

# الخلاصة

لقد تمت دراسة التوصيلية الكهربائية للبولي مثيل ميثاكريلت وللبولي كلوريد الفانيل بالحالة النقية والمخلوطة مع السوائل الأيونية الآتية: سلفونيت الكولين و سلفونيت الأمونيوم و كلوريد الكولين / يوريا. التي أضيفت بنسب وزنية هي ١٠ و ٢٠% من كل سائل أيوني.

لقد تم تحسين التوصيلية الكهربائية لهذه البوليمرات حيث تحولت من العوازل الكهربائية الى ناقل للشحنات المستقرة.

لقد أظهرت النتائج العملية ان التوصيلية الكهربائية تزداد بوضوح مع زيادة النسبة الوزنية من السوائل الأيونية المضافة و كذلك تزداد مع زيادة درجة الحرارة. كما أظهرت النتائج العملية ان بولي كلوريد الفانيل يمتلك أعلى توصيلية كهربائية من بولي مثيل ميثاكريلت في كلتا الحالتين (النقية والمخلوطة مع السائل الأيوني) بالإضافة الى ذلك أظهرت السوائل الأيونية المضافة نفس التأثير تقريبا على كلا البوليمرين. لقد أظهرت هذه السوائل الأيونية تأثيرها على التوصيلية بالاتجاه الآتي:

كلوريد الكولين / يوريا < سلفونيت الأمونيوم < سلفونيت الكولين.

علاوة على ذلك، وجود السوائل الأيونية بكلا النسبتين أدت الى اختزال قيم طاقة التنشيط واستمرارها بالنقصان مع زيادة الوزن المضاف من السوائل الأيونية.

# Abstract

The electrical conductivities of PVC and PMMA were investigated either alone or composite with ionic liquids up to 110 °C, choline dodecyl benzene sulfonate, ammonium dodecyl benzene sulfonate and choline chloride / urea were added in 10 wt % and 20 wt %. The conductivities of both composite polymers were improved changing the behavior of these polymers from insulator into antistatic characterization as their conductivities reach  $10^{-9}$  S. cm<sup>-1</sup>.

The experimental results showed that the D.C electrical conductivities were clearly increased with increasing the added weight of ionic liquids and also increased with increasing the temperature. Where in each cases PVC has higher conductivities than PMMA polymer, in addition added ionic liquids showed almost equal effect on either PVC or PMMA. However, these ionic liquids showed the following trends of influence of conductivity:-

choline chloride / urea > ammonium dodecyl benzene sulfonate > choline dodecyl benzene sulfonate

Furthermore, the presence of ionic liquids in each wt% reduced the D.C activation energy and more decreased with increasing the added weight of ionic liquids.

# CHAPTER 1 General Part

## ***1.1 Polymers:***

Materials classified as polymer are long chain molecules with a repetition of structural unit. The structural units are called monomer, which are connected to each other by covalent bond <sup>(1)</sup>. Macromolecule, big molecule also are used to define polymer term. However, large molecule of complex structure can be cover better by this name "polymer" since the latter carries with it the connection of simple repeating unit. The process of connection is called polymerization. The structural unit may be joined together in a variety of ways to form polymers. The number of these repeated units is called degree of polymerization <sup>(1-3)</sup>.

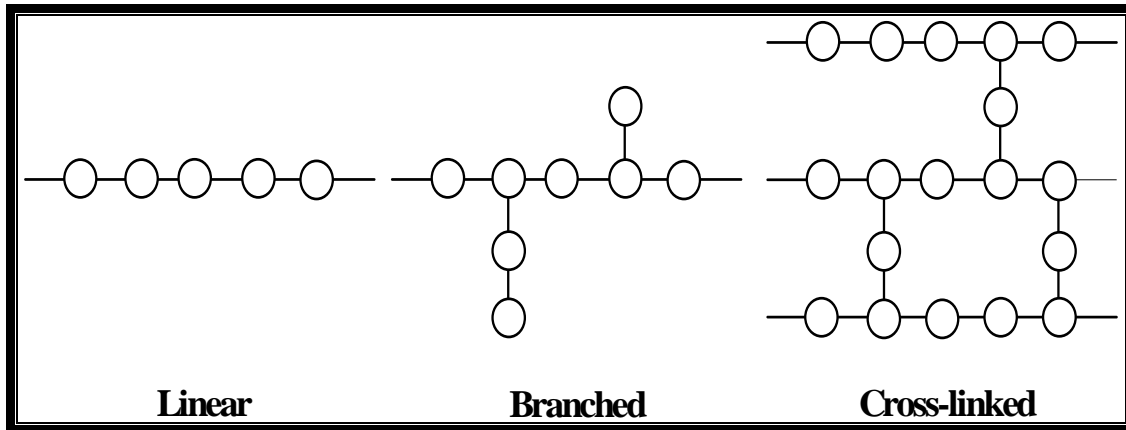
If all the structural units are identical (one kind) the polymer is called (homopolymer), if the polymer incorporating two or more chemically different type of structural units into the chain then it is termed (copolymer), many commercial synthetic polymer are copolymers <sup>(1-5)</sup>.

There are three main structural shapes in which polymer molecules are produced, which can be classified into: <sup>(4)</sup>

1. Linear polymers: - like polyethylene and polyvinyl chloride.
2. Branched polymers: - like low density polyethylene.
3. Cross-linked polymers: - like thermosetting resins, phenoplast, and uroplast.

Depending on the structural shape of the polymer molecule <sup>(1-5)</sup>

The simplified structures of these polymers are given in Fig. (1.1)



**Figure (1.1):- General structure of polymers.**

Polymer materials is used as engineering material specially plastics. Plastics can also be classified into: thermoplastic, thermosets (thermosetting resin).

Thermoplastic: important materials which are softening and flow upon application of heat, and can be remolded many times, in addition to be processed by molding technique and easily deformed. Some of these types of polymers are: polyethylene, polypropylene, polystyrene, polyamide (nylon), polymethyl methacrylate, polyvinyl chloride <sup>(3-7)</sup>.

Thermosets: The thermoset polymers are this once heated, react irreversibility so that subsequent application of heat and pressure do not make them soften and flow. In contrast to thermoplastic polymer thermosets polymers are substances which can not be melted and remelted but set irreversibility, such as phenolic resin, epoxides, unsaturated polyester, polyurethanes and melamine formaldehyde <sup>(3-7)</sup>.

In contrast to many materials, polymers do not have unique molecular weight but are described in terms of an average molecular weight <sup>(8)</sup>. In comparison to well-ordered, covalent, or ionically bonded inorganic materials, polymers are weakly bonded, disordered materials. The functional groups from which they are made up need not to have unique spatial relationships to each other, these differences have distinguished the polymers from other materials. The polymers are in general heat insulators and are usually soft and easily distorted. They are electrically insulator and poor conductor of charges, thus display good exceptionally high chemical resistance <sup>(6)</sup>.

The above properties make polymer materials so popular such that the concept of polymer (or macromolecule) spread rapidly into many areas of natural sciences and technology. In engineering, for example, a series of successes in commercial polymer synthesis established anew sector of international chemical industry devoted to producing and applying polymeric materials, notably plastics and rubber, coating and adhesives. one of related examples are the use of polymers in the field of electro electrophotography and the technological application of different phenomena found in polymers, such as the piezoelectricity and pyroelectricity, in transducers and solar detectors <sup>(2, 9)</sup>.

Polymeric materials are unique because of the range of structural forms that can be synthesized and the way in which changes can be made in the structure in a local or general way. They can exist as amorphous materials, crystalline materials, or mixture of crystalline and amorphous materials <sup>(1, 8)</sup>. Even highly crystalline polymers (e. g. polyethylene, polypropylene, polymethyl pentene) contain considerable amorphous phase. They are molecular materials, that is, each polymer chain has its own individual entity, and the interaction with other polymer chain is usually weak.

Polymer chains can occur in different conformation and can be oriented mechanically.

It is now clear that many polymer materials possess a significant degree of crystallinity. On the other hand, many others are found to be completely amorphous. The presence or absence of crystallinity is determined by molecular structure and thus the division of polymers into crystalline group and an amorphous group.

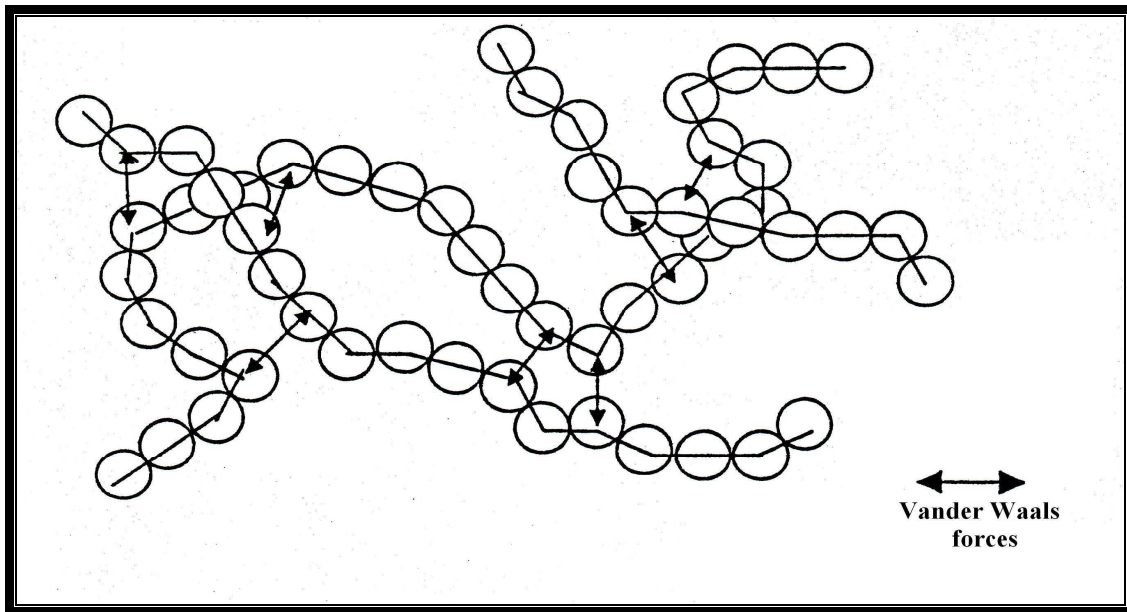
Crystalline polymers include: Stereoregular homopolymers with strong interaction forces and certain block copolymer, for examples: poly ethylene (high and low density), poly propylene, cellulose, polymethyl pentene, polyethylene terephthalate, polyethylene oxide.

Amorphous polymer include: A tactic homopolymer and random copolymer. For example: Chlorinated polyethylene, polystyrene (atactic commercial), acrylonitrile butadiene styrene, polymethyl methacrylate and polyvinyl chloride, and wide cases of thermosets polymers. Many factors affected on crystallization of polymers, include: rate of cooling, presence of orientation, melt temperature, molar mass, chains branching and additives. However, most polymer materials contain some percent of crystallinity and some percent of amorphousity.

One of the important characterizations of polymers is the glass transition temperature ( $T_g$ ) which can be defined as a temperature point where a polymer experiences a significant change in properties. Typically, the  $T_g$  is where a polymer structure turns "rubbery" upon heating and "glassy" upon cooling. Amorphous polymers are structural below  $T_g$ . Amorphous materials go through one stage of the change from a glassy to a rubbery consistency with a simultaneous loss in stiffness. This stage of going from stiff to flowing is over a wide temperature range. Crystalline materials go through a stage of becoming leathery before becoming rubbery.

There is a loss of stiffness in both of these stages. However, crystalline materials have a sharp, defined melting point <sup>(5-7)</sup>.

Polymer may thus consist of linear chains arranged in some way and hold together in the solid by Vander Waals forces between chains and mechanical entanglement. See Fig. (1.2):



**Figure: - (1.2) Linear chains held together by Vender Walls force and mechanical entanglement.**

In comparison with metals, polymers have the following properties <sup>(9)</sup>: Lower densities, lower stiffness, lower thermal conductivities, higher thermal expansively, resistance to chemical environments (weak acids, weak alkalis, and salt solutions), however, they are not to have resistant to organic solvents. In addition, polymers are good electrical insulators, having resistivities which are about ( $10^{18}$ ) times greater than those of metals <sup>(6, 10)</sup>. Although the main interest in the electrical properties of polymers was effectively limited to their electrical insulating properties, considerable science research projects have been devoted to modify some of these

properties. Even though the polymers are almost classified as good insulators, a conducting polymer is a chewable and desirable. A lightweight, readily moldable, desirable conductive material has long been recognized as a worth while goal to work for <sup>(10)</sup>. The thermoplastic polymers (i.e. PVC and PMMA) have been studied in this work which is now being outlined.

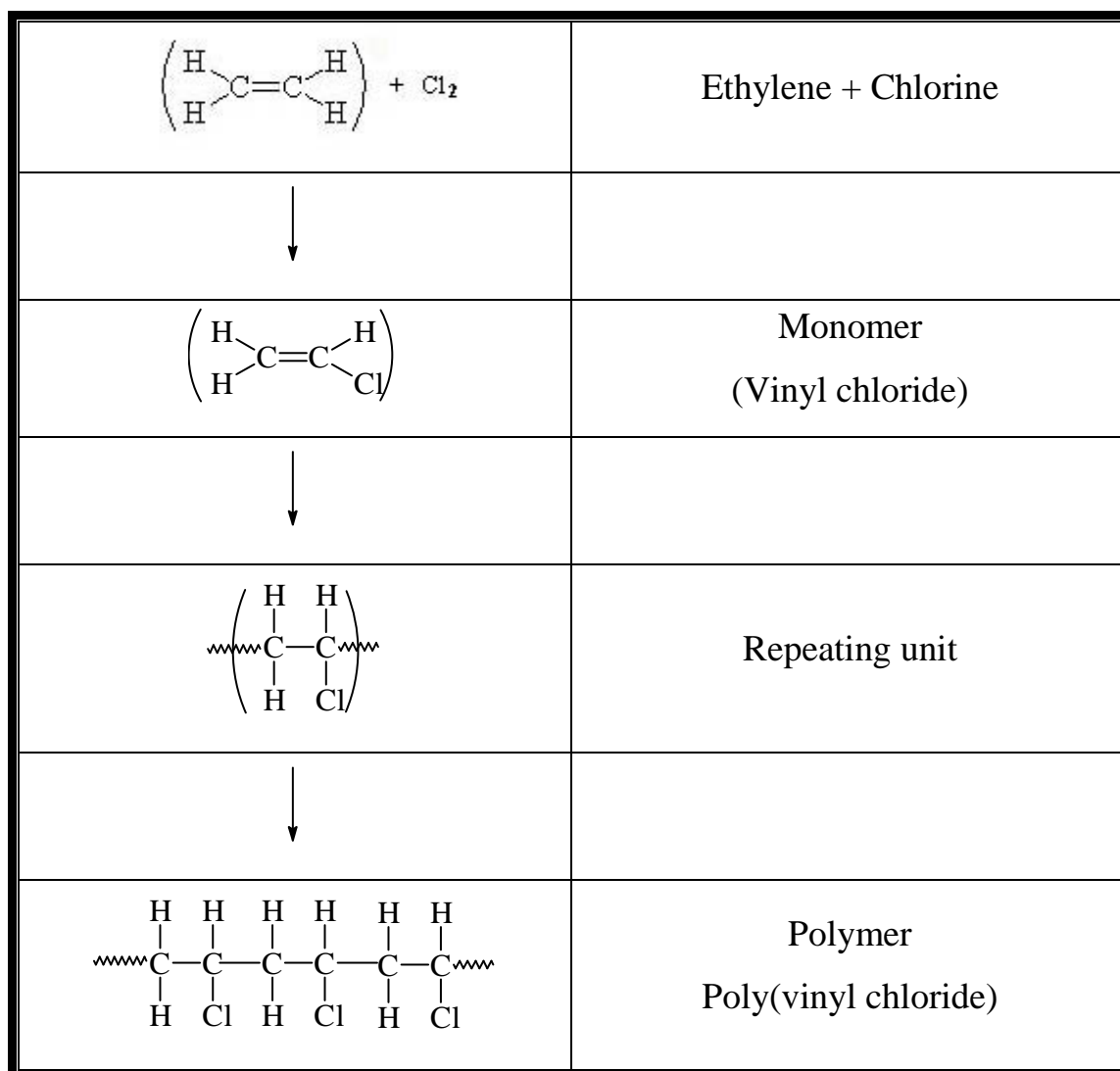
### ***1.1.1 Polyvinyl chloride:***

PVC is a thermoplastic, linear amorphous polymer. Vinyl chloride monomer and its polymers occupy a unique place in the history of plastics. Arriving early in technology of synthetic resins, they have not been displaced by new polymers. To the contrary, they had increasingly important <sup>(11)</sup>.

Vinyl chloride had its beginning in the laboratory of the French chemist Regnault <sup>(12)</sup> in 1835; when he produced vinyl chloride by mixing ethylene dichloride with an alcoholic solution of potassium hydroxide. The material remained laboratory curiosity, however, until Ostromislensky <sup>(13)</sup>, investigated vinyl chloride chemistry in 1912.

The First World War resulted in heavy demands on German's chemical industry. Because of rubber shortage, German chemists again investigated Regnault's work, and in 1918 Klatte and Rollet <sup>(14)</sup>, developed the first practical method of polymerizing vinyl chloride. It found a wide acceptance as substitute for rubber as well as building materials. In the United Kingdom PVC was not produced on commercial scale until the out break of Second World War <sup>(11)</sup>. This polymer is produced by addition polymerization of the monomer vinyl chloride <sup>(15)</sup>, see Fig. (1.3)





**Figure (1.3):- Schematic diagram for Preparation of polyvinyl chloride**

Polyvinyl chloride is a linear- chain polymer with bulky chloride side-groups which prevent crystalline regions occurring normally. PVC is hard and rigid material at room temperature <sup>(16)</sup>. Straight poly (vinyl chloride) is colorless rigid material with Tg about 80 °C. It has relatively high density and low softening point <sup>(17)</sup>.

The presence of the chlorine atom causes to increase in the inter chain attraction, hence an increase in the hardness and stiffness of the polymer is recognized. PVC is also polar polymer because of C-Cl dipole. These properties make PVC polymers as good candidate in the application

involving high frequencies because high dielectric constant and high power factor values higher than polyethylene owing to the polar carbon-chlorine bond <sup>(16)</sup>.

PVC has very limited solubility. The most effective solvents are those which appear to be capable of some form of interaction with polymer. It has been suggested that polyvinyl chloride is a weak proton donor and effective solvents are proton acceptor <sup>(17)</sup>. Thus the PVC polymer is soluble at room temperature in oxygen-containing solvents such as ethers e. g. dioxane, tetrahydrofuran; ketones e. g. cyclohexanone, methyl isobutyl ketone and nitro compounds, e. g. nitrobenzene <sup>(18)</sup>.

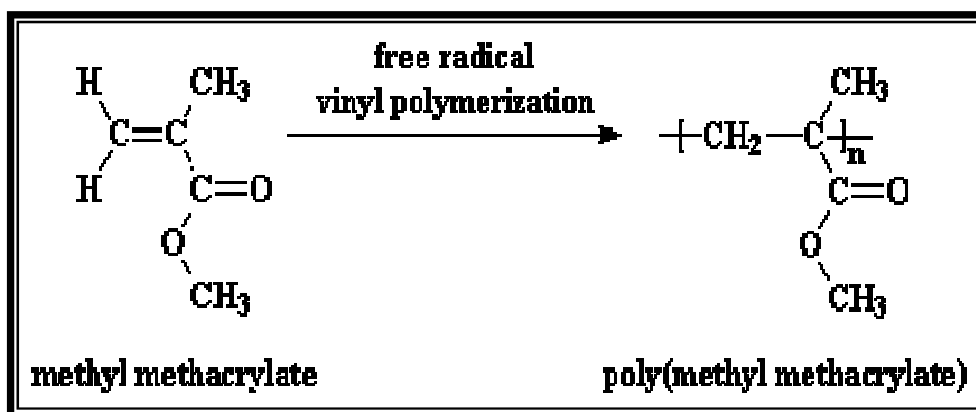
PVC including the various copolymers of vinyl chloride and chlorinated PVC is expected to remain important among thermoplastics because of its compatibility with a large number of other products (e. g., plasticizers, impact modifiers), in contrast to other plastics. Because PVC's mechanical properties can be adjusted over a wide range, yielding everything from rigid to flexible end products, there are many different processing methods and applications for PVC.

The importance of PVC in the field of plastics, in rigid form of PVC, can be extruded into pipe, conduit or sheet, while in flexible form it can be substituted for rubber in low-voltage cables and house wiring <sup>(18)</sup>. This polymer may be regarded as the most widely used plastic material important applications from high volume construction related products to simple electric wire insulating and coatings <sup>(17)</sup>.

### **1.1.2 Polymethyl methacrylate:**

PMMA is a thermoplastic, amorphous polymer. Methacrylic ester monomers have the generic formula  $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOR}$ , and is the nature of the R group that generally determines the properties of the corresponding polymers. PMMA is a member of a family of polymers which chemists call acrylates, methacrylates differ from acrylates in that the  $\alpha$  hydrogen of the acrylates is replaced by a methyl group. It is the  $\alpha$  methyl group of the polymethacrylate that imparts the stability, hardness, and stiffness, of methacrylic polymers <sup>(5)</sup>. Rohm and Bauer <sup>(19)</sup> polymerized methyl methacrylate into transparent sheets in 1932. PMMA is an amorphous plastic with a high surface gloss, high brilliance, a clear transparency of 92 % (inorganic glass also has a transparency of 92 %), and a refractive index of 1.49. PMMA is classified as a hard, rigid, but brittle material, with  $T_g = 105^\circ\text{C}$ . PMMA has good mechanical strength, it is resistance to many chemicals chlorinated but soluble in organic solvents such as ketones (e.g. methyl ethyl keton), chlorinated hydrocarbon (chloroform), esters (ethyl acetate) and ethers (e.g. tetrahydrofuran) <sup>(20, 21)</sup>.

PMMA can be produced using a variety of polymerization mechanisms. The most common technique is the *free radical polymerization* of MMA. The free radical polymerization of MMA can be performed homogeneously, by bulk or solution polymerization, or heterogeneously, by suspension or emulsion polymerization. Free radical polymerizations can be performed relatively easily <sup>(19, 20)</sup>. Radicals can be generated with radiation, heat, or chemical agents (usually in conjunction with radiation or heat). The free radical polymerization of MMA is the predominant industrial mechanism to produce PMMA <sup>(19-22)</sup>. Fig. (1.4) <sup>(21)</sup> show the free radical polymerization of PMMA polymer.



