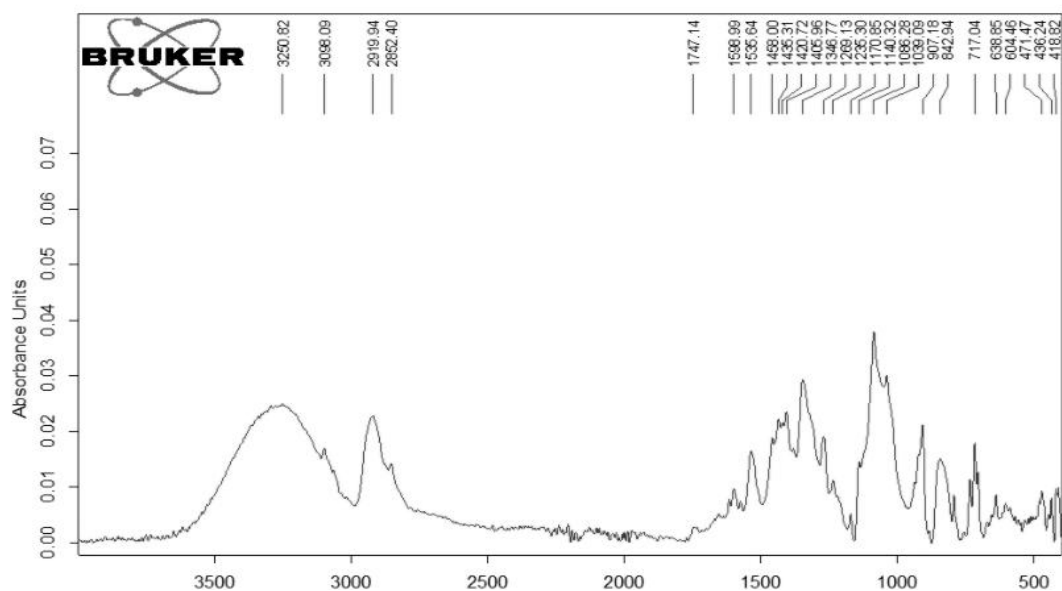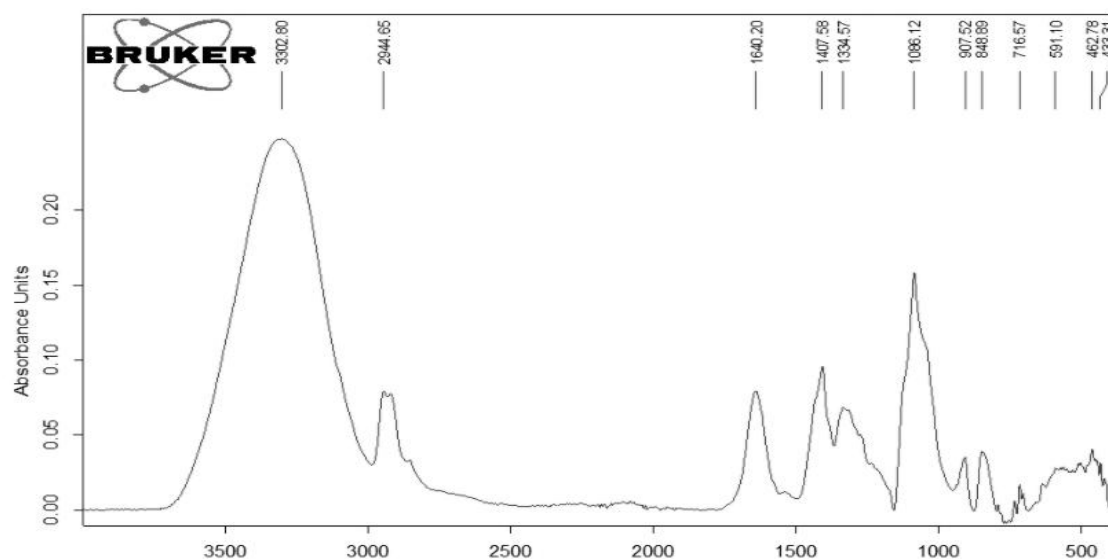
Figure 5 : FT-IR spectrum for pure PVA film

