

## Determined the energy gap and activation energies of some transition metal complexes of liquid crystalline Schiff base .

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### Abstract

The aim of this study is to preparation and characterize some complexes of free liquid crystal material (MBBA) with  $\text{Cu}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$  and  $\text{Cr}^{+3}$  in order to study their electrical properties (DC) and (AC), such as: activation energy and the exponential factor, together with energy gap.

The volume resistivity measurements were performed in the temperature range between (303 to 423 K), the temperature was measured by using thermocouple that contacts the test sample from one side whereas the other side is connected with counter.

A similar effect has been reported in four poly (Schiff bases) and their iron (III) complexes were synthesized and characterized.

\* **Keywords** : *Liquid crystal;  $\text{CH}_3\text{OC}_6\text{H}_4\text{CH:NC}_6\text{H}_4(\text{CH}_2)_3\text{CH}_3$ ; Schiff base; Energy gap; Activation energy.*

(p- methoxybenzylidene-p-butyl aniline) (MBBA)

(303-423)

## Introduction

The mesophases of thermotropic liquid crystals may be divided into three main groups; nematic, cholesteric and smectic phases. The nematic phase, where the rod-like molecules are ordered in the direction of the molecular long axis, although the mass centers of the molecules are not ordered. If a liquid crystal, capable of forming a nematic phase, contains a chiral carbon atom, a helical structure of the nematic phase will form. It is called cholesteric phase. In the smectic phases the molecules are ordered in layers. Different smectic phases are known. They are designated by capital letters A, B and C in chronological order of discovery<sup>(1)</sup>.

Liquid crystals exist in a state that is transitional between that of a solid or liquid. In this intermediate state, liquid crystal molecules tend to point the same way, like the molecules in a solid, but can also move around to different positions, like the molecules in a liquid. This tendency of the liquid crystal molecules to point a long a certain direction results in the liquid crystal displaying certain properties that are specific to the direction to which these properties are measured. This fundamental property of liquid crystals, called anisotropy, is what is exploited in the engineering of liquid crystal displays (LCDs)<sup>(2)</sup>.

## Theory

The energy gap ( $E_g$ ) is the difference in energy between the highest point in the valence band  $E_V$  and the lowest point in the conduction band  $E_C$ . It is defined as the lowest energy to transform charge carrier from the top of valence band to the bottom of conduction band. It represents one of an importance optical property of organic semiconductors. The variation of the

concentration of the current carriers (electrons and holes) to temperature ( $T$ ) can be expressed as follows<sup>(3)</sup>:

$$\sigma = \sigma_0 \exp\left[-\frac{E_g}{2K_B T}\right] \dots (1)$$

where ( $K_B$ ) is Boltzmann's constant, ( $\sigma_0$ ) is the ideal conductivity of monocrystalline structure, and ( $\sigma$ ) is the electrical conductivity. The factor of ( $1/2$ ) in the exponent appears with intrinsic semiconductors because the possible distributions of electrons in the conduction band are independent of the distributions of holes in the valence band. If it is assumed that the mobility of the carrier varies rather slowly with temperature, Eqn.(1) may be then rewritten for the experimental conductivity as follows:

$$\sigma = \sigma_0 \exp\left(-\frac{E_{act.}}{K_B T}\right) \dots (2)$$

where  $E_{act.}$  represent the activation energy. In this equation the energy term is one of the most important factors for the study of organic semiconductors.

The behaviour of semiconductors is based on the reliance of their electrical conductivity upon electric field and applied voltage where conductivity increases with the frequency increase according to the following equation<sup>(4)</sup>.

$$\sigma_{ac}(w) = Aw^s \dots (3)$$

where ( $A$ ) is a constant and ( $S$ ) represent the exponential factor, where  $S$  given in the formal as<sup>(5)</sup>:

$$S = \frac{d[\ln \sigma_{ac}(w)]}{d[\ln w]} \dots (4)$$

To calculate the dielectric loss tangent or dissipation factor we used the equation:

$$\tan \delta = \frac{\epsilon''}{\epsilon'} = \frac{1}{R_p C_p w} \dots (5)$$

where ( $\epsilon''$ ) is called the imaginary dielectric constant (loss factor), ( $\epsilon'$ ) is real dielectric constant, ( $\epsilon'$  and  $\epsilon''$ ) are experimentally observable quantities which may be used to characterize the dielectric dispersion over a range of frequencies and temperatures. The relation between the conductivity, the loss factor and the frequencies is :

$$\begin{aligned}\sigma &= \sigma_{dc} + \sigma_{ac} \\ &= \sigma_{dc} + \epsilon_0 \omega \epsilon'' \dots (6)\end{aligned}$$