**Figure (1.4):- Free radical polymerization of polymethyl methacrylate**

MMA can be polymerized spontaneously with heat (high boiling liquid) this polymerization is extremely slow, however, and of no industrial relevance. MMA has been polymerized anionically. The anionic polymerization is not used industrially because the monomer has to be extremely pure, and the polymerization must be performed at very low temperatures <sup>(19, 22)</sup>.

PMMA has favorable processing properties, good thermoforming, and can be modified with pigments, flame retardant additives, UV absorbent additives, and scratch resistant coatings and extremely good weather resistance <sup>(19, 22)</sup>.

Because of the excellent optical properties, weather resistance, light weight, impact and shatter resistance (compared to inorganic glass), another polymer used as an unbreakable glass substitute is polycarbonate but PMMA is cheaper <sup>(21)</sup>. Heat resistance, and process- ability make PMMA has many profound and diverse uses that affect our lives every day. PMMA also can serve as a conduit for light. The ability to mold PMMA precisely allows complex optical design to be manufactured easily and inexpensively.

PMMA is also used to improve vision external to the body, again due to its excellent optical properties and process ability, as well as its biomedical

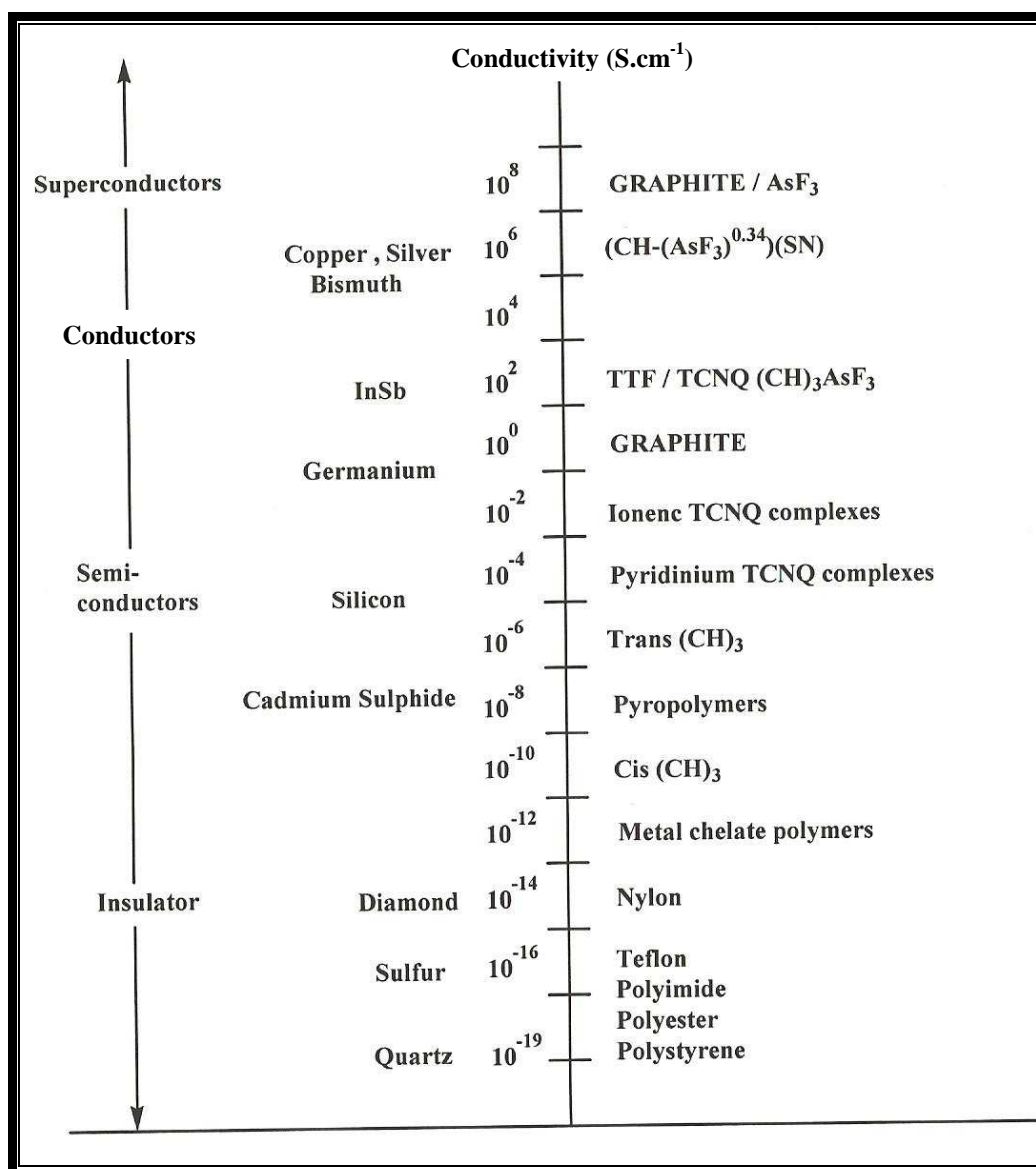
inertness when in contact with the eye, as contact lenses are. Hard and soft contact lenses, and optical spectacles for eyeglasses, are all made commercially from homopolymers and copolymers of PMMA <sup>(19, 22)</sup>.

The bulk and surface resistivities of PMMA are higher than that of most plastic materials. High resistance and non tracking characteristics have resulted in its use in high voltage application, its excellent weather resistance coupled with its electrical properties have promoted the use of polymethyl methacrylate for out door electrical applications <sup>(22)</sup>.

## **1.2 Conductivity of Polymers:**

There are several methods of producing conductive polymers or some times called as (conductive composite). Among these and the most commonly one is achieved by introducing macroscopic pieces of conducting materials into the hosted polymers to obtain conductivity composites with a desirable conductivity. Thus, conductive composites made by inclusion of suitable additives such as graphite powder, carbon black, metal powder, carbon fibers and ionic solid powder in to the bulk of a polymer commonly used. Apart from the obvious application of highly conductive materials for power and signal transmission, there is also a need for materials having intermediate conductive properties for flexible heating elements and graded cable isolation <sup>(10)</sup>. Conducting polymers have also been proposed as promising materials in circuitry element, functioning as passive element (conducting trace) or active elements devices (or p – n junction) <sup>(10, 23)</sup>.

In terms of their electrical conductivity, materials can be ground into four categories: - superconductor, conductor, semiconductor and insulator<sup>(23)</sup>. The range of materials including polymeric materials and their electrical conductivity are illustrated in Fig. (1.5), the range of electrical conductivity is observed in materials which covers a range of (27) orders of magnitude from the best conductors (superconductors) with  $\sigma$  of  $10^8$  S.  $\text{cm}^{-1}$  to the best insulators with  $\sigma$  of  $10^{-19}$  S.  $\text{cm}^{-1}$ .



**Figure (1.5):- The conductivity of materials (including polymers).**

Polymers (i.e. plastics) primarily regarded as insulators. In last three decades, conducting as well as semiconducting polymer were discovered and been widely produced <sup>(23)</sup>. As shown in Fig. (1.5).

Most plastics are naturally non-conductive, hence their wide use as electrical insulators. Because of their ease of fabrication, however, polymers are highly desirable materials of construction. Where some transfer of electrical charge is desired modifications to the polymer must be made to increase conductivity. This has resulted in plastics being formulated for use in four distinct application categories of increasing conductivity:

1. Insulating (e.g. wire coating)
2. Dissipative ("anti-static" polymers)
3. Conductive (materials capable of conducting modest amounts of electrical current)
4. Highly Conductive or Shielding (materials capable of conducting significant amounts of electrical current)

The easiest "conducting" attribute to achieve in a polymer is to make it "anti-static". Anti-static polymers do not conduct electrical charges in a conventional sense. They do, however, permit electrons to move across the surface from areas of high charge to areas of lower charge there by eliminating the tendency to deliver a shock or create a spark. "Anti-static" compositions are generally characterized by surface resistivities of  $10^9$  to  $10^{11}$  Ohm. cm <sup>(24)</sup>.

### **1.2.1 Electrical properties of polymers:**

Electrical properties of polymers are the responses when an electric field applied and the subject of electrical properties of polymers covers a diverse range of molecular phenomena. In contrast to metals, when the electrical response is one of electronic conduction, polymers display a much less striking response.<sup>(10)</sup> As a consequence of the characteristically insulating nature of polymers, any electrostatic charges that they acquire are retained for along time. Since charges may be deposited by mere contact with different material, the charge conditions are frequently encountered with articles made from polymers.

It is worth pointing out here that, although contact charges represent only slight imbalance of charge compared with the total amounts of positive and negative charge present in matter, they can never be less to give arise to electric fields which are high enough to cause sparking in air<sup>(25)</sup>.

Polymer is not completely free of conduction processes, small quantity of charge carriers it may posses low-level conduction, is essentially insulating polymers can take variety of forms. Conduction may very often be contributed by impurities that provide small concentration of charge carriers in the form of electrons or ions. At high fields, the electrodes may inject new carriers (holes and electrons) into the polymers, causing the current to increase more rapidly with voltage than in according with Ohm's law. At very high fields, these and other processes will lead to complete breaking down of polymers as insulating materials<sup>(10, 26)</sup>.



Insulators, most commonly polymers, are widely used as inter level dielectrics, encapsulates, and materials for the packaging and housing of electronic equipment. The electrical insulating quality inherent in most polymers has long been exploited to constrain and protect currents flowing along chosen paths in conductors and to sustain high electric fields without breaking down.

### **1.2.2 Electrical properties:**

Solid can be divided according to their electrical properties as outlined earlier into three classes: conductors, insulators and semiconductors, in terms of their electrical conductivity. Conduction of electric current in materials is the result of the movement of charged particles (ions or electron) under an applied electric field. The electrical conduction in any matter is given in the relation:

$$\sigma = n q \mu \quad (1.1)$$

Where (n) is the concentration of charged carriers, (q) is the value of the charge carriers and ( $\mu$ ) is the mobility of carriers<sup>(10)</sup>.

The phenomenon of conduction exhibits appreciable variation depending on the nature of charge carriers in matter. The basic types of conduction are:

1. Electronic conduction: where the carriers are elementary negatively charged particles-(electrons).
2. Ionic or electrolytic conduction: where the carriers are ions, i.e. the parts of atoms or groups of atoms having a positive or negative charge.

3. Electrophoresis conduction: where the carriers are the charged groups of molecules-motions. The flow of current through the matter is attended by an electrophoresis effect <sup>(27)</sup>. In general the magnitude of conductivity and nature of conduction can essentially change depending on the temperature, structure and impurity

Conductivity depends on temperature: it generally increases with decreasing temperature for “metallic” materials (some of which become superconductive below a certain critical temperature (T<sub>c</sub>), while it generally decreases with lowered temperature for semiconductors and insulators.

### **1.2.3D.C electrical conductivity:**

The electrical conductivity is one of the most widely known varying physical properties. This conduction through a substance sandwiched between metal electrodes has been the subject of interest for theoretical and experimental investigators <sup>(28)</sup>.

Conductivity is defined by Ohm’s law:

$$U = R I \quad (1.2)$$

Where I is the current through a resistor and U is the drop in potential across it, the proportionality constant R is called the “resistance”, , R is measured by applying a known voltage across the resistor and measuring the current through it. The reciprocal of resistance (R<sup>-1</sup>) is called *conductance*.

The resistivity ( $\rho$ ) is a measure of the electrical resistance of a material, being defined by:-

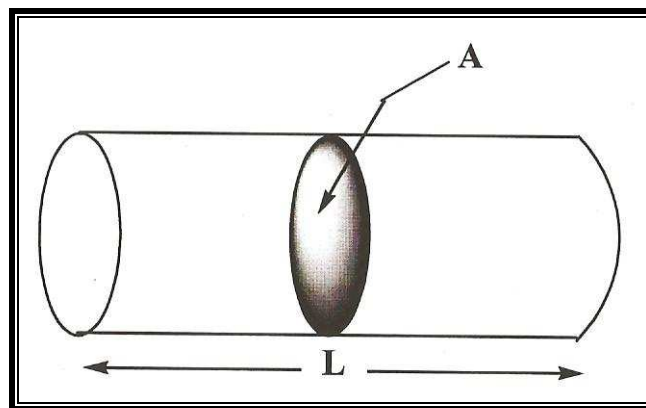
$$\rho = R A / L \quad (1.3)$$

Where R is the resistance of a length (L) of a cross-sectional area (A) which is area of the aluminum electrode, as shown in Fig. (1.6), the unit of resistivity ( $\rho$ ) is the ( $\Omega \cdot \text{cm}$ ).

The electrical conductivity ( $\sigma$ ) is the reciprocal of the resistivity:-

$$\sigma = 1 / \rho = L / RA \quad (1.4)$$

The unit of conductance is the Siemens ( $S = \Omega^{-1}$ ). The unit of conductivity is ( $S \cdot \text{cm}^{-1}$ ). Since conductivity is the reciprocal of the resistivity, an electrical insulator will have a very low conductivity, while an electrical conductor will have a very high conductivity.



**Figure (1.6): Determining the resistivity of the specimen.**

The electrical conductivity for non metallic materials varies exponentially with temperature (T), and is given by an Arrhenius equation <sup>(28)</sup>:-

$$\sigma = \sigma_0 \exp (-E_{ac} / BT) \quad (1.5)$$

Where B is the Boltzman constant and  $E_{ac}$  is the activation energy which is defined as the smallest energy that will raise the free energy of an atom or a molecule to such state so that it can go over the energy barrier.

The rate of this process will be dependent on the number of molecules or particles having sufficient thermal energy to reach the energy barrier and on the velocity of these molecules or atoms will cross this energy barrier.

If the electrical conductivity ( $\sigma$ ) is measured over a wide range of temperature, keeping other parameters constant, the plots of the logarithm of the conductivity against reciprocal of the absolute temperature are straight lines and from its slope, the activation energy ( $E_{ac}$ ) can be calculated for this process <sup>(29)</sup>.

### **1.2.4 Conductive Polymers:**

Conductive polymers are polymers which contain ions. The ions are, however, not very mobile in each of these materials. In polymer electrolytes the chemical structure of the polymer should be optimized for a high ion mobility and long range ion transport, thus for good ion conductivity <sup>(30)</sup>. The science of polymer electrolytes is a highly specialized interdisciplinary field which encompasses the disciplines of electrochemistry, polymer science, organic chemistry, and inorganic chemistry. The field has attracted ever-increasing interest, both in academia and industry, for the past two decades due to the potentially promising applications of such electrolytes,

not only in all solid-state rechargeable lithium or lithium-ion batteries, but also in other electrochemical devices such as supercapacitors, electrochromic windows, and sensors<sup>(31)</sup>.

Understanding the electrical conduction of polymers is important in two main areas:-

1. The generation of high-performance electrical insulators.
2. The synthesis of metallically conducting polymers.<sup>(32)</sup>

Researchers, generally, have demonstrated that conductive polymers can be used as energy storage element in:-

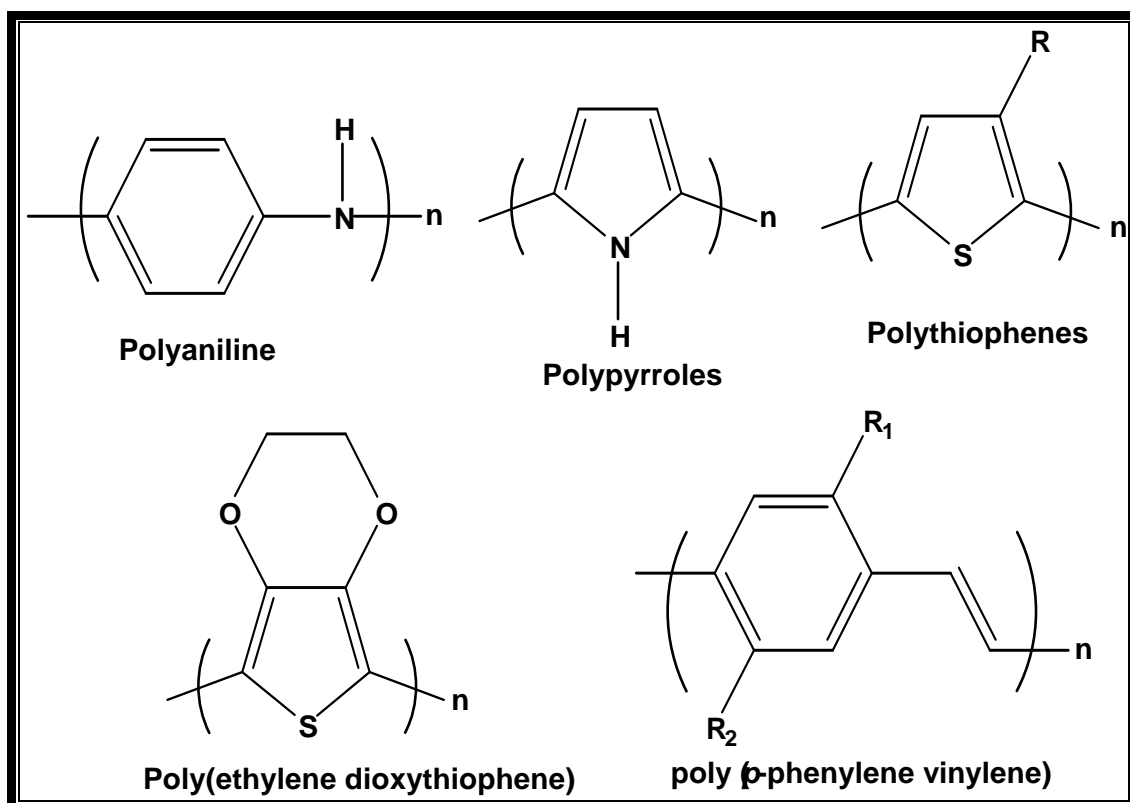
1. Capacitors and secondary batteries.
2. As semiconductor material in diodes.
3. Insulated gate field effect transitions (FET) and light emitting diodes.
4. As conductive layer for electromagnetic shielding (EMI) and electrostatic protection.

Polymers as stated earlier in section (1.4), display conductivity lying between the conductivities of insulators and of metallic conductors, such polymers are said to be conductive, the phenomena of conduction in organic compounds was first observed in certain polymer hydrocarbons and dyes, it was established that conjugated polymers exhibit semiconducting properties the conjugated include polymers made from acetylene polymers, pyrolyzed products, heterocyclic polymers and materials containing metallic atoms in their structure<sup>(32)</sup>. The unique properties of inherently conductive polymers stem from the possibility of fine-tuning the conductivity by adjusting the amount of dopant incorporated within the polymer, doping / undoping

reversibility, and the optical absorption characteristics in the UV-Visible and near infrared as well as its electromagnetic absorption characteristics.

Several polymers have been tested and proved to work in a variety of applications including:- Batteries, capacitors, smart windows, light emitting diodes, transistors, photovoltaic, corrosion control, conductive adhesive and inks, static dissipation, electromagnetic shielding, radar microwave absorption, direct plating, clean room application, sensors, microlithography, electrostatic powder coating, direct plating and drug delivery systems. Examples of some conductive polymers are shown in Fig. (1.7) <sup>(33)</sup>:-

Doped Polyaniline is used as a conductor and for electromagnetic shielding of electronic circuits. Polyaniline is also manufactured as a corrosion inhibitor. The polypyrrole conductive polymer has even higher conductivity than plastic extended with conductive filler shields. The experimental results for the shielding efficiency of polypyrrole films over a wide range of frequencies in radiation field (1MHz- 1GHz) <sup>(34)</sup>. It has been tested as microwave-absorbing “stealth” (radar-invisible) screen coatings and also as the active thin layer of various sensing devices.



**Figure (1.7):- Example of some conductive polymers.**

The polyanilines, polythiophene and polypyrrole are very useful materials for fabricating electro-optical display device<sup>(35)</sup>.

Polythiophene for example show change in color from red to blue on applying voltage, the change color lasts for several hours, thus showing the possibility of being used as an optical memory element. Polythiophene derivatives are promising for field-effect transistors; they may possibly find a use in supermarket checkouts.

Polyethylene dioxythiophene (PEDOT) doped with poly styrene sulfonic acid is manufactured as an antistatic coating material to prevent electrical discharge exposure on photographic emulsions and also serves as a hole injecting electrode material in polymer light-emitting devices.

Several types of polymer electrolytes have been developed and characterized as hosts polymers, such as those based on: polyethylene oxide

(PEO) <sup>(36)</sup>, polyacrylo nitrile (PAN) <sup>(37)</sup>, polymethyl methacrylate (PMMA) <sup>(38)</sup>, polyvinyl chloride (PVC) <sup>(39)</sup>, and polyvinylidene fluoride (PVdF) <sup>(40)</sup>.

Table (1.1): lists some polymers that have been investigated as hosts for polymer electrolytes and their corresponding chemical formulae <sup>(41)</sup>.