Figure 6: The FT-IR Spectrum for PVA/ 0.4 wt.% LiCl film

According to Fig. 5 (FT-IR spectrum for pure PVA film) , The predominant   O–H vibrational band of alcohols at 3250.82 cm^{-1} (3500 – 3200 cm^{-1}) is shifted to 3302.80 cm^{-1} , this mean shifting towards higher wave numbers about 51.2 cm^{-1} and appeared as broad hydroxyl band. The vibration peak at 2919.94 cm^{-1} between (3000-2800) cm^{-1}, which is refers to stretching band (C-H) from alkyl, is shifted to 2944.66 cm^{-1}, this mean that the stretching (C-H) peak is also shifting towards higher wave numbers about to 24.52 cm^{-1}. This gives a strong indication of specific interactions between the polymer matrix and dopant salt. For stretching (C-H) peak, there is also remarkable shifting to higher peak intensities. The acetyl (C-O) stretching bond is shifted from 842 cm^{-1} for pure PVA to 846 cm^{-1}. The observed changes intensity of (C-H) band, shifting of some bonds indicates the formation of complexes between the PVA and LiCl additive [27].

3.4 D.C Electrical Conductivity:
From the results, shown in Fig. 7, one can see the electrical conductivity ($\sigma_{d.c}$) increases with wt.% LiCl. It is clear from these results that the electrical conductivity ($\sigma_{d.c}$) improved about seven orders. This can be referred to ionic salts addition, like LiCl, that will lead formation of additional energy levels between the valance band and conduction band and decreasing the band gab of the material and create new conductive pathways. Increasing the additive concentration will lead to increase the above effects on electrical conductivity due to increase the density and mobility of charge carriers.
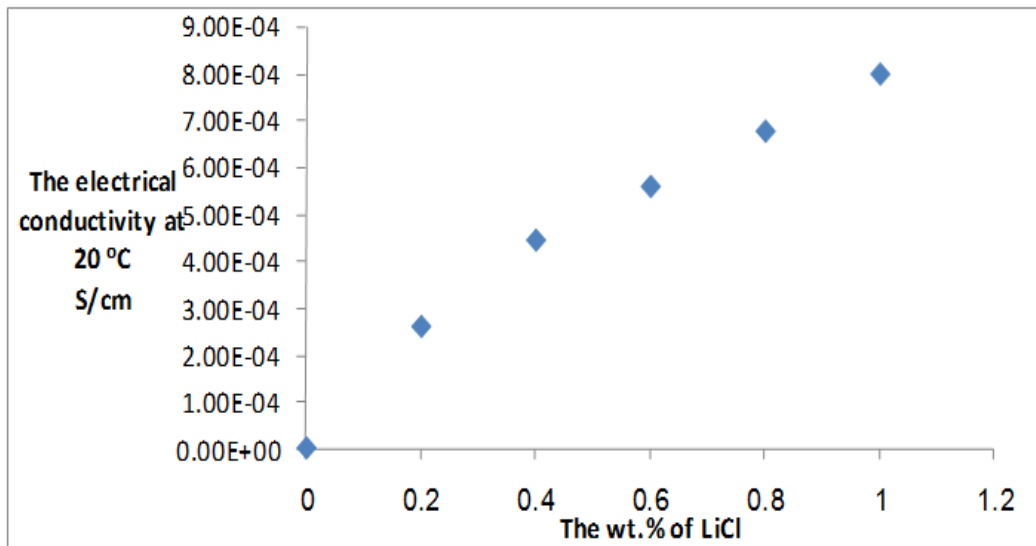
Figure 7: increasing the electrical conductivity with increasing the wt.% of LiCl