The AC electrical conductivity ( $\sigma_{ac}$ ) was calculated from Equation (6) by using the calculated value of dielectric loss and the activation energy ( $E_{act}$ ) was calculated from the slope of the relation between ( $\ln \sigma_{ac}$ ) and reciprocal of temperature for various frequencies as in figure(2). The exponential factor (S) was calculated from slope of ( $\ln \sigma_{ac}$ ) and ( $\ln \omega$ ) through Equation (3). The tangent of loss angle ( $\tan \delta$ ) was calculated from Equation (5). Also, the energy gap was calculated depending on the values of exponential factor by equation below <sup>(6)</sup>:

$$S = 1 - \frac{6K_B T}{E_g} \dots (7)$$

The electron theory of solids aims to give a satisfactory account of electrical conduction in metals, and to explain the existence of metallic, semiconducting and insulating behaviour in different types of solids.

The classical and the quantum theories of electronic gas (free electron) could not explain the great differences in electric conduction of insulator, semiconductor, and conductor solid materials. This is because they do not take into consideration that solid materials have energy band, and that consist of so many adjacent energy

levels. The number of these levels is equal to the number of atoms in the crystal. The band, therefore, seems to be continuous but it is actually discrete with forbidden regions that present conduction electrons from existing there. These regions are called energy gaps <sup>(7)</sup>.

The energy gap in insulator materials is relatively large in comparison with the energy gap in conductor or semiconductor materials. The conductivity of semiconductor materials is affected by temperature, light, electromagnetic field, and is also affected by slight quantities of impurities. The sensitivity of semiconductors towards these factors renders an important material in the electronic applications.

Semiconductor must have its Fermi level within a gap, at least two bands must be important. The normally filled band below ( $\epsilon_F$ ) is called the valence band, the normally empty band above ( $\epsilon_F$ ) is called the conduction band. Any electron excited into the conduction can contribute to the electrical conductivity. However, the absence of an electron from the nearly filled valence band also contributes to the conductivity <sup>(8)</sup>.

A physical transformation of a solid or liquid or a chemical reaction really involves the rearrangement of a group of atoms into a new or more stable configuration. To accomplish this configuration, the reactions or the deformed atoms must be activated to a state of higher energy before the process can occur spontaneously. The smallest energy that will raise the free energy of an atom or a molecule to such a state so that it can go over the energy barrier is called the activation energy. This corresponds to the top of the energy barrier <sup>(9)</sup>.

## Experimental Procedure

A novel Schiff base ligand from liquid crystal material  $\text{CH}_3\text{OC}_6\text{H}_4\text{CH} : \text{NC}_6\text{H}_4(\text{CH}_2)_3\text{CH}_3$  and its transition metal complexes with Cu(II), Co(II), Ni(II) and Cr(III) have been preparation<sup>(10)</sup>.

Electrical conductivity is a material property which has the largest variation in its value. Conducting as well as semiconducting polymers have been widely produced. Table(1) shows the electrical conductivity of metals, semiconductors and insulators<sup>(11)</sup>.

**Table (1) Typical values of conductivity for metals, semiconductors and insulators**

Class of substance	Typical values for conductivity (ohm cm)-1
Metals	10 E+2 to 10 E+8
Inorganic semiconductors	10 E-9 to 10 E+3
Organic semiconductors	10 E-14 to 10 E+2
Insulators	Below 10 E-14

The materials used in this work for the preparation of poly (Schiff bases) and their complexes with Cu(II), Co(II), Ni(II) and Cr(III) were used without further purification, the colour of the

resultant mixture changed immediately, which is indicated that the complex is formed. The physical properties of these poly (Schiff bases) with complexes are listed in Table(2).

**Table (2) Physical properties of the prepared poly (Schiff bases) with complexes.**

Complex symbol	Chemical formula	Color	M.wt (gm.mol-1)
MBBA	$\text{CH}_3\text{OC}_6\text{H}_4\text{CH}:\text{NC}_6\text{H}_4(\text{CH}_2)_3\text{CH}_3$	white	273.37
MBBA-Cu <sup>+2</sup>	$(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{H}_2\text{O}$	dark	693.28
MBBA-Ni <sup>+2</sup>	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	dark	753.45
MBBA-Co <sup>+2</sup>	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	dark brown	770.67
MBBA-Cr <sup>+3</sup>	$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	dark green	826.74

The electrical measurements DC and AC of these compounds and their complexes have been investigated. The samples of study prepared for DC and AC measurements have been made of disk shapes with the diameter (10 mm) and thickness ( $2 \pm 0.5$  mm). The electrical conductivity ranged of organic semiconductors. Energy gaps for these complexes were also calculated by using the exponential factor.