**Table (1.1): Polymers that have been investigated as hosts for polymer electrolytes and their corresponding chemical formulae**

<i>Polymer host</i>	<i>Repeat unit</i>	<i>Glass transition Temperature T<sub>g</sub> (°C)</i>
Poly(ethylene oxide)	$-(\text{CH}_2\text{CH}_2\text{O})_n-$	-64
Poly(propylene oxide)	$-(\text{CH}(-\text{CH}_3)\text{CH}_2\text{O})_n-$	-60
Poly[bis(methoxy ethoxyethoxide)-phosphazene]	$-\text{[N=P}(-\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3)_2\text{]}_n-$	-83
Poly(dimethylsiloxane)	$-\text{[SiO}(-\text{CH}_3)_2\text{]}_n-$	-127
Poly(acrylonitril)	$-(\text{CH}_2\text{CH}(-\text{CN}))_n-$	125
Poly(methyl methacrylate)	$-(\text{CH}_2\text{C}(-\text{CH}_3)(-\text{COOCH}_3))_n-$	105
Poly(vinyl chloride)	$-(\text{CH}_2\text{CHCl})_n-$	82
Poly(vinylidene fluoride)	$-(\text{CH}_2\text{CF}_2)_n-$	-40

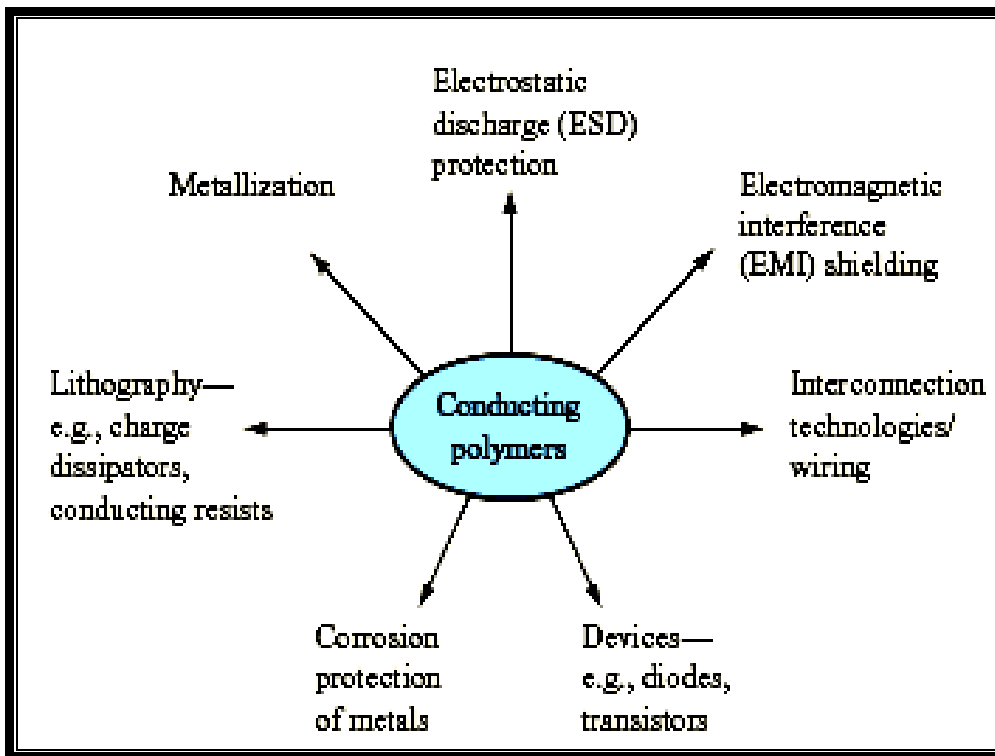


### **1.2.5 Applications of conductive polymers:**

In 2000 the Nobel Prize in Chemistry went to three scientists--Alan Heeger, Hideki Shirakawa and Alan MacDiarmid<sup>(42)</sup> for the discovery and development of Conductive Polymers. This innovation is being realized in commercially viable applications as outlined earlier in section (1.7).

Conducting polymers<sup>(43)</sup> offer a unique combination of properties that make them attractive alternatives for certain materials currently used in microelectronics. Conducting polymers have potential applications at all levels of microelectronics (See Fig. 1.8).

While many highly conducting materials are widely available (e.g. metals), most of these are not easy to economically fabricate into complex shapes. Thermoplastics on the other hand are easily and inexpensively moldable or into an almost unlimited variety of shapes and sizes. Because of their ease of fabrication, plastics that conduct electrical charges are frequently desired for various applications where the conductivity of metal is not required. Plastics can, in fact, be formulated to have specific conductivity characteristics from very low to very high conductivity as necessary and desirable<sup>(24)</sup>.



**Figure (1.8):- Potential applications of conducting polymers in microelectronics.**

In this time, when the technology is going in advance and the nature is suffering a lot of changes, because of this reason, the humanity should look for option that does not cause a lot of damage to the nature. Actually the polymers are in abundance in the world and several of them “have been tested and proved to work in a variety of applications” used all the time and for the majority of the people. *Those are strong reasons to study the properties of the conductive polymers* <sup>(43, 44)</sup>.

### **1.3 Ionic Liquids:**

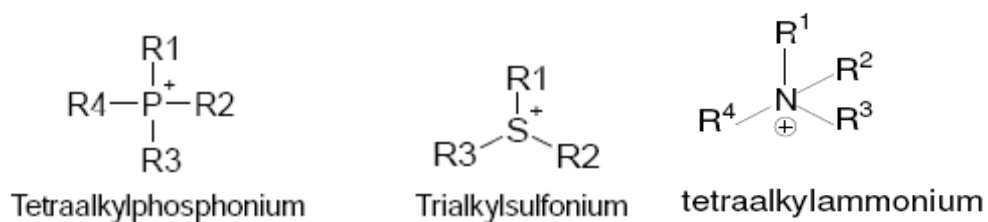
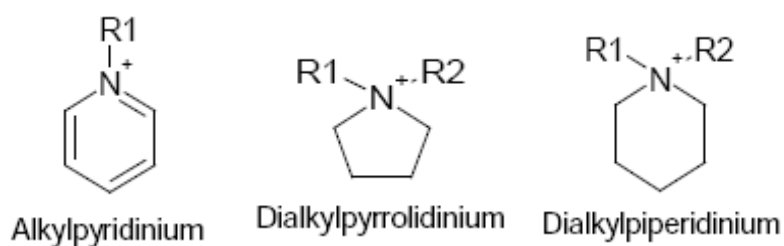
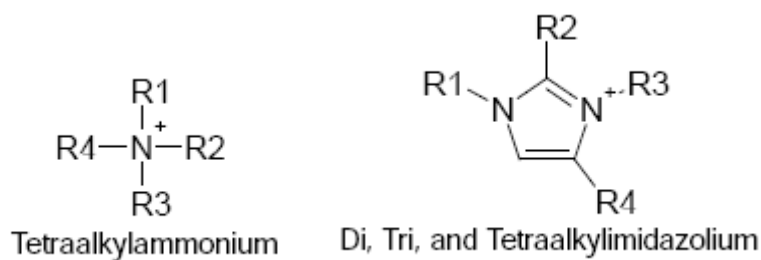
Ionic liquids are solvents consisting entirely of ions resembling the ionic melts of metallic salts, however, ionic liquids are liquids at much lower temperatures (less than 100°C) <sup>(45)</sup>. The ionic liquids generally consist of a combination of organic cations such as imidazolium, pyridinium, pyrrolidinium, ammonium, sulfonium and phosphonium and bulky and soft anions, such as  $\text{CF}_3\text{SO}^-$ ,  $\text{N}^+\text{CF}_3\text{SO}^-$ ,  $\text{PF}_6^-$  and  $\text{BF}_4^-$ . <sup>(46)</sup>

It is also called the "designer's solvent" by changing the types and combination of its basic composition, positive ions and negative ions, it is possible to produce a limitless variety of chemical compounds, as it makes possible the creation of electrolytes, which have new and non-conventional performance through modification of molecular design by changing types and combination of positive ions and negative ions. For this reason, research has advanced worldwide into various industrial applications which take advantage of ionic liquid characteristics <sup>(47)</sup>.

They have unique properties such as high thermal and electrochemical stability, high ionic conductivity, negligible vapor pressure, and non-flammability and resistance to moisture absorption. These properties make ionic liquids potential benign solvent replacements for volatile organics traditionally used in organic synthesis and separation processes and electrochemical application <sup>(45)</sup>.

Ionic liquids are fluids that consist entirely of organic cations and inorganic or organic anions Fig. (1.9) <sup>(48)</sup>. Seddon speaks of about one trillion ( $10^{18}$ ) possible cation / anion combinations to produce ionic liquids <sup>(49)</sup>.

### 1. Common Cations:-



### 2. Common Anions:-

$[\text{Cl}]^-$ ,  $[\text{AlCl}_4]^-$ ,  $[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$ ,  $[\text{BF}_4]^-$ ,  $[\text{PF}_6]^-$ ,  $[\text{CF}_3\text{SO}_3]^-$ .

**Figure (1.9):- (1) Common cations and (2) Common anions for ionic liquids.**

### **1.3.1 Historical aspect of Ionic Liquids:**

Ionic liquids may be considered as a new class of remarkable solvents, yet they have been around for many years dating back to the 1900s<sup>(50)</sup>. Ionic liquids were initially discovered by electrochemists many years ago while looking for ideal electrolytes for batteries<sup>(49)</sup>. The first recorded ionic liquid, ethylammonium nitrate  $[\text{C}_2\text{H}_5\text{NH}_3] [\text{NO}_3]$ , which is a liquid at room temperature, was discovered by Walden in 1914<sup>(51)</sup>. It was first developed by the military for use in liquid propellants<sup>(51)</sup>. Walden measured the physical properties of ethylammonium nitrate,  $[\text{C}_2\text{H}_5\text{NH}_3] [\text{NO}_3]$ , which has a melting point of 12 °C, formed by the reaction of ethylamine with concentrated nitric acid. The modern history of ionic liquids started with the development of aluminum chloride based salts for electroplating in 1948<sup>(52)</sup>.

Then, Hurley and Weir<sup>(53)</sup> stated that a room temperature ionic liquid could be prepared by mixing and warming 1-ethylpyridinium chloride with aluminum chloride. Ionic liquids were in the some period discovered by US scientists Frank Hurley and Tom Weir at the Rice Institute in Texas in 1951 while looking for a cheaper and easier way to electroplate aluminum. The ionic liquid they produced was an alkylpyridinium chloroaluminate<sup>(53)</sup>. The imidazolium cations were discovered by Hussey and Wilkes at the US Air Force Academy while looking for a replacement for the alkylpyridinium cations since they were relatively easy to reduce, both chemically and electrochemically, their particular favorite, [ethyl methyl imidazolium]  $[\text{AlCl}_4]$  had a melting point below room temperature<sup>(54)</sup>. The chloroaluminate ionic liquids act as both catalyst and solvent in many processes, chemical reactions in the chloroaluminate ionic liquids, including Friedel-Crafts<sup>(55)</sup> and oligomerisation reactions<sup>(56)</sup> have been tested successfully. However, they suffered a major drawback: they are air and

water sensitive and therefore their use as solvents in transition metal catalysis is limited.

In 1970s and 1980s, Osteryoung<sup>(57)</sup> and Hussey<sup>(58)</sup> carried out extensive research on organic aluminum chloride ambient temperature ionic liquids and the first major review of room temperature ionic liquids was written by Hussey<sup>(59)</sup>. The ionic liquids based on  $\text{AlCl}_3$  can be regarded as the first generation of ionic liquids.

In 1992, Wilkes and Zaworotko<sup>(60)</sup> reported the first air and moisture stable ionic liquids based on 1-ethyl-3-methylimidazolium cations with either tetrafluoroborate or hexafluorophosphate as anions. The hexafluorophosphate ionic liquids are, however, less stable to moisture and are known to hydrolyse in the presence of water and heat to form HF and/or phosphoric acid. Therefore, ionic liquids based on more hydrophobic anions such as tri-fluoromethanesulfonate ( $\text{CF}_3\text{SO}_3$ ), bis-(trifluoromethanesulfonyl) imide  $[(\text{CF}_3\text{SO}_2)_2\text{N}_-]$  and tris (trifluoromethanesulfonyl) methide  $[(\text{CF}_3\text{SO}_2)_3\text{C}_-]$  have been developed<sup>(61)</sup>. These ionic liquids have received extensive attention not only because of their low reactivity with water but also because of their large electrochemical windows.

### **1.3.2 General advantages of Ionic liquids:**

Green chemistry concentrated its aims on the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances<sup>(62)</sup>. With the rapid advancements in the field of synthetic organic chemistry, more and more environment friendly processes are being developed at rapid rate. Recently, there has been an upsurge in interest in ionic liquids. It is generally accepted that ionic liquids possess relatively low melting points and are less viscous than molten salts. Ionic

liquids have low vapor pressures, are considered by many authors to be environmentally friendly and can be applied in many organic reactions <sup>(63)</sup>.

The very low vapor pressure of ionic liquids has led to their use as a green solvent in environmentally friendly reactions and separation processes <sup>(64)</sup>. This feature of ionic liquids permits their repeated use as benign solvents for green chemical syntheses without solvent loss to the environment due to evaporation <sup>(65)</sup>. Due to these excellent characteristics of ionic liquids which makes them superior to other organic solvents, scientists have done much work on their applications in electrochemistry, liquid-liquid extraction and catalysis, including biocatalysis and polymerization <sup>(66)</sup>.

Ionic liquids have become very popular in recent years and have proven to be versatile alternatives to classic synthetic procedures using common organic solvents. Application in organic synthesis is enormous and still increasing. They have become of great importance in development of laboratory or industrial catalytic processes <sup>(67)</sup> and biocatalysis <sup>(68)</sup>. They have been used in various polymerization processes and preparation of ion conductive polymer electrolytes <sup>(69, 70)</sup>. Technical applications of ionic liquids present big diversity including preparation of photosensitizers <sup>(71)</sup>, solar cells <sup>(72)</sup>, lubricants for steel <sup>(73)</sup>, improvement of aerogels production <sup>(74)</sup> and HPLC methods <sup>(75)</sup>, and even embalming and tissue preservation for biological purposes <sup>(76)</sup>.

B. Weyershausen and K. Lehmann <sup>(77)</sup> believe that due to their unique properties ionic liquids have a great potential to be used as performance additives in many materials and applications. The application of ionic liquids is in accordance with the chemical industry's guidelines and principles concerning the initiatives sustainable development and responsible care <sup>(77)</sup>.

### **1.3.3 Ionic liquids in electrochemistry:**

The physical and electrochemical properties of air stable room-temperature molten salts have been extensively studied for electrochemical application as electrolytes for batteries and capacitors <sup>(78)</sup>. It possesses several properties which make them attractive alternatives to traditional nonaqueous electrolytes and attractive candidates for various electrochemical devices <sup>(79)</sup>. Ionic liquids with different organic cations have also been suggested for electrolyte applications such as metal surface, finishing batteries, capacitors, fuel cells, electrosynthesis, actuators and nuclear waste treatment <sup>(48)</sup>.

Ionic liquids containing various nonchloroaluminate anions, which are stable in air and moisture, are receiving much attention due to their potential applications in many diverse fields <sup>(80, 81)</sup>.

As a large number of combinations of cations and anions are possible, so the physicochemical properties of ionic liquids can be controlled by a suitable choice of the composition of ionic liquid. The physicochemical properties of different hydrophobic and hydrophilic ionic liquids based on imidazolium cations have been reported to depend upon the alkyl chain length of the imidazolium cation and nature of the anion <sup>(82)</sup>.

Central Research Institute of Electric Power Industry has focused on room temperature ionic liquid because it may be useful for producing inherently safer lithium secondary batteries if used as electrolyte due to its superior flame resistance compared to flammable organic liquid electrolytes <sup>(47)</sup>. The applications of ionic liquid as an alternative to more classical non aqueous electrolytes because of their intrinsic properties the hydrophobic ionic liquid can successfully be used as solvents for lithium salts leading to hydrophobic lithium electrolytes of high conductivity <sup>(83)</sup>.



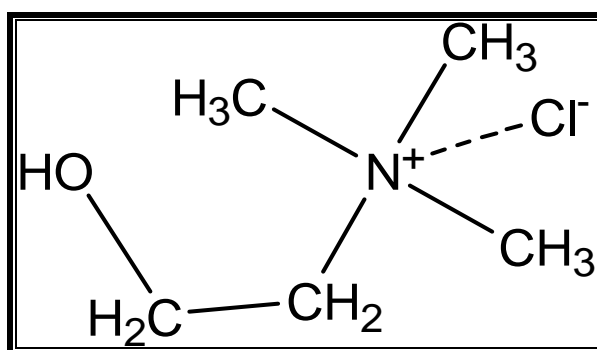
A change in viscosity, density, ion size and degree of dissociation also affects the conductivity of ionic liquid; however it is difficult to estimate the contribution of each parameter separately. However, most of the studies are mainly on ionic liquids containing various fluoroanions and both cations and anions have been reported to be mobile in such ionic liquids, as electrolytes in various electrochemical applications<sup>(84, 85)</sup>.

### 1.3.4 Choline Chloride:

More recently, researchers have been moving away from  $[\text{PF}_6]^-$  and  $[\text{BF}_4]^-$  since they are highly toxic or even away from halogenated compounds completely. Moves towards less toxic cations have been growing, with compounds like ammonium salts such as choline being just as flexible a scaffold as imidazole<sup>(86)</sup>.

Choline chloride is a quaternary amine salt, Ethanaminium, 2-hydroxy-N, N, N-trimethyl-, chloride,  $\text{C}_5\text{H}_{14}\text{NO}.\text{Cl}$

It dissociates in water into the corresponding positively charged quaternary hydroxyl alkylammonium ion and the negatively charged chloride ion. Its structure is illustrated in Fig. (1.10), and physical properties tabulated in table (1.2)<sup>(87)</sup>.



**Figure (1.10):- Structural formula of Choline chloride.**

**Table (1.2):- Physical and chemical properties of choline chloride.**

<i>property</i>	<i>Value</i>
Physical state	White crystalline solid
Melting point	302 °C
Boiling point	Not applicable due to decomposition on heating
Relative density	1.1 g/cm <sup>3</sup>
Viscosity	21 c poise
Vapor pressure	6.6*10 <sup>-8</sup> Pa
Water solubility	650 g/l
Molecular weight	139.63 g/mole

Eutectic mixtures of salts have been utilized for a long time to decrease the temperature for molten salt applications. Ambient temperature molten salts have been formed by mixing quaternary ammonium salts with metal salts.

Halide salts can also form complexes with hydrogen bond donors and previous work has shown that mixtures of urea with alkali metal halides form eutectics with melting points of < 150 °C<sup>(88)</sup>. While a few reports also exist for adducts of urea with other metal salts, their use as solvents has been limited to high temperature applications<sup>(89)</sup>. Recent work<sup>(90)</sup> showed that mixtures of substituted quaternary ammonium salts such as choline chloride with urea produce eutectics that are liquid at ambient temperature and have unusual solvent properties when compared to most molecular solvents and are more typical of the properties observed for ionic liquids. Choline chloride-urea ionic liquids are highly conducting, confirming that the ionic species are dissociated in the liquid and can move independently.

The viscosity and conductivity are strongly affected by the amide and quaternary ammonium salt and hence the fluid properties could be tailored for specific applications <sup>(90)</sup>. The mixtures of amides with quaternary ammonium salts form low melting point eutectics that have unusual solvent properties, additional advantages of this type of mixture is that it is sustainable, biodegradable and a large number of variants can be produced from readily available materials.

#### **1.4 Polymers and ionic liquids:**

Ionic liquids have been incorporated in different polymers to obtain electrolytes in the gel and membrane form, <sup>(91)</sup> for application in a variety of electrochemical devices. The gels are freestanding, flexible films composed of an air-stable. The properties of the novel electrolyte gels are strongly dependent on the type of ionic liquid, the amount of polymer and the preparation method used <sup>(92)</sup>.

The aim of the use of the ionic liquids with polymers to produce leakage-free flexible systems with good conductivity, good transparency, high contrast and response time, ionic liquid polymer electrolytes present high interest for reliability and safety reasons: non volatility, non flammability, relatively high ionic conductivity of the ionic liquid, leakage-free devices and enhanced the mechanical properties of the polymer. Polymer gel electrolytes containing hydrophilic and hydrophobic ionic liquids have been reported to possess high conductivity suitable for applications <sup>(93)</sup>.

Ionic liquids being themselves ionic conductors can find applications in various electrochemical devices and in this direction ion conducting polymer electrolytes containing polymers and ionic liquids prepared in the film form can be interesting electrolytes <sup>(93)</sup>. The blending of ionic liquids with

polymers may lead to the development of new materials (ionic liquids may act as plasticizers, electrolytes dispersed in polymer matrices).

Due to their unique physical and chemical properties, ionic liquids have many advantages when incorporated with polymers materials some of these advantages have been described as follow:

### ***1.4.1 Thermal stability of polymeric gel:***

Polymeric gel systems containing Magnesium salts obtained high ionic conductivity with mixed alkyl carbonates, ethylene carbonate (EC) and dimethyl carbonate (DMC), as a plasticizer <sup>(94)</sup>. However, those low molecular weight organic plasticizers would cause serious troubles when the gel will be applied to practical battery systems at a higher temperature range than their boiling or flash points.

Recently, air- and water-stable organic ionic liquids (also known as room temperature molten salts) have been proposed as non-volatile polar media in variety of electrochemical systems. Especially, much attention has been directed to the combinations of imidazolium cations and specific organic anions <sup>(95)</sup>, Due to their unique characteristics of thermal stability, non-flammability and extremely high ionic conductivity, the ionic liquids can be used for polymeric gel electrolyte as not only the charge carrier but also the plasticizer <sup>(96)</sup>.

The differential scanning calorimeter DSC profiles of the polymeric gel electrolyte did not give any peaks corresponding to the decomposition or evaporation of the gel electrolyte components in the temperature range from  $-150$  to  $300$  °C <sup>(97)</sup>. Thus, M. Morita, T. Shirai and N. Yoshimoto., conclude that the present polymeric gel electrolyte system poly (ethylene oxide)-modified polymethacrylate (PEO-PMA) dissolving 1-ethyl-3-

methylimidazolium (trifluoromethyl sulphonyl) imide (EMITFSI) ionic liquid is stable over a wide temperature range.<sup>(98)</sup>

### **1.4.2 Polymerization in Ionic liquids:**

Ionic liquids, as electrolytes, have also attracted the attention of researchers in the fields of electrochemical polymerization and the synthesis of conducting polymers. Ionic liquids are used as solvents for polymerization processes, and in several systems they indeed show some advantages. In radical polymerization, the  $k_p/k_t$  ratio (where  $k_p$  is the rate constant of propagation and  $k_t$  is the rate constant of termination) is higher than in organic media, and thus better control of the process can be achieved<sup>(99)</sup>.

It has been suggested that the decrease of  $k_t$  is related to the higher viscosity of a solution in an ionic liquid<sup>(100)</sup>. Less obvious is an explanation of the effect of an ionic liquid on  $k_p$ . For homogeneous radical polymerization in an ionic liquid, the  $k_p/k_t$  ratio seems to be considerably higher than that in organic media (in the studied case of MMA polymerization by more than 1 order of magnitude) although it has to be confirmed that this phenomenon is of a general nature.

There are several factors that stimulate the application of ionic liquids as solvents for polymerization processes:

- Ionic liquids are thermally stable and nonvolatile and can be easily recycled.

