Introduction

I-1. General Introduction:

Solid state organic chemistry is unusually a broad area. It includes X-ray crystallography, mechanistic organic chemistry, physical pharmacy, physical chemistry, drug stability, kinetic of solid state reaction, etc. Organic solid state attempts to explain the rates of solid reactions and the change occurring in physical properties of organic compounds in terms of chemical process and crystal structure.

The relationship between the properties of substances and their crystalline structure is widely used by modern technologists (1), not only to increase the rate of their chemical interaction but also for obtaining materials with predetermined properties for various critical purposes such as semiconductors, ferro- and piezo-electrics, etc. These materials are obtained by carefully regulating the crystalline defects.

The electrical conductivities of solids and their dependence on temperature and composition provided the first main challenge to theories of the solid state, and they continue to be among the central concerns of a wide range of scientist concerned with solid and their electronic applications.

During the last four decades semiconductor equipment is being increasingly applied in various fields of science and engineering. Recently semiconducting properties were discovered in organic compound (3). The ever increasing interest in organic materials with semiconducting properties is due to the fact that we can produce a semiconducting materials with a combination of electrical, optical and physicochemical properties which are not encountered in inorganic semiconductors. In particular, some applications of materials made from inorganic semiconducting materials have some disadvantages that limit their applications. For example, technical difficulties are caused by the great variation in parameters of inorganic thermistors with the variation in the content of impurities. But thermistors made from organic semiconducting materials have all properties of inorganic thermistors, and in addition some advantages which will doubtless lead to their wide use in the future.

Interest in the electronic properties of organic solids has grown spectacularly in the last three decades. The speculation that a superconducting transition was occurring near 60K in a high conductivity organic crystals (4) played a big role, in focusing the attention of scientists on the field. More generally, however, it has been recognized that studies of electrical properties of organic substances and organic molecular crystals provide fundamental knowledge applicable to physical, chemical, and biological systems.

Many efforts have been devoted to relating the chemical structures of organic compounds with their electrical properties (5-8). **Garrett** et. al.(9) pointed out that the condensed aromatic hydrocarbons are superconductors on the aromatic scale, since there are no obstacks to the flow of electron within the molecules. The reason for the extremely low conductivities and relatively high energy gaps of hydrocarbons must be sought in the processes involved in the transport of charges across intermolecular barriers. In view of these barriers, it is perhaps surprising that organic molecular solids display any conductivity at all. The explanation may lie in mechanism which allow electronic interaction across the barriers, leading to overlapping of the molecular orbitals of adjacent molecules.

The conducting properties of organic compounds usually correlate with the energy difference between the highest occupied and the lowest empty molecular orbitals, suggesting that the transportation of electrons in these systems involves the non-bonding empty molecular orbitals of the compounds (10).

The crystalline organic semiconductors belong to the category of molecular crystals which have the characteristics of wide energy band gap, low carrier mobility, and low melting point. Most organic semiconductors should really be designated as insulators.

The ionic conductivity in polar as well as dielectric materials may occur as a result of impurities or defects within the structure. This behaviour is observed mainly in the ferroelectric materials with ordered structures (11). Whereas for some organic materials containing hydrogen bonds (9) ,it is necessary to consider the possibility that ionic conductivity may occur at the same time as electronic conduction.

The formation of crystals possessing a polar axis, a property shown by many common organic and inorganic materials, is one of the most remarkable aspects of the chemistry of the solid state (12). The special properties of polar materials have led to their enormous importance in industry. Applications ranging from the microphone and ultrasonic cleaner to frequency-doubling crystals in laser technology depend on the properties of the polar crystalline state. It has been pointed out (1) that polar materials are very promising candidates as a basis of major components of the programmable digital computer such as output and memory. The crystal structure has also played an important historical role in chemistry. It underlays the recognition of the relationship between optical activity and molecular structure and was fundamental to the first resolution of an organic compound (13).

Many investigators have reported that the conductivity of some organic semiconductors under AC fields may be higher by several orders of magnitude than that under DC fields (14). This phenomenon may be associated with the polarization of the molecules.

A study of organic specimes with different specific conductivities has revealed that the lower the specific conductivity the stronger is the frequency dependence of the conductivity (15). Both the dielectric constant and the specific conductivity can be considered to be associated with the carrier transport.