The activation energy ( $E_{\text{act}}$ ) determine from logarithmic ( $\sigma_{\text{dc}}$ ) values and plotted as a function to the reciprocal of temperature. A similar effect has been reported in four poly (Schiff bases) and their iron(III) complexes were synthesized and characterized<sup>(12)</sup>.

## Results

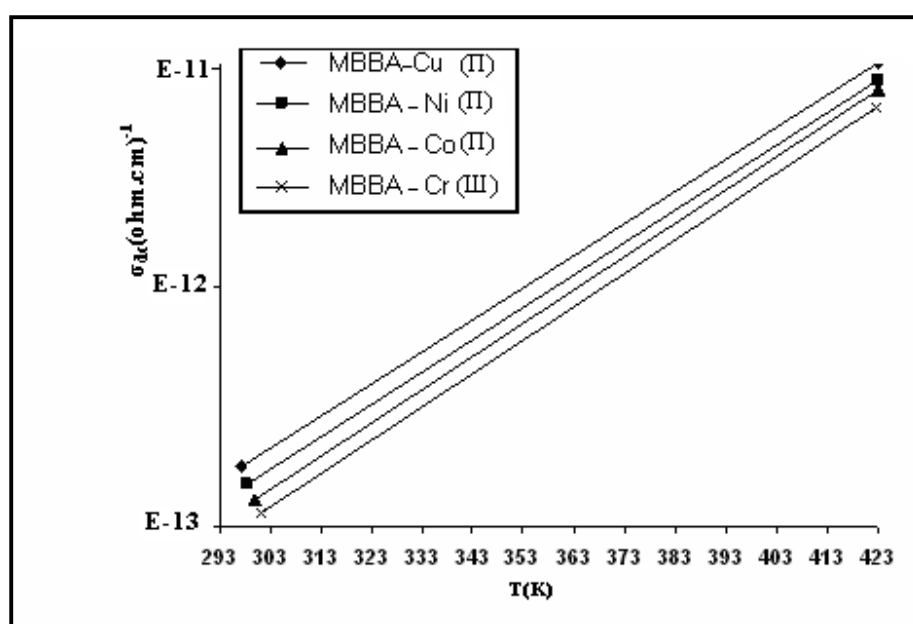
There are many relationships between electrical conductivity and (LCM) structure. In (MBBA), for

example, a pair of electrons forms each bond (CH = N). If adjacent hydrogen atoms to carbon are removed a series of conjugated double bands are formed<sup>(13)</sup>.

The conductivity measurements and its variation as a result of complexation have been carried out at a temperature ranged from (303 to 423)K, the dependence of DC electrical conductivity on temperature is established.

At low temperature the DC electrical conductivity is low and increased with the rise of temperature, i.e., the temperature coefficient of resistance is negative and this is a characteristic of a semiconductor<sup>(14-16)</sup>.

Figure (1) shows the relationship between the values of DC electrical conductivity with temperatures of samples as used in the paper. The figure defer to the characterized like to the semiconductor conduction mechanism.



**Figure (1) : The DC electrical conductivity as a function of temperature**

The values of energy gap ranged from (2.178 – 0.423) eV and there are consistent with the electrical conductivity DC and AC of organic