- Because of their special solvent properties, new homogeneous or heterogeneous polymerization systems may be developed, and the course of polymerization may be favorably affected.
- Because of the large electrochemical window, they are especially suitable as reaction media for electrochemical (and also chemically induced) polymerization processes leading to conducting polymers.

Ionic liquids may simply serve as thermally stable, neutral liquid reaction media for polymerization processes. Thus, they may act as moderators in exothermic polymerization reactions. It has been shown that the thermal polymerization of styrene and acrylonitrile in ionic liquids provides safer processes, reducing the exothermic activity and decreasing product decomposition that may be a source of toxic gases <sup>(101)</sup>.

In addition, the application of ionic liquids as solvents in atom transfer radical polymerizations facilitates the separation of the catalyst residue from the polymer. Because of the good solubility of the catalyst in the ionic liquid, the polymer can be easily extracted with a suitable solvent, whereas essentially all the catalyst remains in the ionic liquid phase <sup>(102)</sup>.

### **1.4.3 Reduce humidification by Ionic liquids:**

Fuel cells which must be operated at 120<sup>o</sup>C or greater, with minimal backpressure and low relative humidity, for stationary applications, the operating conditions requiring temperatures greater than 150<sup>o</sup>C at extremely low relative humidity; Thus, B. Pivovar, R. Gilbertson, Y. Kim, B. Orlor approach to exploring this problem is to investigate ‘free’ proton-containing ionic liquids, are based on imidazole cations and dihydrogen phosphate

( $\text{H}_2\text{PO}_4^-$ ) or bisulfate ( $\text{HSO}_4^-$ ) anions capable of proton conduction (hopping candidates). While these substances have the ability to act as anhydrous proton conductors, they may exhibit greatly increased conductivity even at relatively low relative humidity <sup>(103)</sup>.

#### **1.4.4 Ionic liquids in polymer transducer:**

Ionic liquids have shown promise as replacements for water in ionic polymer transducers. Ionic liquids are non-volatile and have a larger electrochemical stability window than water and a high inherent ionic conductivity. Therefore, transducers employing ionic liquids can be operated for long periods of time in air and can be actuated with higher voltages, thus increasing the transducers energy density. Furthermore, transducers based on ionic liquids do not exhibit the characteristic back relaxation that is common with water-swollen materials. Water has several disadvantages as a solvent for ionic polymer transducers, however. First, water is volatile and will quickly evaporate out of the membrane. This prohibits the use of these devices for long periods of time in an air environment. Water-swollen transducers could also clearly not be used in space applications. Second, the maximum voltage that can be applied to an ionic polymer transducer is determined by the electrochemical stability limit of the solvent. For a platinum electrode, electrolysis of water will occur at a potential of 1.23 V. <sup>(104)</sup>.

### **1.4.5 Ionic liquids as plasticizers:**

One of the unique applications of ionic liquids is as novel plasticizers, as has been shown in a number of publications<sup>(105-109)</sup>. Considering the diverse challenges associated with different traditional plasticizers<sup>(110)</sup>, ionic liquids hold prospects as alternative plasticizers in the rapidly growing plastic industry.

Recently, the possible application of imidazolium ionic liquids as plasticizers for poly methyl methacrylate and poly vinyl chloride has been investigated. As plasticizers, ionic liquids were initially found to have better compatibility with poly (methyl methacrylate) than di-(2-ethylhexyl)-phtalate<sup>(105-107)</sup>. It was also found that they were capable of lowering the Tg of PMMA much more than di-(2-ethylhexyl)-phtalate does, while improving the high temperature stability of PMMA and also providing a wide temperature range for flexible PMMA-based plastics<sup>(105-107)</sup>, and the thermal stability of the polymer can be improved considerably in comparison with that of the most commonly used plasticizer, namely di-(2-ethylhexyl)-phtalate<sup>(105-107)</sup>. Due to the structural similarity of many ionic liquids with traditional phthalate and trimellitate plasticizers, and also based on preliminary results obtained<sup>(105)</sup>, ionic liquids have been proposed to be potential plasticizers for PVC. The phthalates, trimellitates and ionic liquids also share common aliphatic hydrocarbon segments in their structures. Therefore, similar performances were expected with ionic liquids in terms of integrating with polymer chains and providing flexibility. Ammonium, imidazolium and phosphonium cations were able to produce flexible PVC films, as confirmed by the lowered Tg of PVC samples<sup>(108)</sup>.



Encouraging results have also been obtained for PVC. Ionic liquid plasticizers have shown much less of a tendency for leaching and excellent migration resistance. This area of application of ionic liquids has been recently reviewed <sup>(108-109)</sup>.

Mechanical test such as tensile tests on the PVA (poly(vinyl-alcohol)) and Nafion membranes with varying amounts of the ionic liquid, 1-ethyl-3-methylimidazolium dicyanamide [EMIM][N(CN)<sub>2</sub>], show that the ionic liquid acts as a plasticizer - modulus decreases, while the elongation to break increases with increasing ionic liquid. Thermogravimetric analysis shows the representative ionic liquid-polymer membranes are stable above 200°C and scanning electron micrographs reveal phase separation between the ionic liquid and polymer. These results may provide insights into the interactions between ionic liquid and the host polymer, which may aid in the design of new polyelectrolyte membranes <sup>(110)</sup>.

## **1.5 AIM OF THE WORK:**

Ionic liquids are growing materials and their excellent properties such as negligible vapor pressure, high degradation temperature, large electrochemical windows and high ionic conductivities make them growing widely. Although the research on using ionic liquids in polymer system is still in its infancy, several interesting possibilities have already emerged that attracted the attention of polymer chemists in recent years.

In the last two decades, many scientists have studied the electrical behavior of modified polymeric materials <sup>(23)</sup>. These polymers are important for modern technological applications. Thus, the present work is focused on the effect of the addition of the ionic liquids with different concentration as conductive additives on the electrical properties of (polymethyl methacrylate and polyvinyl chloride) thermoplastic insulating polymers.

The ionic liquids incorporated with those polymers are:

- 1- Choline dodecyl benzene sulfonate.
- 2- Ammonium dodecyl benzene sulfonate.
- 3- Choline chloride / Urea.

It is also intended to evaluate the effect of ionic liquids concentration and elevating temperature on the electrical properties of the prepared composites polymers films.

# CHAPTER 3

## Results & Discussion

### **3.1 Composite Materials:**

Composite materials may be defined in general, as the combination of two or more different materials. The purpose for making composites polymers is to improve electrical and mechanical properties of polymers by incorporating suitable fillers to polymer matrix such as: metals, organic and inorganic salts <sup>(113)</sup>.

There are some side effects due to introducing fillers like deterioration the mechanical properties of polymers such as: flexural modulus, tensile properties, impact behavior and elongation, there for its need to plasticizers materials to enhance polymer flexibility are needed. Common problems with plasticizers, however, include evaporation and leakage from the surface, instability at high temperatures, lack of lubrication at low temperatures, migration within polymer and toxicity <sup>(106-109)</sup>.

Recently, ionic liquids have been reported to increase the electrical conductivity of polymers with the improvement of their plasticity <sup>(84, 93, 98)</sup>. The newly prepared room temperature ionic liquids of choline chloride/urea which is a liquid at room temperature with conductive properties though to improve the conductivity of polymers and would also expected to improve polymer plasticity like other ionic liquids <sup>(111)</sup>. In addition to this new ionic liquids, a newly prepared ionic liquids based on dodecyl benzene sulfonate it's also used in an attempt to improve electrical and elastic properties of PMMA and PVC.

### **3.2 D.C Electrical properties of PMMA-Choline dodecyl benzene Sulfonate Composite:**

The D.C electrical resistivity ( $\rho$ ) and the electrical conductivity ( $\sigma$ ) were determined by adopting equations (1.3) and (1.4). It is generally accepted that both the contents of added ionic liquids and temperature greatly affect on the D.C electrical conductivity characteristics of polymers <sup>(10)</sup>.

The measured values and these calculated values of resistivities and corresponding conductivities for PMMA film alone and composites films of PMMA with 10 and 20% choline dodecyl benzene sulfonate are shown in Tables (3.1), (3.2) and (3.3) respectively.

**Table (3.1):- Values of measured resistance and calculated resistivities, conductivities,  $\ln\sigma$  and  $1000/T$  at various temperatures, for polymethyl methacrylate film.**

<i>Temperature K</i>	<i>1000/T K<sup>-1</sup></i>	<i>R*10<sup>-6</sup> Ohm</i>	<i><math>\rho</math> *10<sup>-5</sup> Ohm. cm</i>	<i><math>\sigma</math> *10<sup>11</sup> S. cm<sup>-1</sup></i>	<i>Ln <math>\sigma</math></i>
303	3.30	700	1177470	0.85	-25.49
313	3.19	640	1076544	0.93	-25.40
323	3.09	580	975618	1.02	-25.30
333	3.00	520	874691	1.14	-25.19
343	2.91	460	773766	1.29	-25.07
353	2.83	400	672840	1.49	-24.93
363	2.75	330	555093	1.80	-24.74
373	2.68	210	353241	2.83	-24.29
383	2.61	100	168210	5.94	-23.55

**Table (3.2):- Values of measured resistance and calculated resistivities, Conductivities,  $\ln\sigma$  and  $1000/T$  at variable temperatures, for PMMA with 10% choline dodecyl benzene sulfonate.**

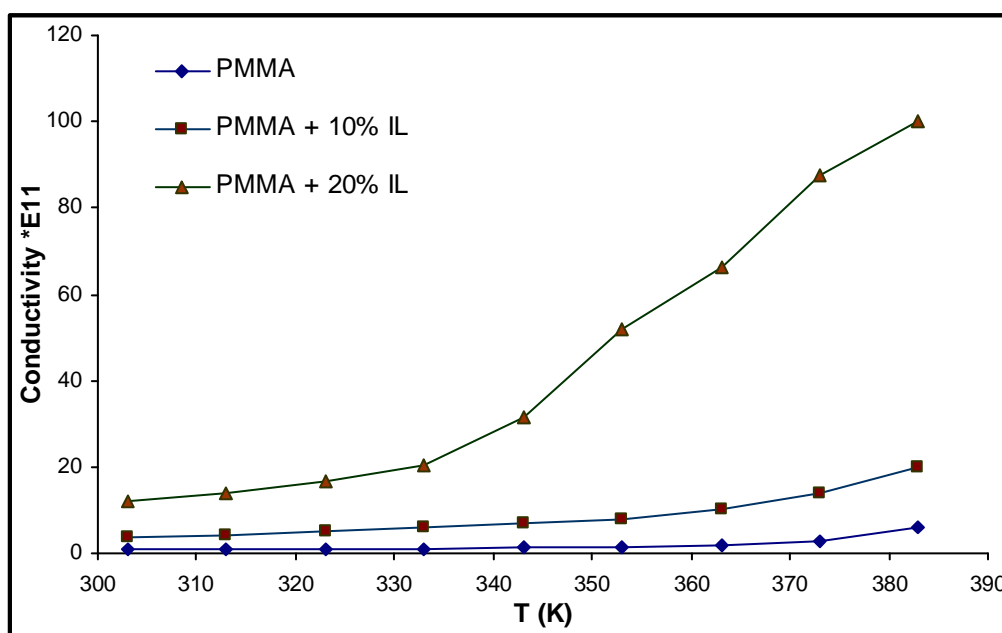
<i>Temperature K</i>	<i>1000/T K<sup>-1</sup></i>	<i>R*10<sup>-6</sup> Ohm</i>	<i><math>\rho</math> *10<sup>-5</sup> Ohm. cm</i>	<i><math>\sigma</math> *10<sup>11</sup> S. cm<sup>-1</sup></i>	<i>Ln <math>\sigma</math></i>
303	3.30	170	285957	3.5	-24.08
313	3.19	148	248950.8	4.02	-23.94
323	3.09	122	205216.2	4.87	-23.74
333	3.00	99	166527.9	6.01	-23.54
343	2.91	86	144660.6	6.91	-23.40
353	2.83	75	126157.5	7.93	-23.26
363	2.75	57	95879.7	10.4	-22.98
373	2.68	42	70648.2	14.1	-22.68
383	2.61	30	50463.0	19.8	-22.34

**Table (3.3):- Values of measured resistance and calculated resistivities, conductivities,  $\ln\sigma$  and  $1000/T$  at variable temperatures, for PMMA with 20% choline dodecyl benzene sulfonate.**

<i>Temperature K</i>	<i>1000/T K<sup>-1</sup></i>	<i>R*10<sup>-6</sup> Ohm</i>	<i><math>\rho</math> *10<sup>-5</sup> Ohm. cm</i>	<i><math>\sigma</math> *10<sup>11</sup> S. cm<sup>-1</sup></i>	<i>Ln <math>\sigma</math></i>
303	3.30	50	84105	11.9	-22.85
313	3.19	43	72330.3	13.8	-22.70
323	3.09	36	60555.6	16.5	-22.52
333	3.00	29	48780.9	20.5	-22.31
343	2.91	19	31959.9	31.3	-21.88
353	2.83	11.5	19344.15	51.7	-21.38
363	2.75	9	15138.9	66.1	-21.14
373	2.68	6.8	11438.28	87.4	-20.86
383	2.61	5	8410.5	100	-20.55

Fig. (3.1) shows the variation of the D.C electrical conductivity for PMMA alone and composite with 10 and 20 Wt% of choline dodecyl benzene sulfonate with various temperature.

The Fig. shows that the D.C electrical conductivity clearly increased with increasing the added weight of ionic liquid to PMMA and that the increase in the conductivity for the samples of high content of ionic liquid is about two orders of magnitude as compared with the conductivity of neat PMMA film (see Tables (3.1) and (3.3)). The electrical conductivity could also be increased as a result of increasing of ionic charge carriers which can be increased due to increasing ionic liquid content <sup>(114, 115)</sup>. There are in agreement with the observed decrease in resistance with increasing the amount of added ionic liquids as shown in Fig. (3.1).



**Figure (3.1):- Variation of D.C electrical conductivity for PMMA-choline dodecyl benzene sulfonate composites with temperature.**

Fig. (3.1) also indicates that the conductivities are directly proportion to temperature. The conductivity was found to have almost identical range of increased values to these of either PMMA alone and composite with both 10 and 20% of choline dodecyl benzene sulfonate ionic liquids. This behavior can be related to the increasing of the ionic charge carriers as well as increasing of polymer segmental motion as a result of increasing temperature for the amorphous polymer in a behavior similar to that of semiconductors materials<sup>(116, 117)</sup>.

From these results, it could be said that the difference in the extent to which the conductivities are affected by the temperature can be attributed to the difference in the chain length since the charge transfer in the polymer chain was shown to be easier than in simple molecules this is in contrast to the behavior of conductivity in metals when increasing the temperature gradually decrease the conductivity due to the vibration and impingements take place between electrons<sup>(118)</sup>.

**Activation energy ( $E_{ac}$ ):**- The activation energy is defined as the amount of energy required to make an electron excitement from the valance band to conduction band. The relationship between conductivity and activation energy is inversely one.

To find the activation energy for the D.C electrical conductivity Arrhenius equation [equation (1.5)] has been used.

$$[\ln \sigma = \ln \sigma_0 - 1/T * E_{ac}/B] * 1000/1000$$

$\ln \sigma_0$  negligible

( $\ln \sigma$ ) was plotted as the [Y axis] and  $(1000 / T \text{ K}^{-1})$  as the [X axis]

Therefore:

$$\text{Slope} = E_{ac} / B * 10^3$$

$$B = 8.62 * 10^{-5} \text{ eV/K}$$

$$E_{ac} = \text{slope} * 8.62 * 10^{-2}$$

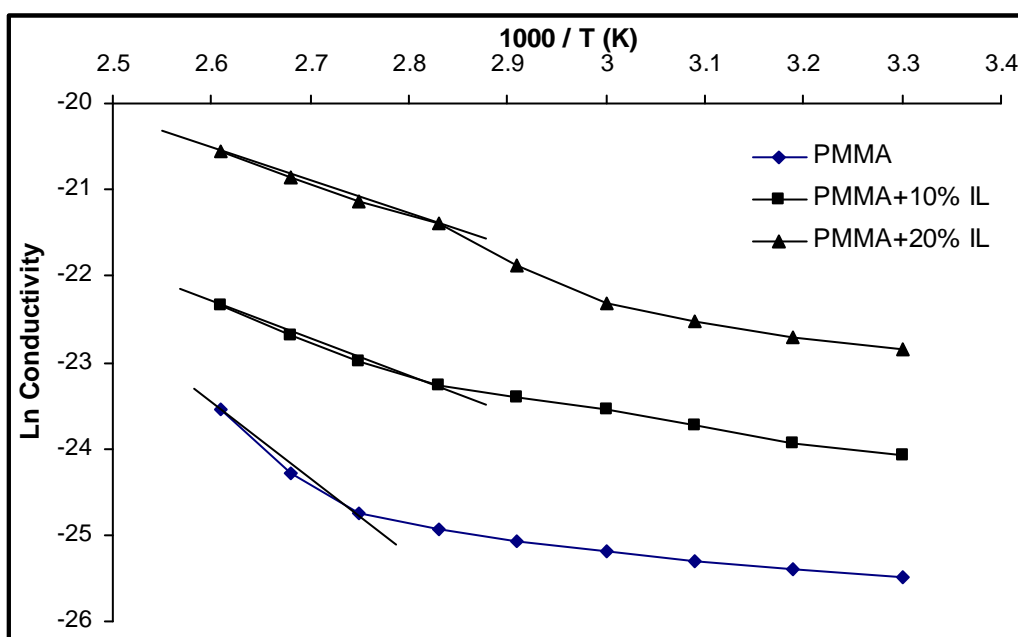
Fig. (3.2) show the plot of  $\ln\sigma$  against the corresponding  $1000/T$  values. The Fig. indicates that PMMA alone has high activation energy value, as given in Table (3.4), while the film of 10% and 20% choline dodecyl benzene sulfonate content have low activation energy values. This behavior can be attributed to the thermal movement of the ions and the molecules of polymer alone, whereas the low activation energy values for the films containing of the ionic liquid can be related to the diffusion of the ionic liquid particles in polymer matrix, the activation energy more decreased with 20 wt % ionic liquid content due to decrease of the distance between the ionic liquid particles. Higher ionic liquid concentration would enhance shorter distance between ionic liquid particles.

The  $T_g$  play the important role in determination the slope for calculate the  $E_{ac}$ , the curve was non linear [due to amorphous nature for the polymers were used] and have three transfer regions; before, through and after  $T_g$ , we take the slope after  $T_g$  for the points have one linearity to determine the lowest  $E_{ac}$  value due to high temperature and higher conductivity.

The conductivity of PMMA alone highly increased above  $T_g$  due to transfer the polymer from the glassy to rubber state; in the rubbery state the polymer chains being easy in movement and the molecule in fresher. Therefore, transitions of the charge carriers become very easy. This behavior can leads to increasing in conductivity after  $T_g$ .



The  $T_g$  decreased when the system (polymer matrix) contains the ionic liquids. This suggests explained by; the interaction between the polymer matrix and ionic liquid is weak. In other words, partial crystallization of the repeated polymer units would be debilitated by the interaction of the repeated polymer units with ions consists of ionic liquids <sup>(98)</sup>. Therefore, ionic liquids would act as electrolytes and plasticizers by decreasing the  $T_g$ . This is, however, was observed as the plasticity of the polymer increased when ionic liquid was composite with the polymers, at less to the manual.