In general, the conductivity decreases with increasing frequency in the case of band conduction process, while it increases with increasing frequency in the case of hopping conduction process (4).

The available experimental results about the frequency dependence of AC- conductivity have revealed a considerable similarity of behaviour for a very wide range of ordered and disordered materials, conducting by electrons, holes, ions, polarons, ... etc.; involving various types of chemical bonds and various electronic energy levels (14).

Generally, the molecules which are the building blocks of all substances, are composed of nuclei and electrons. So when a field acts on a molecule, it will polarize. There are different types of polarization processes depending on the structure of the molecules which constitute the solid. If the molecule has a permanent moment, i.e. a moment even in the absence of an electric field , we speak on a dipolar molecule. When an electric field is applied to a dipolar system in which the dipoles are able to rotate freely as in gas or liquid; so before the field was applied, the dipoles were oriented randomly, resulting in a vanishing average polarization. But when a field is applied to the substance, the molecular dipoles tend to align with the field resulting in a net nonvanishing polarization. This leads to the so-called "dipolar polarizability". The dipolar polarizability in a solid depends on the particular solid and on the range of temperature.

If the molecule contains ionic bonds, then the field tends to stretch the lengths of these bonds. The effect of this change in length is to produce a net dipole moment in the unit cell. Since the polarization here is due to the relative displacements of oppositely charged ions, we speak of " ionic polarizability ".

The electronic polarizability is a type of polarization which arises when a field is applied on the individual ions or atoms in a molecule which are themselves polarized by the field. Thus the ion or atom is polarized because the electrons in its various shells are displaced to the left relative to the nucleus. Or nucleus is displaced from the center of the sphere. Various shells are displaced to the left relative to the nucleus or nucleus is displaced from the center of the sphere. The interfacial polarization is another type of polarization which produces from different sources. Interfacial polarization at electrodes resulting from the migration of ions by the electric field and accumulated at the electrodes(11). While interfacial polarization at crystallites produced mainly from the formation of charges at the surface of crystallites in the glasses or in heterogeneous crystalline medium. The different types of polarization are shown in Fig.(1-1).

The types of dielectric can be classified into: simple dielectrics, paraelectrics and ferroelectric which subdivided into ferrielectric and antiferroelectric. Add to subdivisions, the term electret to distinguish between the macroscopic properties of simple dielectrics and paraelectrics; we must define the former which is exhibiting only the ionic and electronic polarization. This is characterized by a permittivity less than 40 that is little dependent on the structure. By contrast, paraelectrics contain a strong permanent electric dipole in each unit cell that is associated with permittivity greater than 20 up to 10000 or more. Those low- permittivity substances having small concentrations of permanent dipoles are referred to as 'polar'; they are intermediate between simple dielectrics and paraelectrics. Generally ,ferroelectrics