PVA films electrical conductivity ($\sigma_{d.c}$ were measured using equation 2 and 3 at different temperatures (293 - 373)°K. Fig. 8 represents ln $\sigma_{d.c}$ vs 1000/T for different concentrations of LiCl in PVA matrix. As shown the electrical conductivity increases with temperature for all salt concentration in PVA films used in this work. The films would exhibit semiconductors behavior.
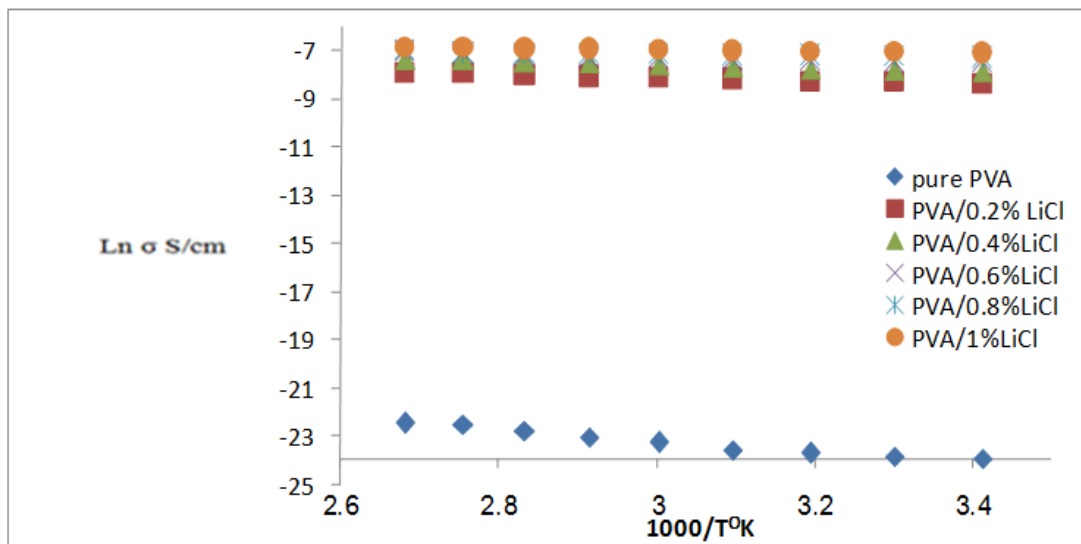

Figure 8: ln σ vs 1000/T for different compositions of PVA / LiCl films

Activation energy, measured by using equation 1, decreases with increasing LiCl concentration in PVA films till 0.8wt. % LiCl then increased for PVA/ 1% LiCl films. This can be explained as a result of increasing the dopant concentration (LiCl), a new unfilled valance band will be created which had a higher value than the other films [28].

Table (1): The activation energy and the electrical conductivity $\sigma_{d.c}$ of different compositions of PVA/LiCl films

The films composition	The activation energy (eV)	$\sigma_{d.c}$ conductivity (S/cm) at 20 °C
Pure PVA film	0.171	4.0112×10^{-11}
PVA/ 0.2wt.% LiCl	0.0368	2.6578×10^{-4}
PVA / 0.4wt.% LiCl	0.03321	4.4451×10^{-4}
PVA / 0.6wt.% LiCl	0.02415	5.5981×10^{-4}
PVA / 0.8wt. % LiCl	0.02101	6.7701×10^{-4}
PVA / 1wt.% LiCl	0.0278	8.003×10^{-4}

IV.   CONCLUSIONS

LiCl affects the electrical conductivity of PVA solution and films. In this work it was found that: LiCl in PVA solution increased their electrical conductivity due to increment of charge carriers density, PVA films exhibit a semiconductor behavior since their electrical conductivity increased with investigation temperature, PVA films electrical conductivity increased seven orders by the addition of LiCl and the activation energy decreases with increasing LiCl concentration in PVA films.

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