**Figure (3.2):- Variation of Ln D.C electrical conductivity with reciprocal absolute temperature for PMMA-choline dodecyl benzene sulfonate composite.**

**Table (3.4):- Values of slope and D.C activation energy for PMMA-Choline dodecyl benzene sulfonate composite.**

<i>Choline dodecyl benzene sulfonate %</i>	<i>Slope</i>	<i>E<sub>ac</sub> (eV)</i>	<i>Temperature range</i>
0%	8.500	0.733	363-383 K
10%	4.182	0.361	353-383 K
20%	3.773	0.325	353-383 K

### **3.3 D.C Electrical properties of PMMA-Ammonium dodecyl benzene Sulfonate Composite:**

**Table (3.5):- Values of measured resistance and calculated resistivities, conductivities,  $\ln\sigma$  and  $1000/T$  at various temperatures, for PMMA with 10% ammonium dodecyl benzene sulfonate.**

<i>Temperature K</i>	<i>1000/T K<sup>-1</sup></i>	<i>R*10<sup>-6</sup> Ohm</i>	<i><math>\rho *10^{-5}</math> Ohm. cm</i>	<i><math>\sigma *10^{11}</math> S. cm<sup>-1</sup></i>	<i>Ln <math>\sigma</math></i>
303	3.30	130	218673	4.57	-23.81
313	3.19	115	193441.5	5.17	-23.69
323	3.09	99	166527.9	6.01	-23.53
333	3.00	81	136250.1	7.34	-23.33
343	2.91	66	111018.6	9.01	-23.13
353	2.83	60	100926	9.91	-23.03
363	2.75	46	77376.6	12.9	-22.77
373	2.68	35	58873.5	17.0	-22.50
383	2.61	25	42052.5	23.8	-22.16

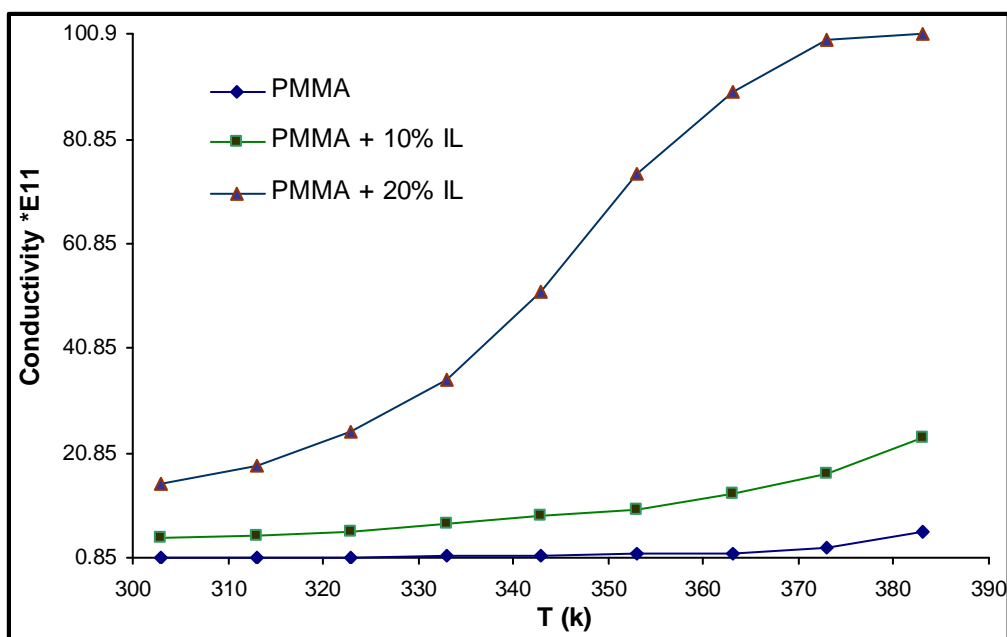
**Table (3.6):- Values of measured resistance and calculated resistivities, conductivities,  $\ln \sigma$  and  $1000/T$  at various temperatures, for PMMA with 20% ammonium dodecyl benzene sulfonate.**

<i>Temperature K</i>	<i>1000/T K<sup>-1</sup></i>	<i>R*10<sup>-6</sup> Ohm</i>	<i><math>\rho</math> *10<sup>-5</sup> Ohm. cm</i>	<i><math>\sigma</math> *10<sup>11</sup> S. cm<sup>-1</sup></i>	<i>Ln <math>\sigma</math></i>
303	3.30	40	67284	14.9	-22.63
313	3.19	32	53827.2	18.6	-22.41
323	3.09	24	40370.4	24.8	-22.12
333	3.00	17	28595.7	35.0	-21.77
343	2.91	11.5	19344.15	51.7	-21.38
353	2.83	8	13456.8	74.3	-21.02
363	2.75	6.6	11101.86	90.1	-20.83
373	2.68	5.2	8746.92	100	-20.59
383	2.61	4	6728.4	101	-20.33

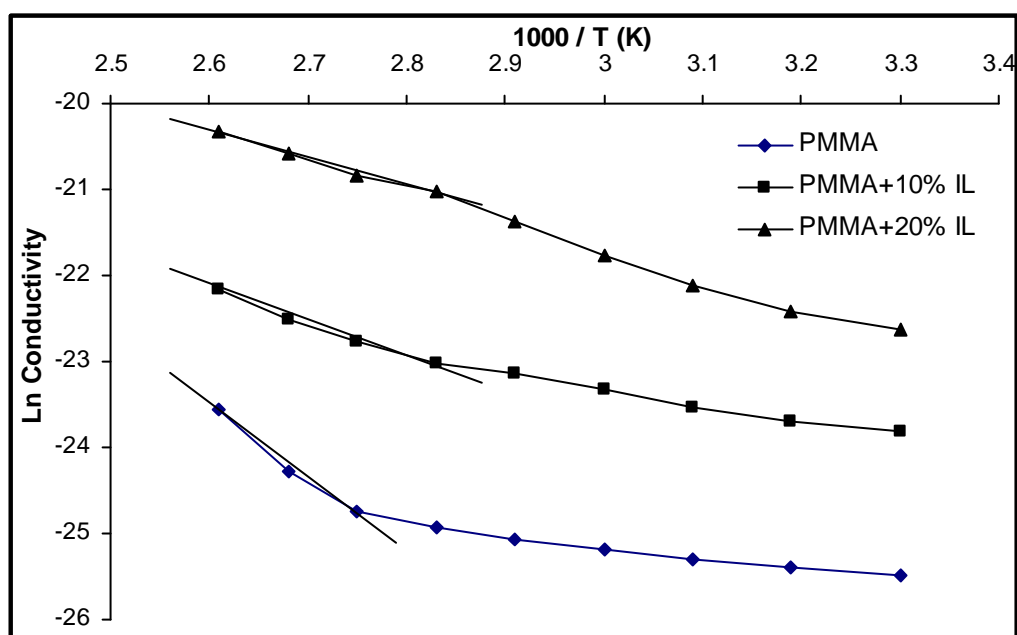
The variation of D.C electrical conductivity with temperature at different ionic liquid content is shown in Fig. (3.3). The Figure shows the dependence of D.C electrical conductivity on ammonium dodecyl benzene sulfonate concentration, the conductivity increase with increasing ionic liquid content.

Fig. (3.3) also indicates that the conductivities were increased with increasing the temperature. The dependence of D.C electrical conductivity of PMMA alone and its composites on temperature indicates in Fig. (3.4).

The relation of  $\ln \sigma$  against the reciprocal absolute temperature is shown in Fig. (3.4), from this Fig. we can calculate the activation energy which has been listed in Table (3.7), the  $E_{ac}$  decrease with increasing ammonium dodecyl benzene sulfonate ionic liquid content. The high  $E_{ac}$  can be attributed to the thermal movement of the ions and the molecules, whereas the low  $E_{ac}$  values for the films containing of ammonium dodecyl benzene sulfonate resulted from the diffusion the ionic liquid particles then decreasing of the distance between the ionic liquids particles in polymer matrix.



**Figure (3.3):-** Variation of D.C electrical conductivity for PMMA-ammonium dodecyl benzene sulfonate composite with temperature.



**Figure (3.4):-** Variation of ln D.C electrical conductivity with reciprocal absolute temperature for PMMA-ammonium dodecyl benzene sulfonate composite.

**Table (3.7):- Values of slope and D.C activation energy for PMMA-Ammonium dodecyl benzene sulfonate composites.**

<i>Ammonium dodecyl benzene sulfonate %</i>	<i>Slope</i>	<i>E<sub>ac</sub> (eV)</i>	<i>Temperature range</i>
0%	8.500	0.733	363-383 K
10%	3.954	0.341	353-383 K
20%	3.136	0.270	353-383 K

PMMA with both choline dodecyl benzene sulfonate and ammonium dodecyl benzene sulfonate ionic liquids composites films exhibits clear view under the microscope lens and not show any recognized particles, it showed a photograph similar to that of the film of PMMA alone as in Fig. (3.7 [a]). These ionic liquids do not show net of electrolyte particles on the surface of polymer film, this apparent behavior pointing to that, the choline dodecyl benzene sulfonate and ammonium dodecyl benzene sulfonate materials are completely immiscible with PMMA (i.e. they are compounds probably dissolved and accommodated in the voids of the polymer matrix and do not migrates to the surface of the polymer film due probably some strong interaction with the polymer.

### 3.4 D.C Electrical properties of PMMA-Choline chloride / Urea Composite:

**Table (3.8):- Values of measured resistance and calculated resistivities, conductivities,  $\ln\sigma$  and  $1000/T$  at various temperatures, for PMMA with 10% choline chloride / urea.**

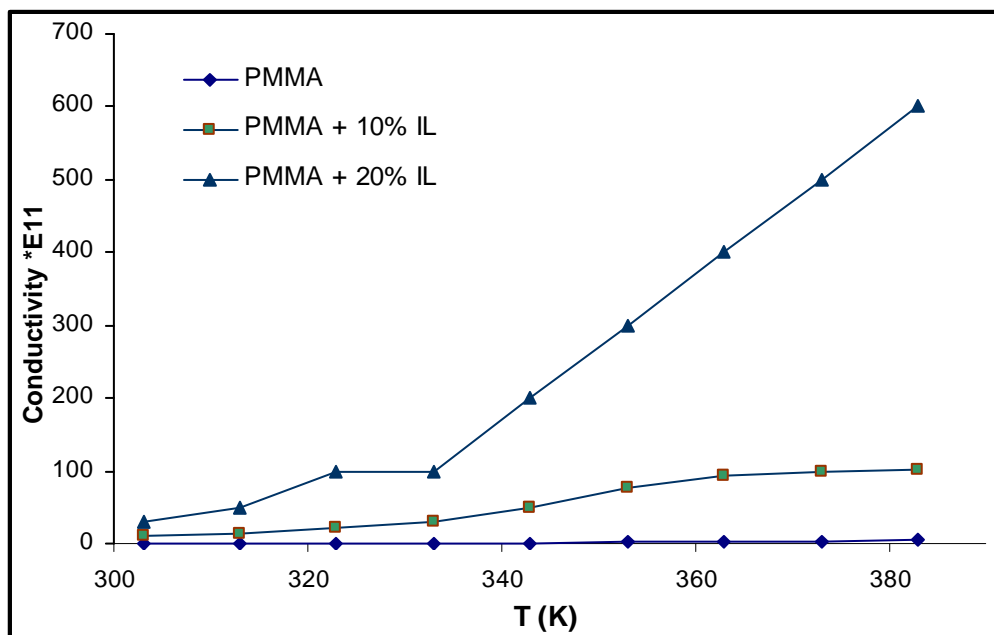
<i>Temperature K</i>	<i>1000/T K<sup>-1</sup></i>	<i>R*10<sup>-6</sup> Ohm</i>	<i><math>\rho</math> *10<sup>-5</sup> Ohm. cm</i>	<i><math>\sigma</math> *10<sup>11</sup> S. cm<sup>-1</sup></i>	<i>Ln <math>\sigma</math></i>
303	3.30	59.4	99916.74	10.1	-23.02
313	3.19	44	74012.4	13.5	-22.72
323	3.09	28	47098.8	21.2	-22.27
333	3.00	19	31959.9	31.3	-21.88
343	2.91	12	20185.2	49.5	-21.42
353	2.83	7.8	13120.38	76.2	-20.99
363	2.75	6.3	10597.23	94.4	-20.78
373	2.68	4.9	8242.29	100	-20.53
383	2.61	4	6728.4	102	-20.33

**Table (3.9):- Values of measured resistance and calculated resistivities, conductivities,  $\ln\sigma$  and  $1000/T$  at various temperatures, for PMMA with 20% cholin chloride / urea.**

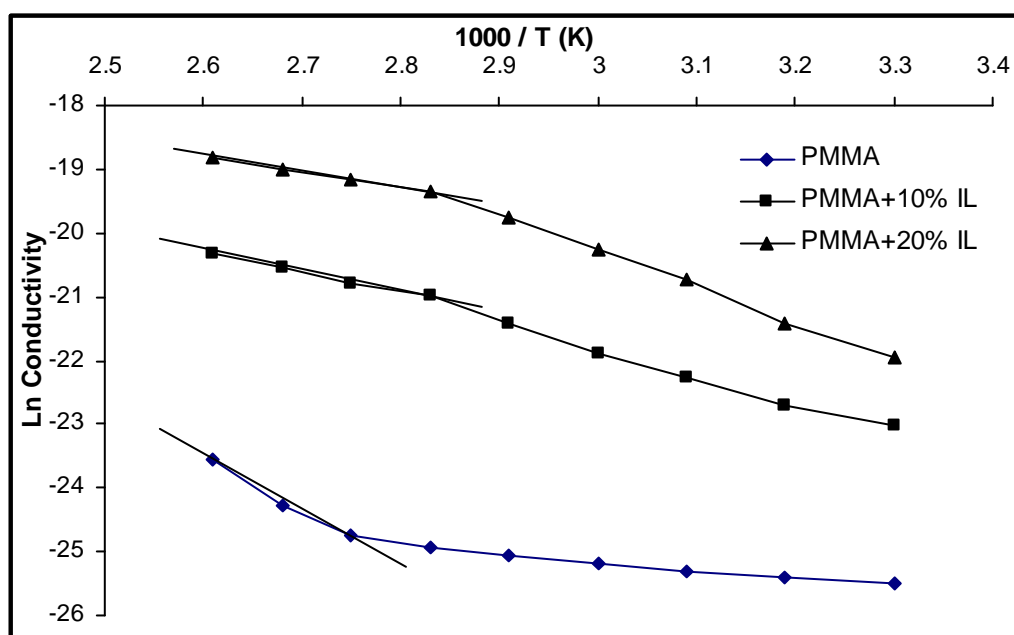
<i>Temperature K</i>	<i>1000/T K<sup>-1</sup></i>	<i>R*10<sup>-6</sup> Ohm</i>	<i><math>\rho</math> *10<sup>-5</sup> Ohm. cm</i>	<i><math>\sigma</math> *10<sup>11</sup> S. cm<sup>-1</sup></i>	<i>Ln <math>\sigma</math></i>
303	3.30	20	33642	29.7	-21.94
313	3.19	12	20185.2	49.5	-21.42
323	3.09	6	10092.6	99.1	-20.73
333	3.00	3.7	6223.77	100	-20.25
343	2.91	2.3	3868.83	200	-19.77
353	2.83	1.50	2523.15	300	-19.35
363	2.75	1.25	2102.625	400	-19.16
373	2.68	1.05	1766.205	500	-18.99
383	2.61	0.9	1513.89	600	-18.83

The D.C electrical conductivity of PMMA-choline chloride/urea ionic liquid composites as a function of temperature, are shown in Fig. (3.5). The Figure shows that when ionic liquids content increase the conductivity increased as a result of the increase charge density in polymer matrix. This Figure indicate too that the conductivity increase with increasing the temperature, the Figure shows that for all samples of zero, 10 and 20 wt % choline chloride / urea ionic liquid content the conductivity is increased with increasing temperature.

The relation of  $\ln \sigma$  against the reciprocal absolute temperature is shown in Fig. (3.6). From this Figure we can calculate the slope then the activation energy by Arrhinus equation, this figure indicates that the neat PMMA sample has high activation energy value, see Table (3.10), while the films of 10 and 20 wt % cholin chloride / urea content has low activation energy values. This behavior can be attributed to the thermal movement of ions and molecules, the low  $E_{ac}$  values for the films of containing ionic liquid can be attributed to the net formation from ionic liquid particles in the polymer matrix then decreasing of the distance between the ionic liquid particles due to increasing ionic liquid content as have been indicated in Fig. (3.7).



**Figure (3.5):-** Variation of D.C electrical conductivity for PMMA-choline chloride / urea composite with temperature.



**Figure (3.6):-** Variation of ln D.C electrical conductivity with reciprocal absolute temperature for PMMA-choline chloride / urea composite.



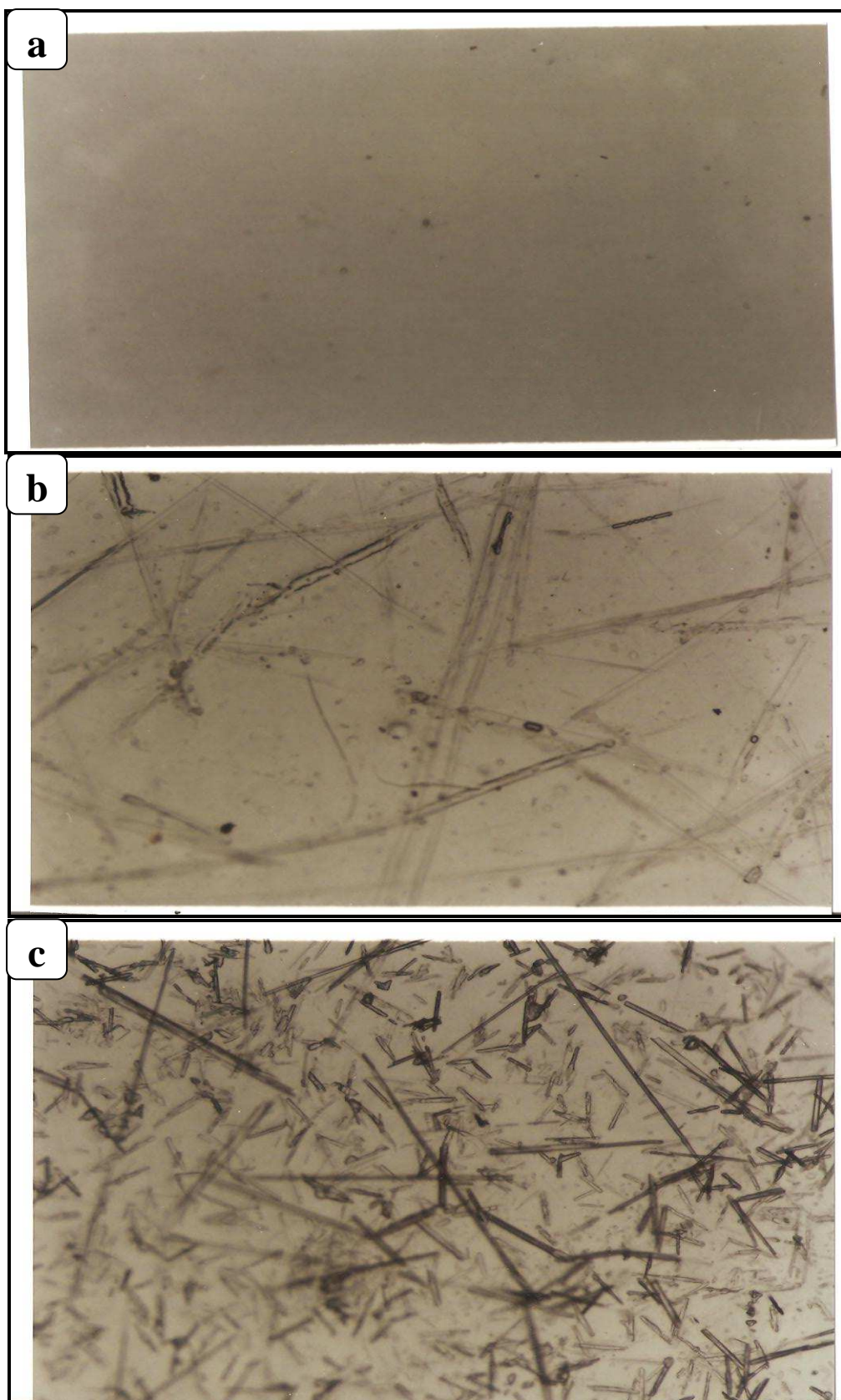
**Table (3.10):- Values of slope and D.C activation energy for PMMA-Choline chloride / urea ionic liquid composite.**

<i>Choline chloride / urea %</i>	<i>Slope</i>	<i>E<sub>ac</sub> (eV)</i>	<i>Temperature range</i>
0%	8.500	0.733	363-383 K
10%	3.000	0.259	353-383 K
20%	2.364	0.204	353-383 K

The increment in the D.C electrical conductivity values of PMMA-choline chloride/urea composites is ascribed to the rearrangements of the electrolyte particles through out the polymer matrix as indicate in Fig. (3.7).

choline chloride/urea may have limited solubility and/or compatibility with the polymer because of that some of choline chloride/urea migrates to the surface of the polymer a phenomenon known with the ionic liquid antistatic additive. It's migrated to the surface of polymer film forming net of choline chloride/urea particles which are randomly distributed on the polymer surface and connected to each other.

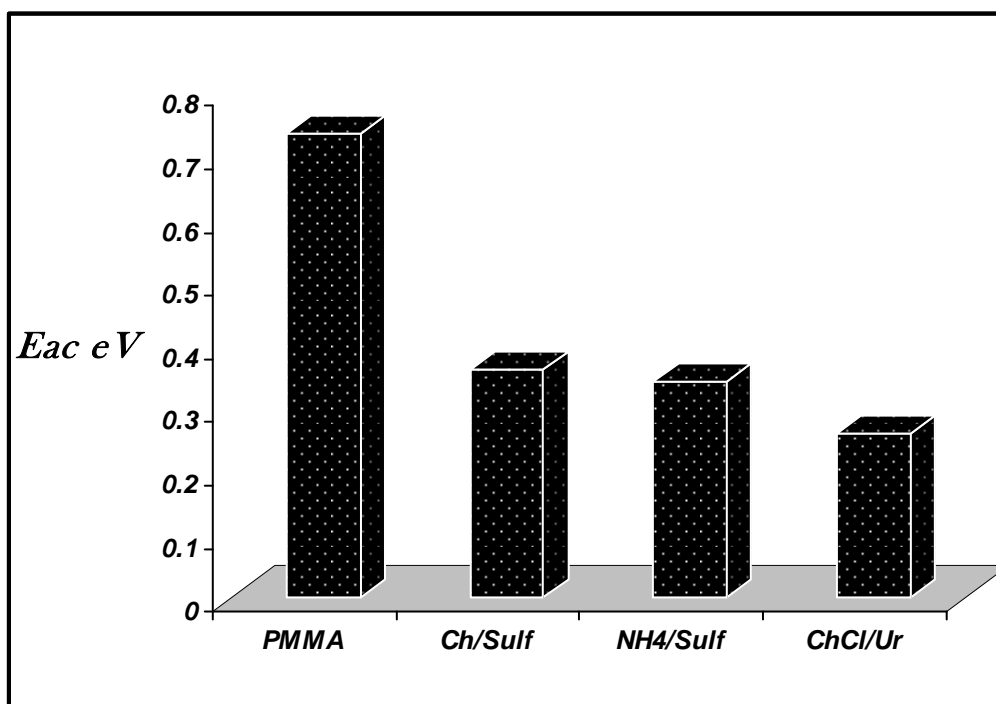
Fig. (3.7 [b] And [c]) showed the effect of increasing the content of ionic liquid as when the amount of added ionic liquid increased from 10 to 20 wt % the migrated particles increased on the surface of PMMA film (compare Fig. (3.7 [b] And [c])). Such net interaction would ease the dissipation of charges from the surface of the polymer film. The above approach which described the dependence of the electrical conductivity on the rearrangement of the filler particles is similar to that observed by other workers<sup>(114)</sup>.