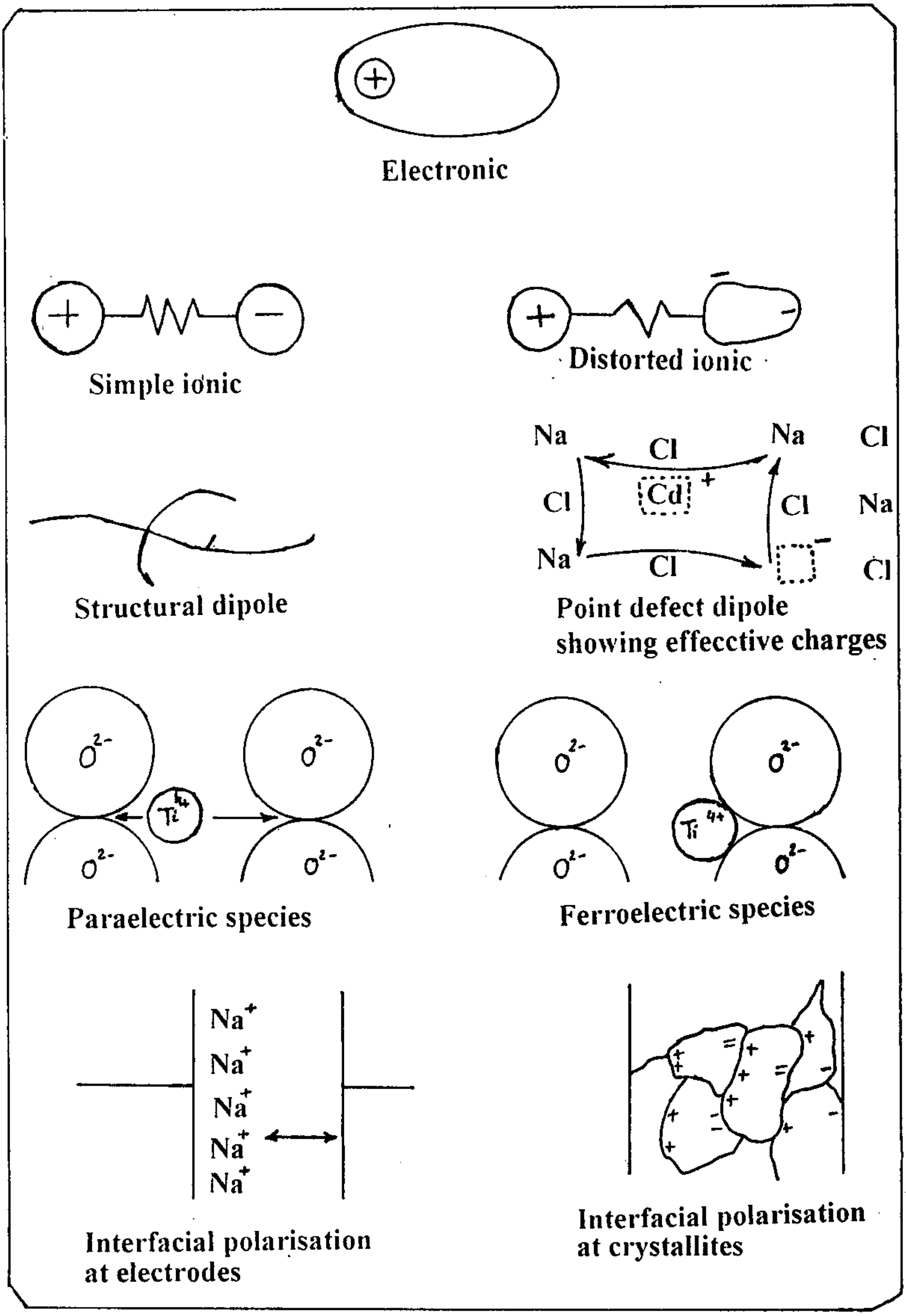

Fig.(I-1): Polarization types in materials.

exhibit polarization that is not a linear function of applied fields, while ferrielectric and antiferroelectric states exist when permanent electric dipoles in positions respectively incompletely and completely balance out.

I-2. Literature Survey:

The metal hydrogen tartrates form a class of compounds of general molecular formula $MHC_4H_4O_6.xH_2O$ where M^+ is the univalent ion Na^+, K^+,Rb^+ … and/or NH_4^+, and x is the number of water molecules (x=0,1,2,3,….). The resistivity, dielectric constant and thermal properties (thermal heat capacity C_p, thermal conductivity and thermal diffusivity σ) as a function of temperature in the range $303 < T < 413K$ were studied (16) for sodium hydrogen tartrate monohydrate, $NaHC_2H_4O_6.H_2O$. The results showed the presence of a structural phase transition at about 356K, in addition to a phase transformation due to the loss of water (dehydration). The data are correlated to the restricted rotation of the tartrate ions as well as to the hydrogen bonding scheme.

The electrical, magnetic and thermal properties of some tartrate molecules [$M_2C_4H_4O_6.xH_2O$, where M^+ is a univalent ion such as Na^+, K^+, ... and NH_4^+ [x=0,1,2,3 and 4] were studied (17) at temperatures higher than room temperature. Also the calorimetric properties (thermal specific, heat capacity, thermal conductivity and thermal diffusivity) as well as the electrical properties (DC-resistance, dielectric constant and pyroelectric current) of the ammonium tartrate single crystal

$(NH_4)_2C_4H_4O_6$ in a temperature range of $303 < T < 413K$ were also investigated. Anomalies behaviours were reported for the physical properties investigated due to a phase transition occurring in the crystal structure.