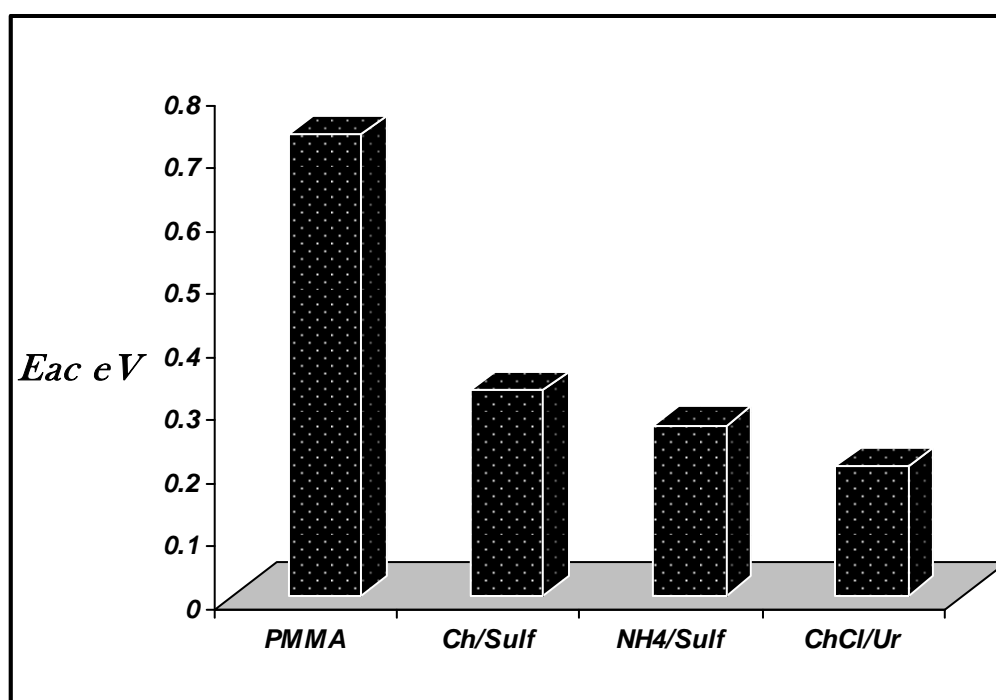
**Figure (3.7):-** Photomicrographs (x40) for (a) pure PMMA, (b) with 10 wt % and (c) with 20 wt % of choline chloride / urea ionic liquid respectively.

Fig. (3.8 And 3.9) show the activation energy for PMMA alone in comparison with added wt % of ionic liquids. These Figures showed the same trend of decreasing activation energy when these ionic liquids were added to PMMA, the activation energy highly reducing from PMMA alone [see Tables (3.4), (3.7) and (3.10)], although when ionic liquids were added in twice the amount of the wt. in 10 and 20%, did not show a similar reduction in activation energy. These reductions from 10 % to 20 % illustrated in these Tables. However the activation energy, it for example Figures (3.8 or 3.9) was taken, showed a gradual decrease when choline dodecyl benzene sulfonate (**Ch/Sulf**), ammonium dodecyl benzene sulfonate (**NH<sub>4</sub>/Sulf**) and choline chloride / urea (**ChCl/Ur**) were used. The lowest activation energy found with choline chloride / urea may be attributed to not only the net formation on the surface but may be due to also the dissolved ionic liquid by the polymer or even to the differences between their ionic conductivity in their pure state.

Additionally ionic liquids materials may result in a decrease of the T<sub>g</sub> value of polymers which lead to increase segmental mobility i.e. increasing conductivity resulted in low activation energy. The variation in the activation energy of D.C electrical conductance for ionic liquids in PMMA may also be attributed to the presence of chloride ions (Cl<sup>-</sup>) in choline chloride and high electrons density by nitrogen atoms and oxygen in urea enhance the electrical conductivity of the PMMA-choline chloride/urea composites.



**Figure (3.8):-** Variations of the D.C activation energy of PMMA alone and with added 10% (Ch/Sulf), (NH<sub>4</sub>/Sulf) and (ChCl/Ur) respectively.



**Figure (3.9):-** Variation of the D.C activation energy of PMMA alone and with added 20% (Ch/Sulf), (NH<sub>4</sub>/Sulf) and (ChCl/Ur) respectively.

### 3.5 D.C Electrical properties of PVC-Choline dodecyl benzene Sulfonate Composite:

**Table (3.11):- Values of measured resistance and calculated resistivities, conductivities,  $\ln\sigma$  and  $1000/T$  at various temperatures, for polyvinyl chloride film.**

<i>Temperature K</i>	<i>1000/T K<sup>-1</sup></i>	<i>R*10<sup>-6</sup> Ohm</i>	<i><math>\rho</math> *10<sup>-5</sup> Ohm. cm</i>	<i><math>\sigma</math> *10<sup>11</sup> S. cm<sup>-1</sup></i>	<i>Ln <math>\sigma</math></i>
303	3.30	500	841050	1.19	-25.15
313	3.19	470	790587	1.26	-25.09
323	3.09	440	740124	1.35	-25.03
333	3.00	410	689661	1.45	-24.96
343	2.91	380	639198	1.56	-24.88
353	2.83	180	302778	3.3	-24.13
363	2.75	140	235494	4.25	-23.88
373	2.68	105	176620.5	5.66	-23.59
383	2.61	70	117747	8.49	-23.19

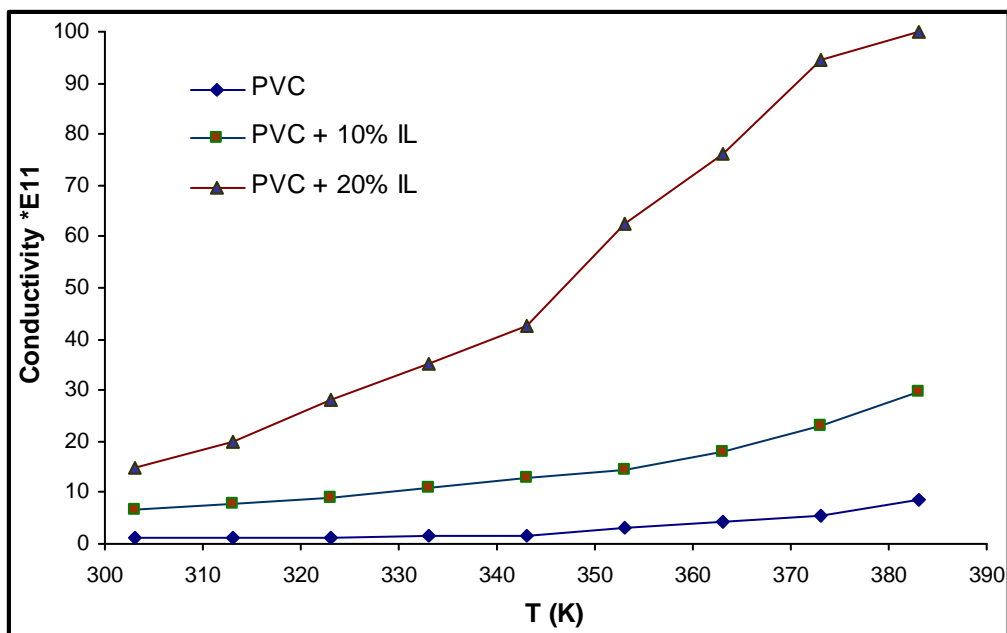
**Table (3.12):- Values of measured resistance and calculated resistivities, conductivities,  $\ln\sigma$  and  $1000/T$  at various temperatures, for PVC with 10% choline dodecyl benzene sulfonate.**

<i>Temperature K</i>	<i>1000/T K<sup>-1</sup></i>	<i>R*10<sup>-6</sup> Ohm</i>	<i><math>\rho</math> *10<sup>-5</sup> Ohm. cm</i>	<i><math>\sigma</math> *10<sup>11</sup> S. cm<sup>-1</sup></i>	<i>Ln <math>\sigma</math></i>
303	3.30	90	151389	6.61	-23.44
313	3.19	76	127839.6	7.82	-23.27
323	3.09	66	111018.6	9.01	-23.13
333	3.00	54	90833.4	11	-22.93
343	2.91	46	77376.6	12.9	-22.77
353	2.83	41	68966.1	14.5	-22.65
363	2.75	33	55509.3	18	-22.44
373	2.68	26	43734.6	22.9	-22.20
383	2.61	20	33642	29.7	-21.94

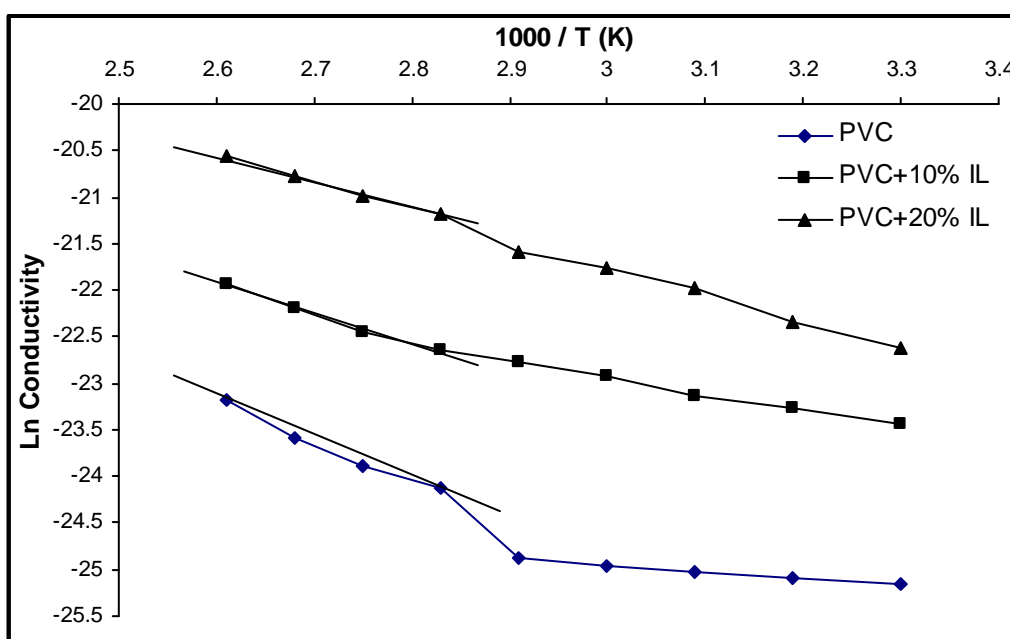
**Table (3.13):- Values of measured resistance and calculated resistivities, conductivities,  $\ln\sigma$  and  $1000/T$  at various temperatures, for PVC with 20% choline dodecyl benzene sulfonate.**

<i>Temperature K</i>	<i>1000/T K<sup>-1</sup></i>	<i>R*10<sup>-6</sup> Ohm</i>	<i><math>\rho</math> *10<sup>-5</sup> Ohm. cm</i>	<i><math>\sigma</math> *10<sup>11</sup> S. cm<sup>-1</sup></i>	<i>Ln <math>\sigma</math></i>
303	3.30	40	67284	14.9	-22.63
313	3.19	30	50463	19.8	-22.34
323	3.09	21	35324.1	28.3	-21.98
333	3.00	17	28595.7	35	-21.77
343	2.91	14	23549.4	42.5	-21.58
353	2.83	9.5	15979.95	62.6	-21.19
363	2.75	7.8	13120.38	76.2	-20.99
373	2.68	6.3	10597.23	94.4	-20.78
383	2.61	5	8410.5	100	-20.55

The D.C electrical conductivity of alone polyvinyl chloride film and composite with choline dodecyl benzene sulfonate as a function of temperature are shown in Fig. (3.10), the electrical conductivity for polyvinyl chloride is increased with ionic liquid additive concentration is increased as a result of the increase charge carriers density in polymer matrix. The variation of D.C electrical conductivity for polyvinyl chloride-choline dodecyl benzene sulfonate ionic liquid composites of different ionic liquid concentration with temperature indicates in Fig. (3.10) too, the conductivity for all the samples of zero, 10 and 20 wt % choline dodecyl benzene sulfonate ionic liquid content is increased with increasing the temperature in behavior similar to that of semiconductor materials.



**Figure (3.10):-** Variation of D.C electrical conductivity for PVC-choline dodecyl benzene sulfonate composite with temperature.



**Figure (3.11):-** Variation of ln D.C electrical conductivity with reciprocal absolute temperature for PVC-choline dodecyl benzene sulfonate composite.

Fig. (3.11) shows the plot of  $\ln\sigma$  against the corresponding  $1000/T$  values, this figure indicates that pure PVC sample has high activation energy value, Table (3.14), while the films of 10 and 20% choline dodecyl benzene sulfonate ionic liquid content have low activation energy values. This behavior can be attributed to the thermal movement of ions and molecules, the low activation energy values can be related to the present of ionic liquid particles in the polymer matrix then decreasing of the distance between these particles due to increasing of the ionic liquid content.

**Table (3.14):- Value of slope and D.C activation energy for PVC-Choline dodecyl benzene sulfonate ionic liquid composite.**

<i>Choline dodecyl benzene sulfonate %</i>	<i>Slope</i>	<i>E<sub>ac</sub> (eV)</i>	<i>Temperature range</i>
0%	4.046	0.349	353-383 K
10%	3.227	0.278	353-383 K
20%	2.909	0.251	353-383 K



### **3.6 D.C Electrical properties of PVC-Ammonium dodecyl benzene Sulfonate Composite:**

**Table (3.15):- Values of measured resistance and calculated resistivities, conductivities,  $\ln\sigma$  and  $1000/T$  at variable temperatures, for PVC with 10% ammonium dodecyl benzene sulfonate.**

<i>Temperature K</i>	<i>1000/T K<sup>-1</sup></i>	<i>R*10<sup>-6</sup> Ohm</i>	<i><math>\rho *10^{-5}</math> Ohm. cm</i>	<i><math>\sigma *10^{11}</math> S. cm<sup>-1</sup></i>	<i>Ln <math>\sigma</math></i>
303	3.30	60	100926	9.91	-23.03
313	3.19	48	80740.8	12.4	-22.81
323	3.09	38	63919.8	15.6	-22.58
333	3.00	29	48780.9	20.5	-22.31
343	2.91	26	43734.6	22.9	-22.20
353	2.83	24	40370.4	24.8	-22.12
363	2.75	20	33642.0	29.7	-21.94
373	2.68	16	26913.6	37.2	-21.71
383	2.61	13	21867.3	45.7	-21.51

**Table (3.16):- Values of measured resistance and calculated resistivities, conductivities,  $\ln\sigma$  and  $1000/T$  at variable temperatures, for PVC with 20% ammonium dodecyl benzene sulfonate.**

<i>Temperature K</i>	<i>1000/T K<sup>-1</sup></i>	<i>R*10<sup>-6</sup> Ohm</i>	<i><math>\rho *10^{-5}</math> Ohm. cm</i>	<i><math>\sigma *10^{11}</math> S. cm<sup>-1</sup></i>	<i>Ln <math>\sigma</math></i>
303	3.30	30	50463	19.8	-22.34
313	3.19	25	42052.5	23.8	-22.16
323	3.09	21	35324.1	28.3	-21.98
333	3.00	17	28595.7	35	-21.77
343	2.91	12	20185.2	49.5	-21.43
353	2.83	8.6	14466.06	69.1	-21.09
363	2.75	7.3	12279.33	81.4	-20.93
373	2.68	6.1	10260.81	97.5	-20.75
383	2.61	5	8410.5	100	-20.55

Fig. (3.12) shows the dependence of D.C electrical conductivity on temperature at different ionic liquid content; the figure shows the conductivity increase with increasing ammonium dodecyl benzene sulfonate ionic liquid content.

The Fig. so shows that the conductivity increase with increasing the temperature for all the samples of zero, 10 and 20 wt % from ionic liquid.

The relation of  $\ln \sigma$  against the reciprocal absolute temperature is shown in Fig. (3.13), from this Fig. we can calculate the activation energy. Which have been listed in Table (3.17), the  $E_{ac}$  decrease with addition of ammonium dodecyl benzene sulfonate ionic liquid.

Both choline dodecyl benzene sulfonate and ammonium dodecyl benzene sulfonate ionic liquids with PVC composites in all concentrations exhibits clear view (similar to that of the pure PVC sample in Fig. (3.16 [a])). Under the microscope lens and not show any recognized region, this is pointing to completely immiscible between this ionic liquids and polymer matrix (PVC) due to some strong interaction with the polymer and do not a migration of added ionic liquids as observed for choline chloride/urea ionic liquid.

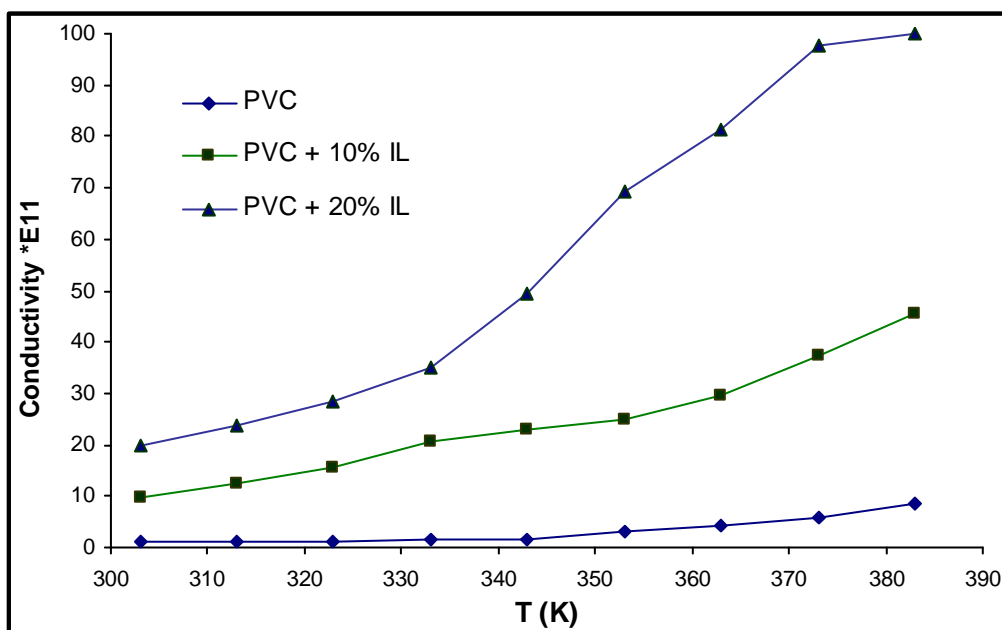


Figure (3.12):- Variation of D.C electrical conductivity for PVC-ammonium dodecyl benzene sulfonate composite with temperature.

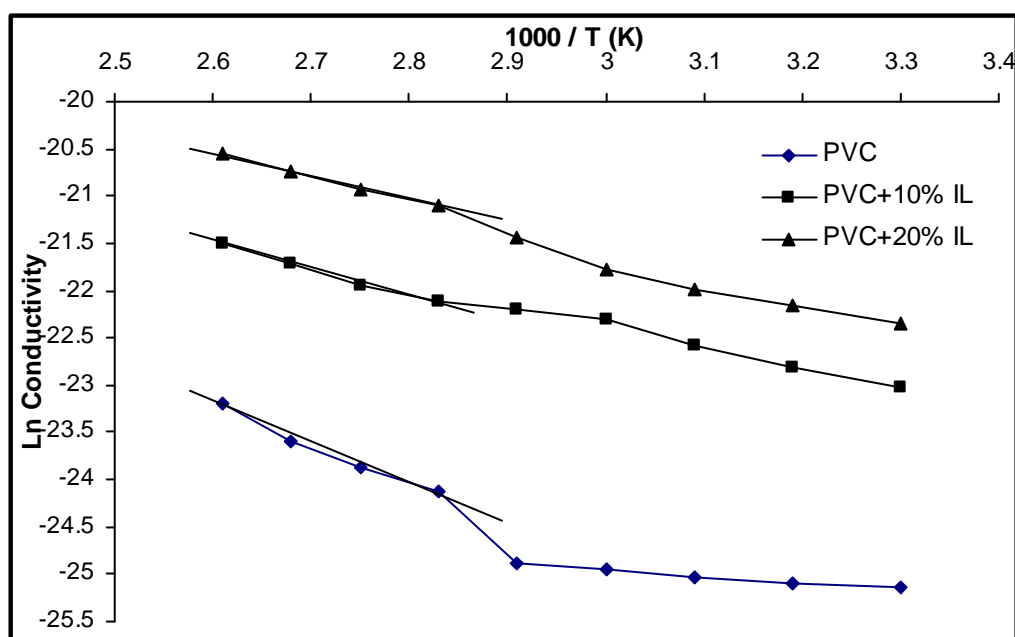


Figure (3.13):- Variation of ln D.C electrical conductivity with reciprocal absolute temperature for PVC-ammonium dodecyl benzene sulfonate composite.

**Table (3.17):- Values of slope and D.C activation energy for PVC-Ammonium dodecyl benzene sulfonate ionic liquid composite.**

<i>Ammonium dodecyl benzene sulfonate %</i>	<i>Slope</i>	<i>E<sub>ac</sub> (eV)</i>	<i>Temperature range</i>
0%	4.046	0.349	353-383 K
10%	2.773	0.239	353-383 K
20%	2.454	0.211	353-383 K

### 3.7 D.C Electrical properties of PVC-Choline chloride / Urea Composite:

**Table (3.18):- Values of measured resistance and calculated resistivities, conductivities,  $\ln\sigma$  and  $1000/T$  at variable temperatures, for PVC with 10% choline chloride / urea.**

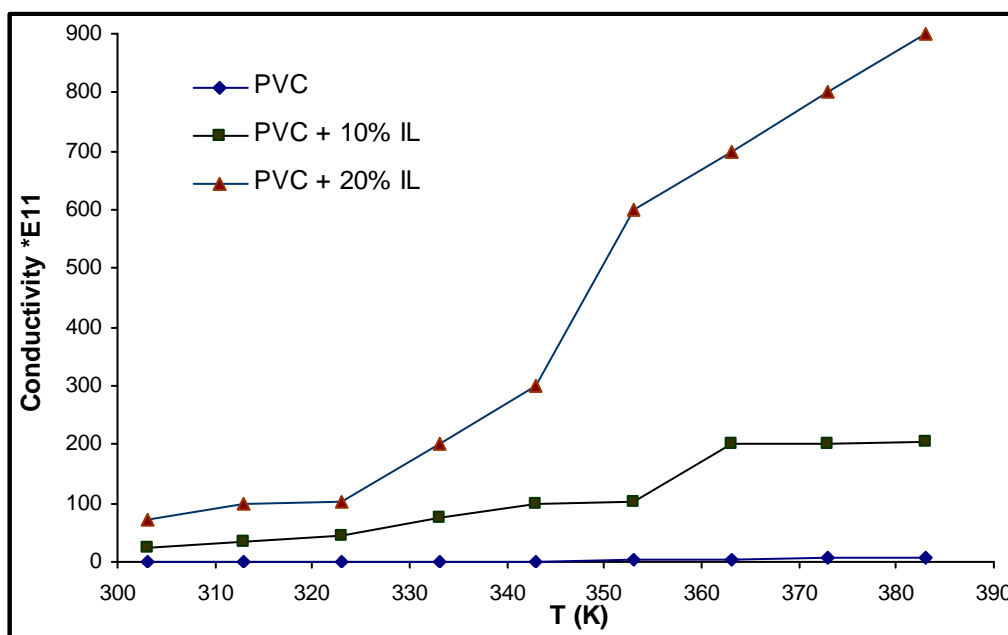
<i>Temperature K</i>	<i>1000/T K<sup>-1</sup></i>	<i>R*10<sup>-6</sup> Ohm</i>	<i><math>\rho</math> *10<sup>-5</sup> Ohm. cm</i>	<i><math>\sigma</math> *10<sup>11</sup> S. cm<sup>-1</sup></i>	<i>Ln <math>\sigma</math></i>
303	3.30	25	42052.5	23.8	-22.16
313	3.19	18	30277.8	33	-21.83
323	3.09	13	21867.3	45.7	-21.51
333	3.00	8	13456.8	74.3	-21.02
343	2.91	4.7	7905.87	100	-20.49
353	2.83	3.35	5635.035	102	-20.14
363	2.75	2.85	4793.985	200	-19.99
373	2.68	2.4	4037.04	201	-19.82
383	2.61	2	3364.2	203	-19.63

**Table (3.19):- Values of measured resistance and calculated resistivities, conductivities,  $\ln\sigma$  and  $1000/T$  at variable temperatures, for PVC with 20% choline chloride / urea.**

<i>Temperature K</i>	<i>1000/T K<sup>-1</sup></i>	<i>R*10<sup>-6</sup> Ohm</i>	<i><math>\rho</math> *10<sup>-5</sup> Ohm. cm</i>	<i><math>\sigma</math> *10<sup>11</sup> S. cm<sup>-1</sup></i>	<i>Ln <math>\sigma</math></i>
303	3.30	8.5	14297.85	69.9	-21.08
313	3.19	5.2	8746.92	100	-20.59
323	3.09	3.2	5382.72	102	-20.10
333	3.00	2.2	3700.62	200	-19.73
343	2.91	1.55	2607.255	300	-19.38
353	2.83	0.9	1513.89	600	-18.83
363	2.75	0.8	1345.68	700	-18.72
373	2.68	0.7	1177.47	800	-18.58
383	2.61	0.6	1009.26	900	-18.43

The variations of D.C electrical conductivity as a function temperature at different ionic liquid content are shown in Fig. (3.14), the conductivity starts to increase when ionic liquid concentration increase. The Fig. so shown that the conductivity increase with increasing temperature.