Sodium potassium tartrate tetrahydrate $(NaKC_4H_4O_6).4H_2O$, known as Rochelle salt, was found to exhibit ferroelectricity (18) between 255K and 297K and a structure of (orthorhombic, $P2_12_12$) (19) for the upper and the lower paraelectric phases having similar symmetry. An anomalous dielectric behaviour at low frequencies and a temperature of ≈297K was also reported by **Ramirez** *et. al.* (20). They reported also the temperature dependence of the dielectric constant and dielectric loss at several frequencies in the range 20Hz to 500Hz. The dielectric dispersion (21) for Rochelle salt was also studied near their Curie points. The dispersion was found to depend on whether the measurements were made during heating or cooling.

The frequency and temperature dependences of the dielectric relaxation of Rochelle salt single crystals were also investigated at a frequency range of 10kHz-1000kHz and over temperatures of (289-301K) (22). The dielectric spectrum of the Rochelle salt was also studied in weak fields at 288-291K (23). Ferroelectric properties are observed along the orthorhombic axis a and are characterized by an anomalous magnitude of dielectric constant ε.

Samedov *et. al.*(24) studied the phase transitions in Rochelle salt at field up to 10kV. The nature of the curie points (255K and 297K) was discussed, and it was found that both the non-polar phase and the antiferroelectric exist below 255K.

Rubidium hydrogen tartrate (RHT) crystal was found to have considerable interset due to their ferroelectric, piezoelectric, optical and other pertinent characteristics. It is extensively used for controlling laser emission. **Desal** *et. al.*(25) studied the electrical conductivity of RHT at different temperatures and explain the mechanism of charge transport in it. Potassium hydrogen tartrate was found to crystalize (26) in orthorhombic structure, $P2_12_12_1$.

Several structural studies of maleic acid/maleate salts have been performed. It has been focused on the conformation of the maleate group or on the symmetry characteristics of the short intermolecular hydrogen bond occurring in the acid maleate salts (27). The potassium hydrogen maleate monohydrate, $KH[C_4H_4O_5].H_2O$ was found to crystallize in monoclinic, with space group Cc (28), while the crystal of sodium hydrogen maleate trihydrate, $NaH[C_4H_2O_4].3H_2O$, at 120K, showed triclinic structure with space group P1 (27).

Disodium maleate monohydrate was found to crystallize in monoclinic with space group C_2/C (27).

The malonic acid shows triclinic crystal structure with space group P1 (30). And sodium hydrogen malonate shows monoclinic crystal structure with space group $P2_1/C$ (31). While potassium hydrogen malonate, $KH(C_3H_2O_4)$, crystallize in the monoclinic system with diffraction symbol C*/* (32). The crystals of the disodium malonate monohydrate, showed orthorhombic structure with space group $PbC2_1$ (33).

The thermal analysis of malonic acid and alkali metal malonates was studied using TG-DTG-DTA and DSC (34). The kinetic parameters for various steps were reported (34-36).

Crystal studies on succinic acid have been carried out (37) at 77K and 300K. At both temperatures unit cells showed monoclinic, space group $P2_1/C$ have been reported.

Ammonium hydrogen succinate showed phase transition at ≈ 170K (38). X-ray crystal structure analysis, above and below 170K, was investigated. The results showed no ordering of the H-atom positions in the short bonds due to phase transition, and the space group was found to be P_1 at 150K and 190K.

Mallinson et. al.(39) studied the structure of sodium hydrogen succinate at 123K, the compound showed a monoclinic structure with space group C/2c. While lithium succinate, $(CH_2COOLi)_2$, showed a trigonal crystal (space group R_3) with 9 formula units in the hexagonal unit cell (40). The succinate ion has a center of symmetry between the central C atoms. The C-C distances are 1.525 and 1.518Å. Four oxygen atoms form a slightly deformed tetrahadron around the Li ion with Li–O distances ranging between 1.945 and 1.961Å. Sodium succinate hexahydrate $Na_2[C_4H_4O_4].6H_2O$ shows triclinic crystal structure with space group P1 (41).

The crystal studies of oxalic acid showed a monoclinic crystal structure (42) with space group $P2_1/n$. While the crystal of sodium hydrogen oxalate monohydrate ($NaHC_2O_4.H_2O$), at 120K, showed a triclinic structure with space group $P\bar{1}$ (43). And the structure of potassium oxalate monohydrate ($K_2C_2O_4.H_2O$) at look, was found to be monoclinic with space group C2/C (44).

The kinetics of thermal dehydration of powdered and single crystal $K_2C_2O_4.H_2O$ were investigated by a differential scanning calorimeter DSC (45). The thermal decomposition of a series of NaH dicarboxylates, $HOOC(CH_2)_nCOONa$ ($n=0-8$), was studied (46) at 373-523K by means of TGA and DTA. An ion exchange reaction between Na^+ and H^+ was found to occur through intermediate processes. The transition temperatures at which the intermediates occur were found to vary alternately with the increase in the carbon number of the acid salts in a manner similar to that of the melting points of the dicarboxylic acids. The reaction mechanism is discussed from the view point of the crystal structure of the acid salt. The kinetic of thermal decomposition and thermal stabilities of many metal organic acids were studied by many authors (47-51).

Phthalate salts have an interesting physical and chemical properties (52). Potassium acid phthalate, for example, has wide technological applications due to its high piezoelectric coefficient and its mica-like structure (53). The elastic properties of sodium, potassium and rubidium acid phthalates were also investigated (54).

The crystal structures of a series of alkali hydrogen phthalate have been determined by a number of workers (55-62). For the sodium and potassium acid phthalate (55,61) the cations were found to be surrounded by six oxygen atoms, four from the ionized carboxyl groups, one from an ionized carboxyl group and one from the water molecule. Due to steric hindrance, the carboxyl groups are not in the plane of the benzene ring; the angles between the two carboxyl planes and the plane of the benzene ring have values of 27° and 67° as well as 31.7° and 75.4° for the sodium and potassium acid phthalate salts, respectively. For the KNa phthalate it may be tentatively assumed that the salt has approximately similar main structural features to the acid phthalate (52).

Thermal analysis for potassium hydrogen phthalate KHP, commonly known as potassium acid phthalate, was investigated by **Varma** (63). It was found that (KHP) crystals decompose into phthalic anhydride and KOH at ≈520K. Electrical properties of KHP crystals were also investigated.

The dielectric constant, loss tangent, specific heat and pyroelectric coefficient for potassium hydrogen phthalate were studied as a function of temperature (64). It was found that each of the dielectric constant and tan δ decreases with increasing the frequency.

The electrical properties of KNaP (sodium potassium phthalate) such as the resistance, dielectric constant, dielectric loss and pyroelectric current as a function of temperature, at a temperature range of $303<T<413$K were investigated (52). An anomalies behaviour in the electrical measurements was observed and explained on the basis of the occurance of possible phase transitions associated with structural rearrangement in the phthalate groups.

The crystal structure of NH_4H terephthalate, $C_6H_4COOHCOONH_4$, has been determined (65). The space group was found to be C_2/C with 4 molecules in the monoclinic unit cell. The crystal structure consists of chains of centrosymmetric terephthalate ions linked by short H-bonds across centers of symmetry (O…O distance of 2.51Å), and these chains are linked via the NH_4 ions to form a 3-dimensional H-bonding network. The carboxyl groups are twisted 9° out of the plane of the benzene ring to form H bonds with NH_4 ions.

Potassium terephthalate was found to crystallize in monoclinic structure and its space group is $P2_1/C$ (66). On heating it above 230°C, transformation to an orthorhombic phase was observed. It is found that the dipotassium terephthalate is thermodynamically more stable than potassium hydrogen terephthalate.

I-3. Aim of Work:

Due to the deficient information concerning the electrical properties of organic acids and their salts, the present work was designed to study the electrical properties of organic acids (oxalic, succinic, malonic, maleic, tartaric, citric, phthalic, terephthalic) and their potassium and sodium salts at lower temperature range 78-400K, in order to give more information on the electrical properties of the acids and their salts especially at lower temperatures .Also, the effect of chemical and crystal structure on the electrical properties of some aliphatic and aromatic compounds was studied. We are also looking to find economically feasible substances for application can be used in electronic field.