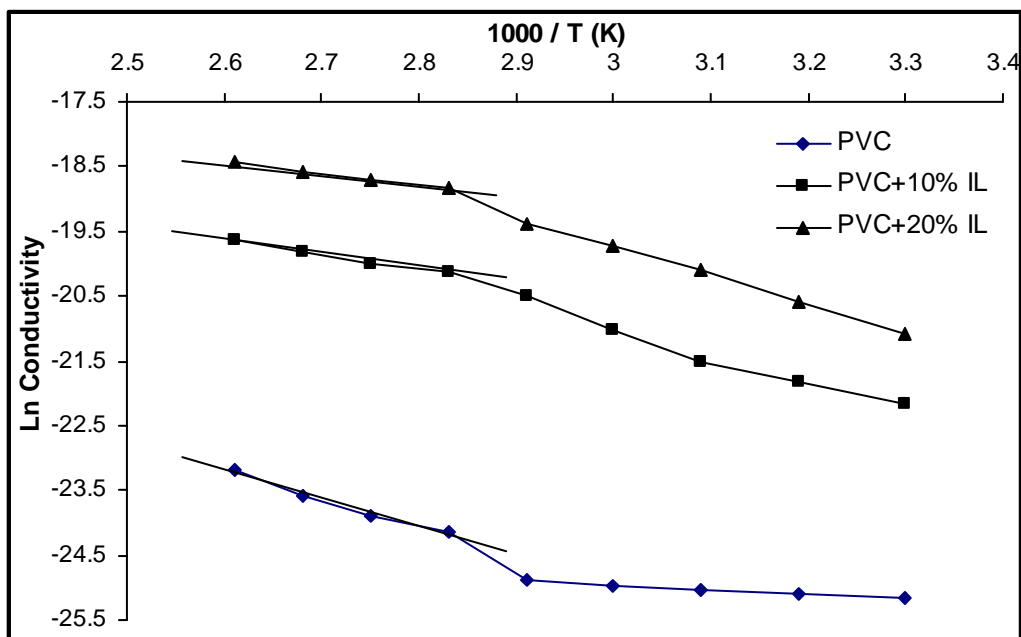
The relation of  $\ln \sigma$  against the reciprocal absolute temperature is shown in Fig. (3.15). From this Figure we can calculate the activation energy values which have been listed in Table (3.20), the activation energy decrease with increasing choline chloride / urea ionic liquid contents. The high  $E_{ac}$  value can be attributed to the thermal movement of the ions and the molecules, whereas the low  $E_{ac}$  values for the films containing of choline chloride / urea ionic liquid can be attributed to the diffusion of the ionic liquid particles in the polymer matrix then decreasing of the distance between these particles due to increasing of the ionic liquid contents as have been indicated in Fig. (3.16).



**Figure (3.14):- Variation of D.C electrical conductivity for PVC-choline chloride / urea composite with temperature.**

The increment in the D.C electrical conductivity values of PVC-choline chloride/urea composites is ascribed to the rearrangements of the electrolyte particles through out the polymer matrix as indicate in Fig. (3.16).

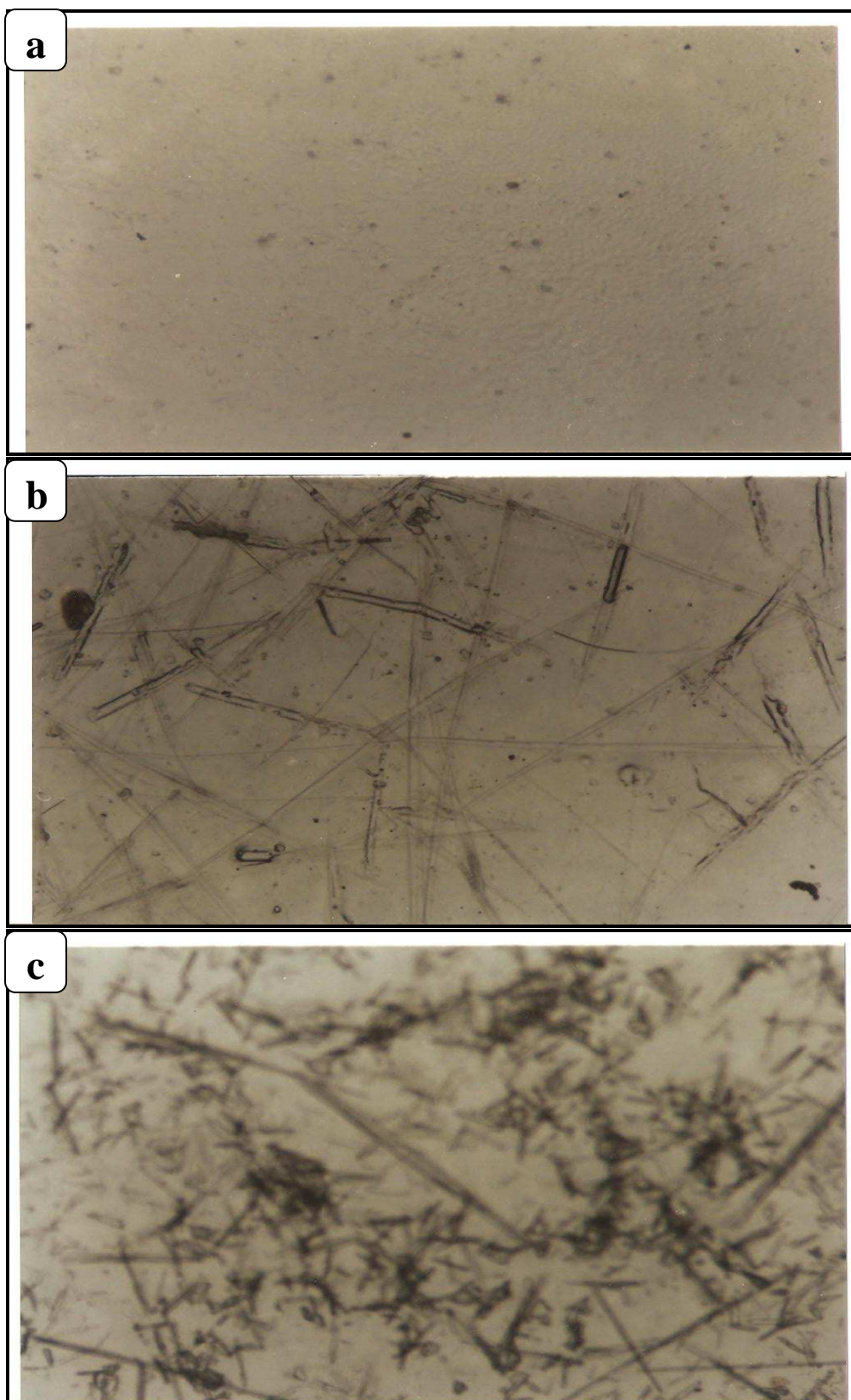
choline chloride/urea material migrate to the surface of the polymer (i.e. they are materials have limited solubility in polymer matrix). It's migrated to the surface of polymer film forming net of choline chloride/urea particles which are randomly distributed on the polymer surface. Fig. (3.16 [b] and [c]) showed the effect of increasing the content of ionic liquid as when the amount of added ionic liquid increased from 10 to 20 wt % the migrated particles increased on the surface of PVC film (compare Fig. (3.16 [b] and [c]) such net interaction would ease the dissipation of charges from the surface of the polymer film. This observation is also reported by other workers<sup>(114)</sup>.



**Figure (3.15):-** Variation of  $\ln$  D.C electrical conductivity with reciprocal absolute temperature for PVC-choline chloride / urea composite.

**Table (3.20):-** Values of slope and D.C activation energy for PVC-Choline chloride / urea composite.

<i>Choline chloride / urea</i> %	<i>Slope</i>	$E_{ac}$ (eV)	<i>Temperature range</i>
0%	4.046	0.349	353-383 K
10%	2.318	0.200	353-383 K
20%	1.818	0.157	353-383 K

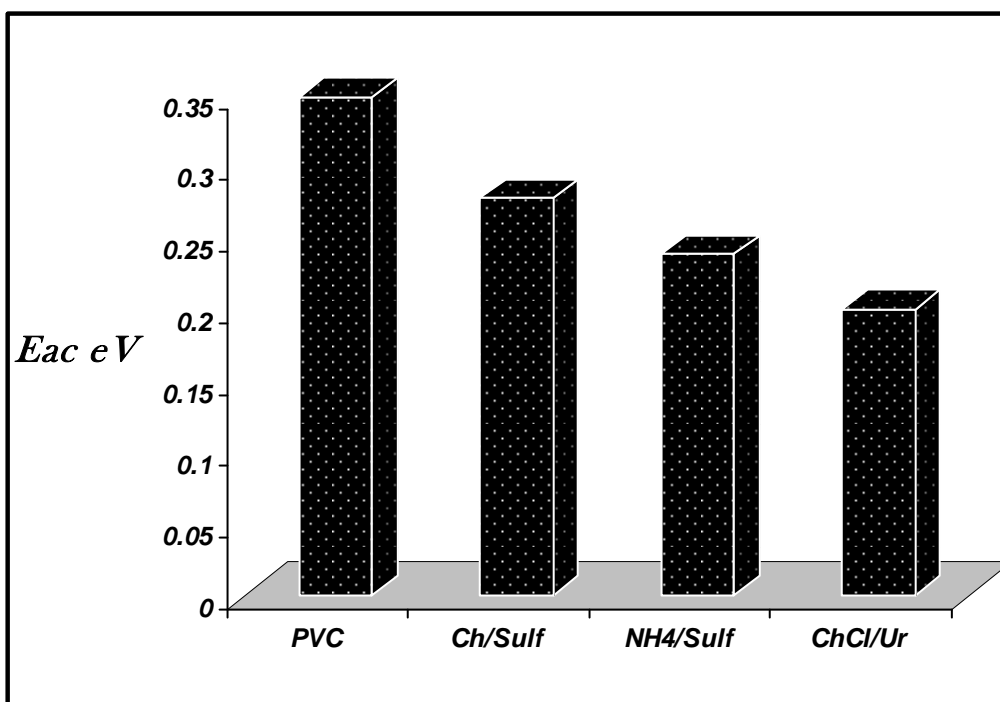


**Figure (3.16):- Photomicrographs (x40) for (a) pure PVC, (b) with 10 wt % and (c) with 20 wt % of choline chloride / urea ionic liquid respectively.**

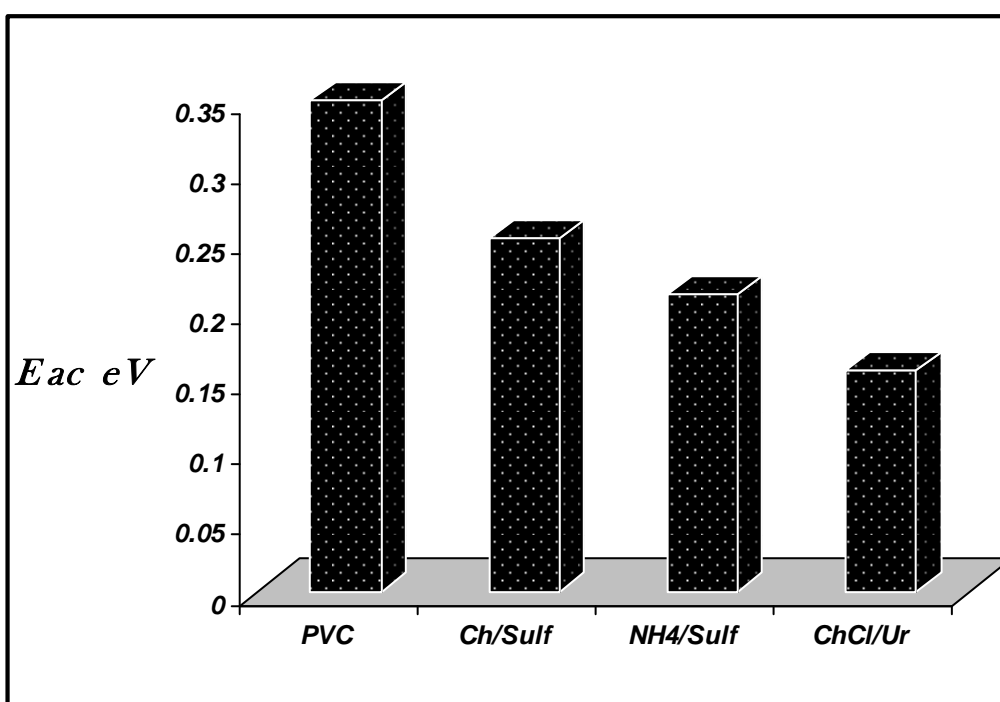


Figures (3.17 and 3.18) show the activation energy for PVC alone in comparison with added wt % of ionic liquids. These Figures showed the same trend of decreasing activation energy when these ionic liquids were added to PVC, the activation energy highly reducing from PVC alone [see Tables (3.14), (3.17) and (3.20)], although when ionic liquids were added in twice the amount of the wt. in 10 and 20%, did not show a similar reduction in activation energy. These reductions from 10 % to 20 % illustrated in Table (3.10). However, the activation energy it for example Figures (3.17 or 3.18) was taken, showed a gradual decrease when choline dodecyl benzene sulfonate, ammonium dodecyl benzene sulfonate and choline chloride / urea were used. the lowest activation energy found with choline chloride / urea may be attributed to not only the net formation on the surface but may be due to also the dissolved ionic liquid by the polymer or even to the differences between their ionic conductivity in their pure state.

Additionally ionic liquids materials may result in a decrease of the T<sub>g</sub> value of polymers which lead to increase segmental mobility i.e. increasing conductivity resulted in low activation energy. The variation in the activation energy of D.C electrical conductance for ionic liquids in PVC may also be attributed to the presence of chloride ions (Cl<sup>-</sup>) in choline chloride and high electrons density by nitrogen atoms and oxygen in urea enhance the electrical conductivity of the PVC-choline chloride/urea composites.



**Figure (3.17):-** Variation of the D.C activation energy of PVC alone and with added 10% (Ch/Sulf), (NH4/Sulf) and (ChCl/Ur) respectively.



**Figure (3.18):-** Variation of the D.C activation energy of PVC alone and with added 20% (Ch/Sulf), (NH4/Sulf) and (ChCl/Ur) respectively.

Table (3.21) show the activation energy values for both PVC and PMMA polymers in pure and composites with ionic liquids. The Table indicated that the values of activation energy for PVC were lowered than PMMA values in pure state (about 50% < PMMA) and composites state (about 75% < PMMA).

**Table (3.21):- Values of D.C activation energy for the pure and composites both PVC and PMMA.**

<i>Composite polymer with</i>	<i>Activation energy (eV) of PVC+% of added materials</i>	<i>Activation energy (eV) of PMMA+% of added materials</i>
<i>Polymer alone</i>	0.349	0.733
<i>Choline dodecyl benzene sulfonate</i>	10% 0.278	10% 0.361
	20% 0.251	20% 0.325
<i>Ammonium dodecyl benzene sulfonate</i>	10% 0.239	10% 0.341
	20% 0.211	20% 0.270
<i>Choline chloride / urea</i>	10% 0.200	10% 0.259
	20% 0.157	20% 0.204

These differences may be attributed to either the lower glass transition temperature of PVC than that of PMMA (compare 80 °C with 105 °C). This would imply that the mobility of PVC chains is more than that of PMMA chains. As a consequence, the segmental motion of the PVC polymer would be easier than PMMA segments.

In addition, PVC considered a polar polymer due to the presence of C-Cl dipole in comparison with PMMA monomer which tend to be nonpolar due to having two methyl groups lead to make PMMA more interstitial hindering than PVC chains (hinders in particles transfer during electric current) therefore PVC posses higher ionic conductivity than PMMA despite of present the oxygen atoms in the PMMA monomer.

For all the samples we have determined *Temperature Coefficient resistance* ( $\alpha$ ) value by plotting between R and T; See Fig. (3.19 And 3.20) by using the following equation:

$$\mathbf{R = R_0 + R_0 \alpha T (K)}$$

When:

R; corresponding Y axis, which is the resistance values for each sample measured from 303-383 K

T (K); corresponding X axis

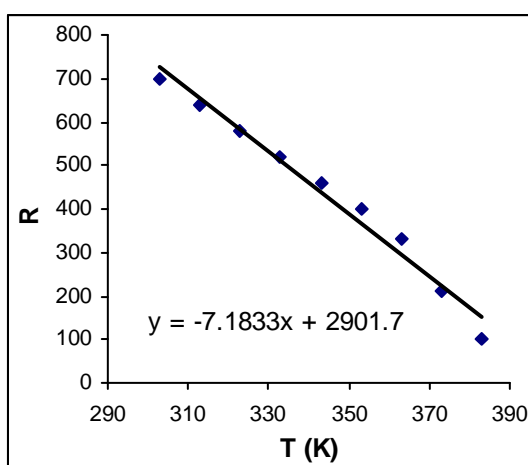
R<sub>0</sub> = the intercept which is resistance at 0 °C

Slope = R<sub>0</sub>  $\alpha$

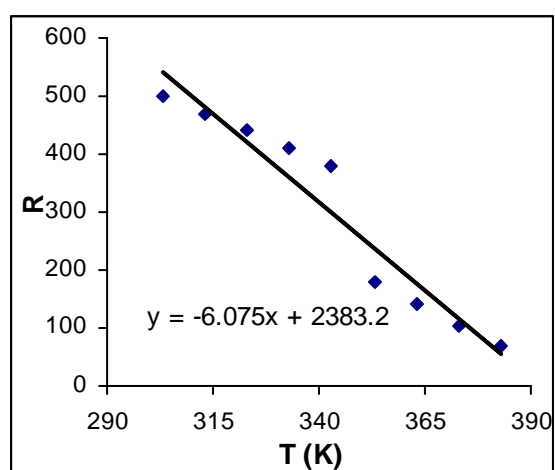
The values of determine R<sub>0</sub> and slope (from the curve by linear square method) and calculated  $\alpha$  were listed in Table (3.22). From this Table we have concluded that the R<sub>0</sub> values decrease with increasing the added weight of ionic liquid due to the electrical behavior of the ionic liquids materials as conductive additives.

**Table (3.22):** Values of slope,  $R_0$  and  $\alpha$  for all the samples were prepared in this work.

<i>Samples</i>	<i>Slope</i>	<i>R<sub>0</sub></i>	<i><math>\alpha \cdot 10^3</math></i>
<i>PMMA</i>	7.1833	2901.7	2.47
<i>PMMA + 10% Ch/Sul</i>	1.7200	682.07	2.52
<i>PMMA + 20% Ch/Sul</i>	0.6002	229.11	2.62
<i>PMMA + 10% NH<sub>4</sub>/Sul</i>	1.3117	522.9	2.51
<i>PMMA + 20% NH<sub>4</sub>/Sul</i>	0.447	169.8	2.63
<i>PMMA + 10% ChCl/Ur</i>	0.6558	245.55	2.67
<i>PMMA + 20% ChCl/Ur</i>	0.2016	74.554	2.70
<i>PVC</i>	6.075	2383.2	2.55
<i>PVC + 10% Ch/Sul</i>	0.8483	341.2	2.49
<i>PVC + 20% Ch/Sul</i>	0.4083	156.79	2.60
<i>PVC + 10% NH<sub>4</sub>/Sul</i>	0.5417	216.24	2.50
<i>PVC + 20% NH<sub>4</sub>/Sul</i>	0.3208	124.71	2.57
<i>PVC + 10% ChCl/Ur</i>	0.2729	102.42	2.66
<i>PVC + 20% ChCl/Ur</i>	0.0853	31.897	2.67



**Fig. (3.19):** Variation resistance Against temperature for PMMA



**Fig. (3.20):** Variation resistance Against temperature for PVC

### **3.8 General Conclusions:**

Polymers composites films were prepared for both PMMA and PVC when they contained 10 and 20 wt % of ionic materials. These films showed an increase in conductivity with added ionic materials or increasing temperature. As consequences, the activation energies were found to be smaller in composite films than in pure polymers.

The electrical conductivities of composite films have been found to depend on the type of ionic materials used and found to follow the sequence:

choline chloride/urea > ammonium/sulfonate > choline/sulfonate.

Although the conductivity of PVC was larger than the PMMA either alone or composite, but the conductivity of PMMA was increased by two order of magnitude while in PVC only increased by one order of magnitude.

In general, flexibility of composites film was improved when ionic materials were used with the polymers and the conductivity transferred the polymers from insulators into antistatic polymers.

### ***3.9 Suggestion for the Future work:***

The improvement of incorporating ionic materials with PMMA and PVC polymers encourage further studies such as:

- 1- Investigation the effect of there ionic materials with other polymers such as polyethylene oxide, polypropylene oxide and polyvinylidene fluoride.
- 2- Investigation the addition of other salt material such as lithium salts in addition of ionic liquids in an attempt to enhance the conductivity further.
- 3- Studying the mechanical properties of composite materials (polymer-ionic liquid).

# CHAPTER 2

## Experimental Part

### 2.1 Chemicals:

The chemical materials used in this work were listed in Table (2.1)

**Table (2.1):- Chemical materials used in this work and its sources**

Materials	Supplier Source	Purity %
PMMA	Penturem Company (Germany)	99.99
PVC	Petkim Company (Turkey)	98.99
Tetrahydrofurane	Thomas beaker (India)	99.95
Choline chloride	Merck	99.00
Urea	BDH	99.00
Potassium hydroxide	BDH	99.00
Ammonium chloride	BDH	99.98
Dodecyl benzene sulfonic acid	The general company for vegetable oils, production (Iraq)	98.00
DMSO	Fluka	99.00
Ethanol	Fluka	99.90
Chloroform	Fluka	98.99
Acetonitril	BDH	99.00
Aluminum wires	Balzer company	99.99



## **2.2 Ionic liquids preparation:**

Three types of ionic liquids were implemented in this study to improve the conductivity of PMMA and PVC polymers. They were choline chloride / urea of 1:2 mole ratio and was prepared as stated by Abbott <sup>(90)</sup>, when the mixture was heated to 80 °C liquid state of the mixture was achieved. under cooled down to room temperature it was still liquid having a freezing point of 12 °C <sup>(90)</sup>.

The other two ionic liquids were choline dodecyl benzene sulfonate with melting point of 118°C and ammonium dodecyl benzene sulfonate with freezing point of -5 °C. the latter two ionic liquids were provided by Ahad Deewan <sup>(111)</sup> as these ionic liquids have been synthesis and are to be presented in a MSc thesis requirement in due time.

## **2.3 polymers-Ionic liquid composite films preparations:**

The composites polymers films were prepared by using a solvent casting method, where 10 wt % and 20 wt % of each ionic liquid were mixed with either PMMA or PVC. Details of preparation of each film are explained as following:

The mechanical balanced of accuracy  $10^{-4}$  have been used to obtain a weight amount 0.07 g and 0.14 g of each ionic liquid (see 2.2) were weighted and added to conical flask containing 25ml of Tetrahydrofuran solvent. A continues magnetic stirring was applied and the mixture were found to be completely soluble after 1.5 hours for choline chloride / urea mixture but immediately for choline dodecyl benzene sulfonate and ammonium dodecyl benzene sulfonate finally clear homogenous liquid were formed. To these clear liquids mixtures a corresponding weight of 0.63 g and 0.56 g of PMMA and PVC were added to these solutions to make composites mixtures of 10 wt % and 20 wt % of ionic liquids / polymers mixtures. When the above weights of polymers where added to the

corresponding ionic liquid solutions they dissolved immediately forming a clear solutions. The final solution then was cast into glass sheet better dish allowing the solvent to be evaporated naturally for 24 hours where ionic liquid / polymer composites flexible films were finally formed having a thickness of about ( $105 \pm 10$  micron) when measured by micro vernia.

## **2.4 Other solvents:**

Tetrahydrofuran (THF) was the best solvent used for preparation of all polymer-ionic liquid composites films in two types of polymers and with three types of ionic liquids.

However, ethanol and chloroform were also used to prepare the composites films but they did not result in elastic film but rigid easy to be break non homogenous films in both PMMA and PVC composites films preparation. in addition, DMSO was also used to prepare the composites films this solvent was found to have good solubilization power yet the natural evaporation process would require a very long time and may not reach completion without unfavorable heating the mixture. Therefore only THF solvent was used in the preparation of the polymer composites specimens.

## **2.5 Preparation of Aluminum-electrodes:**

A coating unit model Edwards (Varian NCR 3116), which is shown in Fig. (2.1), has been used for deposition of thin aluminum layers on both sides of each sample to act as electrodes. The shape of thin layer is circular and the diameter is (1.5 cm), the deposition of aluminum is done under highly reduced pressure. The purpose for these electrodes is to minimize the contact resistance and eliminate the space charge effect. The coating unit consists of two evacuation pumps, rotary pump, which produce an initial pressure of about ( $10^{-3}$ ) torr, and a diffusion pump which produces low

pressure about ( $10^{-3}$ - $10^{-6}$ ) torr with the help of the rotary pump and cooling system. The pressure is measured by using pirani and pining gauges.

### **1. Masks:**

The items used for the desired shape of the deposited electrode are called "masks" and that are made of aluminum sheets. Fig. (2.2a) shows the shape of the masks which have been used in this work. The shape of masks has been used has a circular area ( $1.76625$ )  $\text{cm}^2$ . These masks have been cleaned by de-ionized water and detergent powder, then are immersed in the ethanol solution for ten minutes and dried at room temperature. This is done because these masks are actually attached with samples and fixed by the coating unit holder.

### **2. Deposition of Al electrode:**

The evaporation started when the vacuum reached ( $10^{-6}$ ) torr. The thickness satisfying a good electrical conduction is ( $3000\text{A}^0$ ) and the substrate was kept at room temperature.

### **3. Evaporation Source (Boats):**

For evaporation process, it is necessary to use a special boat which must have the following properties:

- 1- The melting and boiling points of the boat material must be higher than those of the evaporated material.
- 2- There must be no chemical reaction between the boat and evaporated material, Tungsten spiral boat shown in Fig. (2.2b) was used as a source.

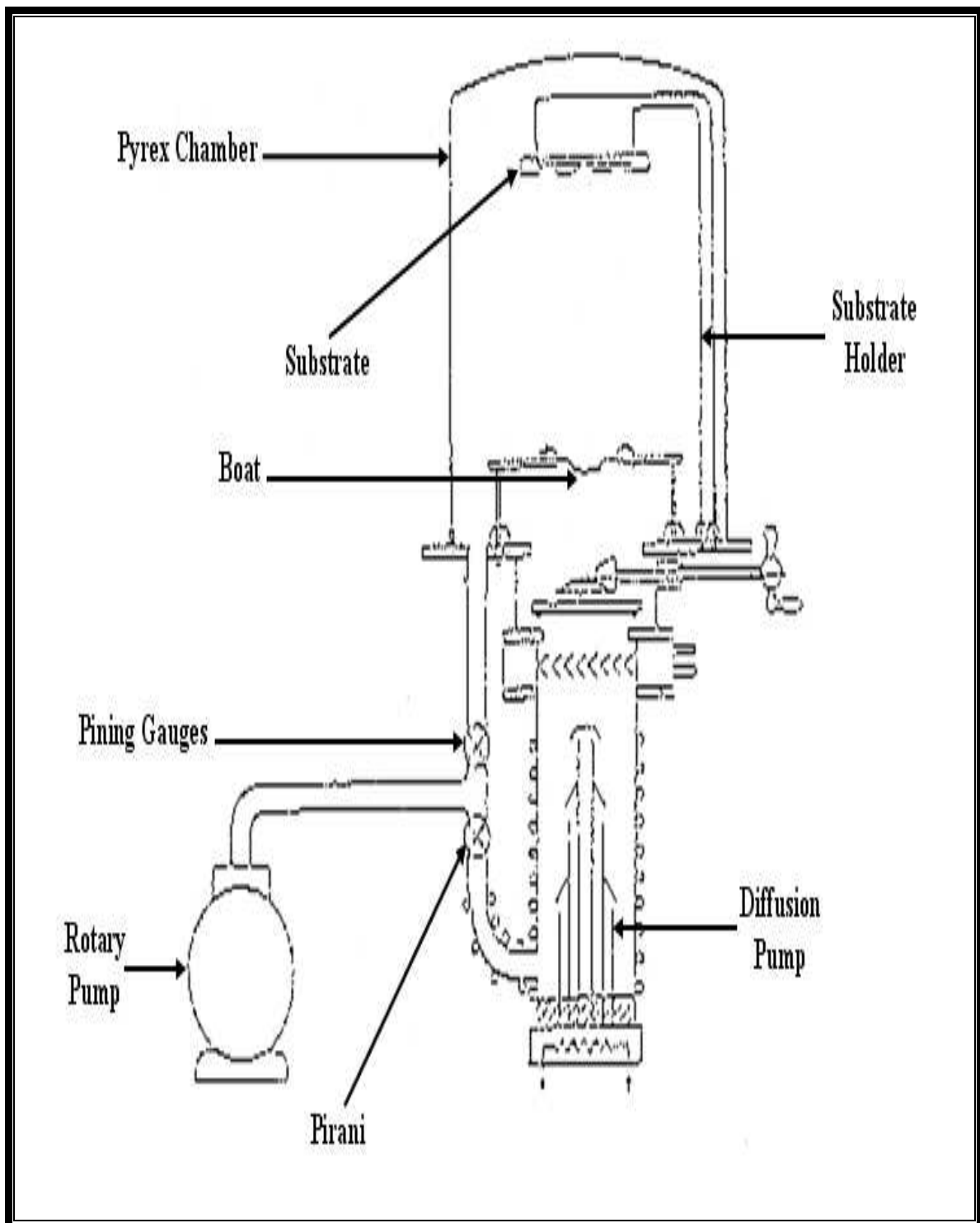
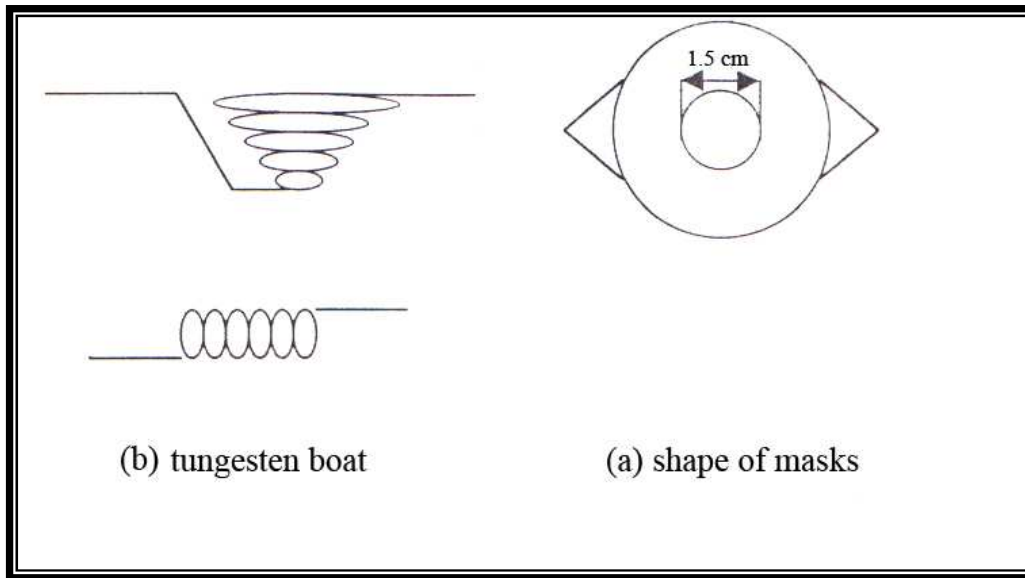
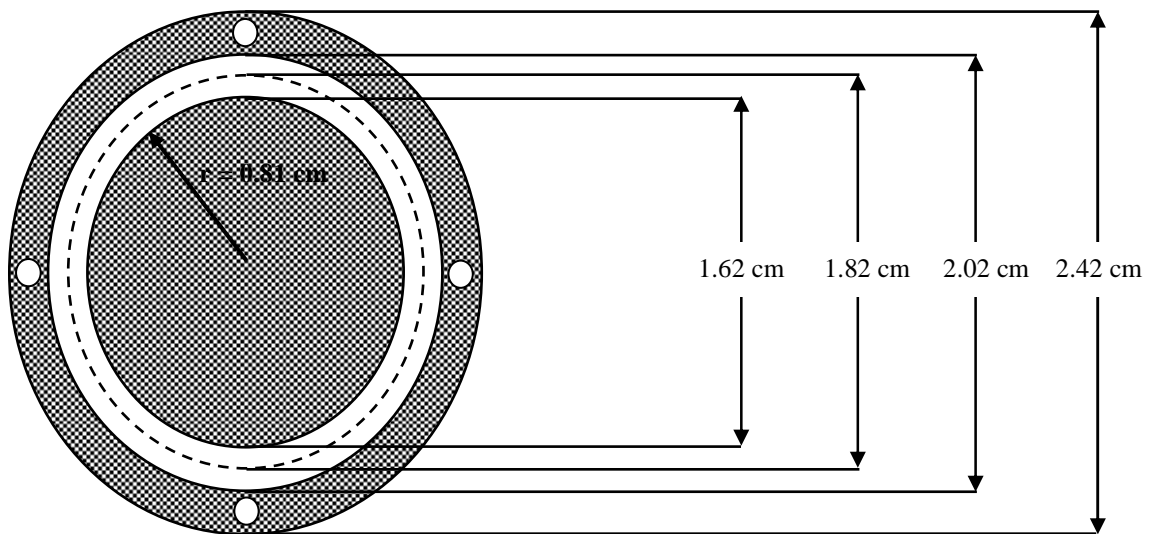


Figure (2.1):- Simplified diagram for the coating units model (Edwards).



**Figure (2.2):- A: Shape of the masks. B: Shape of the tungsten boat.**



**Figure (2.3):- Schematic diagram of the electrode used in measuring the resistance of the specimens of alone and composite polymers.**

## **2.6 Measurement of D.C resistivity:**

There are different methods for determination of D.C resistivity of insulating materials. According to ASTM (D257-78) standard method recommendation <sup>(112)</sup>, for measured of electrical resistance of insulating materials. Guard ring electrode method has been adopted in this work to study the effect of the concentration of ionic liquid additions and the temperature on the resistivity of the polymer composites.

There are two main reasons for an adoption of this method. The first one is that in guard ring electrode system the leakage current can be minimized over the surface of the specimen and can be collected by the guard electrode which is not included in the measured current (i.e. the surface resistance can be separated from resistance considerable extent). The second reason is the ability of this system to decrease the effect of the fringing of the field at the edges. The conductivity was calculated as outlined earlier in equations (1.3) and (1.4).

The schematic diagram of the electrode and its dimensions indicate in Fig. (2.3). A suitable measuring system is used to study and measure the electrical properties of the polymer in both pure and mixed with ionic liquids state, the complete system is shown in Fig. (2.4) and the supplied voltage was 220V.

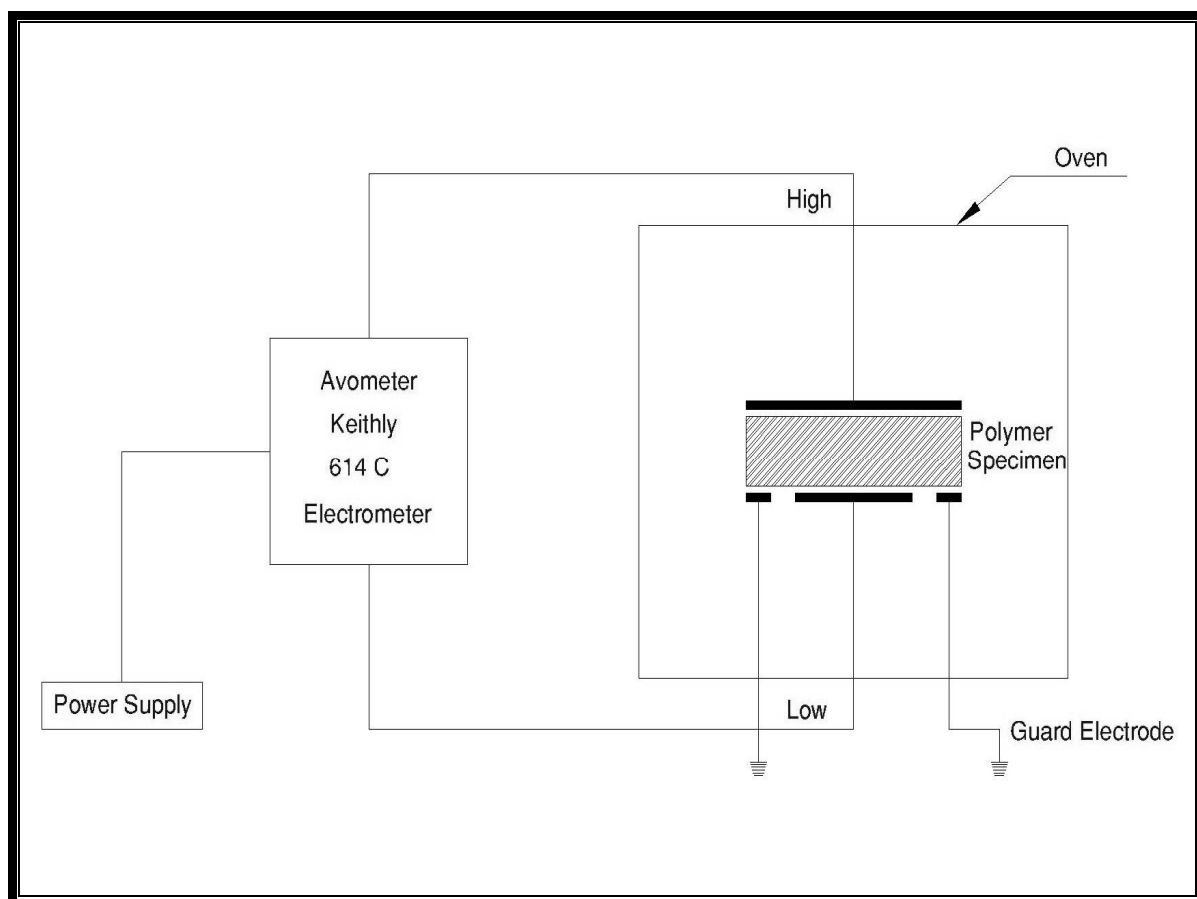
The electrodes were made of copper metal, and two adjustable screws applied a uniform pressure on the specimens. The resistance was measured by using Keithly 614 digital-solid state electrometer.

The test sample is sandwiched between the electrodes and put it in temperature controlled oven (Hereaus electronic). The resistance calculated

for each reading and average (R) has been taken. The resistance measurements were performed in the temperature range (303-383 K).

### **2.7 Microscopic Observations:**

The samples were examined by using the optical microscope from (Olympus BH-2) which has a maximum magnification power of (x 500) and equipped with light intensity automatic controlled camera.



**Figure (2.4):- Schematic diagram for D.C volume resistivity measurement.**

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**دراسة التوصيلية الكهربائية المستمرة لمتراكبات *PVC***

**و *PMMA* مع بعض السوائل الأيونية في درجات**

**حرارية مختلفة**

Republic of Iraq  
Ministry of Higher Education and Scientific Research  
Al-Nahrain University  
College of Science  
Department of Chemistry



*Investigation of the D.C Electrical  
Conductivities of PVC and PMMA  
Composites with some Ionic liquids at variable  
Temperatures*

A Thesis

Submitted to the College of Science at Al-Nahrain University in  
partial fulfillment of the requirements for the Degree of Master  
of Science in Chemistry

By

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(B. Sc. 2005)

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# Symbols and Abbreviations List

<b>Symbols</b>	<b>Full meaning used in theses</b>	<b>Units</b>
<b>T<sub>g</sub></b>	Glass transition temperature	Centigrade
<b>PVC</b>	Polyvinyl chloride	/
<b>PMMA</b>	Poly methyl methacrylate	/
<b>MMA</b>	Methyl methacrylate	/
<b><math>\sigma</math></b>	Conductivity	S.cm <sup>-1</sup>
<b>T<sub>c</sub></b>	Critical temperature	Centigrade
<b>U</b>	Drop in potential	Volt
<b>I</b>	Current	Ampere
<b>R</b>	Resistance	Ohm = $\Omega$
<b><math>\rho</math></b>	Resistivity	Ohm. cm
<b>S</b>	Siemens	Ohm <sup>-1</sup>
<b>R<sup>-1</sup></b>	Conductance	Siemens
<b>B</b>	Boltzman constant = $8.62 \times 10^{-5}$	eV/K
<b>E<sub>ac</sub></b>	Activation energy	eV
<b>D.C</b>	Direct current	Ampere
<b>A</b>	Guard electrode effective area	Cm <sup>2</sup>
<b>R<sub>0</sub></b>	Resistance at 0 °C	Ohm
<b><math>\alpha</math></b>	Temperature coefficient resistance	K <sup>-1</sup>

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

شَهِدَ اللَّهُ أَنَّهُ لَا إِلَهَ إِلَّا هُوَ وَالْمَلَائِكَةُ وَأُولُوا الْعِلْمِ قَائِمًا

بِالْقِسْطِ لَا إِلَهَ إِلَّا هُوَ الْعَزِيزُ الْحَكِيمُ

صدق الله العظيم

آل عمران الآية (١٨)

# *DEDICATION*

*To all who suffer to raise the name of*

*Mesopotamia*

*With honors and dignity*

*To...*

*My motherland IRAQ*

*My Father*

*My Mother*

*My Family and My Friends for their Kindness,*

*Attention and encouragement*

*RASHA*



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**RASHA**



جمهورية العراق  
وزارة التعليم العالي والبحث العلمي  
جامعة النهريين  
كلية العلوم  
قسم الكيمياء

## دراسة التوصيلية الكهربائية المستمرة لمتراكبات *PVC* و *PMMA* مع بعض السوائل الأيونية في درجات حرارية مختلفة

رسالة  
مقدمة الى كلية العلوم- جامعة النهريين  
وهي جزء من متطلبات نيل درجة الماجستير في الكيمياء

من قِبَل  
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بإشراف  
الدكتور هادي محمد علي عبود

جمادي الاخرة ١٤٢٩ هـ

حزيران ٢٠٠٨ م

CHAPTER 1

General Part



CHAPTER 2

Experimental Part

CHAPTER 3

Results & Discussion

# References