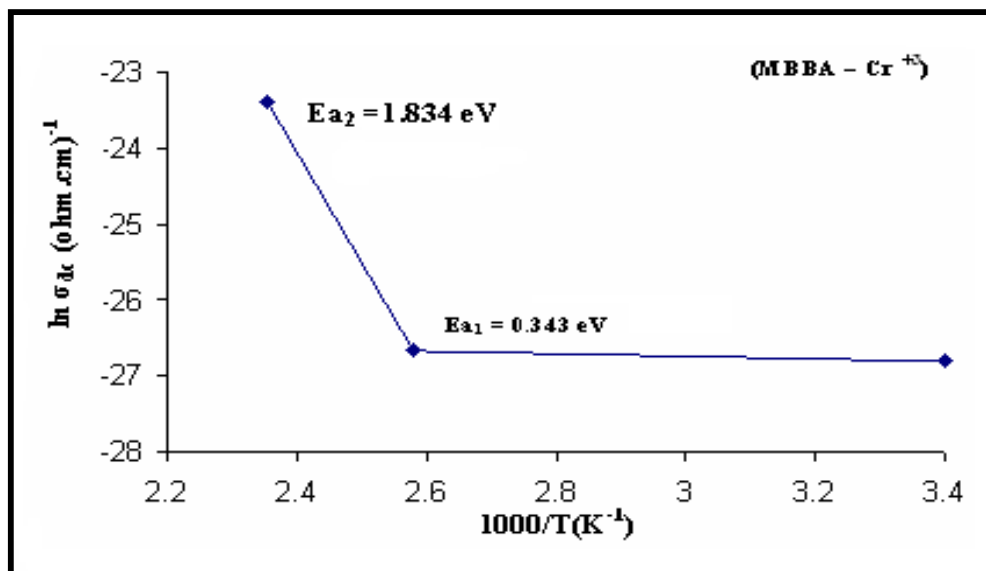
semiconductors ( $10^{-14} - 10^2$ ) ( $\text{ohm.cm}^{-1}$ ). The values of the activation energy are listed in table (3).

**Table(3): The value of activation energy for complexes**

Samples	Activation Energy (eV)	
	Ea1 (303-353)K	Ea2 (363-423)K
MBBA-Cu <sup>+2</sup>	0.524	1.942
MBBA-Ni <sup>+2</sup>	0.622	2.121
MBBA-Co <sup>+2</sup>	0.711	2.727
MBBA-Cr <sup>+3</sup>	0.343	1.834

The first activation energy ( $E_{a1}$ ) occurs at low temperature while the second is at high temperature<sup>(17,18)</sup>. The second activation energy ( $E_{a2}$ ) by the charge transfer at high temperatures is due to the thermal excitation of the carriers at the grain boundaries<sup>(18)</sup>.

The values of the activation energy  $E_{a1}$  and  $E_{a2}$  are shown in Figure (2) and we take the slope of best fit straight line of these curves, all the activation energy are determined by using Equation (2).



**Figure (2): The variation of  $\ln \sigma_{dc}$  with reciprocal temperature for sample (MBBA-Cr<sup>+3</sup>)**

The plot between  $\ln \sigma_{dc}$  and  $\frac{1}{T}$  for complexes (Cu<sup>+2</sup>, Ni<sup>+2</sup>, Co<sup>+2</sup>) are similar line in figure(2), but only different in values of activation energy ( $E_{a1}$ ,  $E_{a2}$ ) that gives in table(3).

### Conclusion

With the physicists came the solid state concepts developed chiefly for the understanding of inorganic

semiconductors, bonded covalently or ionically. The typical organic solid, is neither a covalently nor an ionically bonded crystal but a molecular crystal.

The central problem in the study of organic semiconductors is to understand how electric charge enters and is transported through a molecular and often highly disordered solid over distances which are very large on an atomic or molecular scale, a problem

which touches on a very wide spectrum of other fields of science, especially those in the realm of biology.

Generally, all charge transfer complexes show a markedly increased conductivity and decreased in value of activation energy compared with that of either components.

For these poly (Schiff bases) samples it was found that ( $\sigma_{dc}$ ) increases steadily with rising temperature.

The values of ( $E_{a1}$ ) ranged from (0.343 – 0.711) eV and as already discussed, is attributed to the hopping processes.

The values of ( $E_{a2}$ ) vary between ( 1.834 – 2.727) eV where decreased with increasing double bond conjugation in the poly (Schiff bases) studied. These results for ( $E_{a1}$ ) and ( $E_{a2}$ ) are expected for organic semiconductors.

### References

- 1- Demus, D. and Richter, L. (1978). Textures of liquid crystals, VEB Deutscher Verlag für Grudstoffindustrie, Leipzig, pp.(16-26).
- 2- Hall, C. (1989). Polymer materials, Macmillon Education Ltd., London, ch.(1).
- 3- Blakemore, J.S. (1974). Solid State Physics, 2<sup>nd</sup>. Edition by W.B. Saunders Company
- 4- Long ,A.R. (1982). Advance in Physics, Vol. 31, No.5,553.
- 5- Kao ,K.C. and Hwong, W. (1981). "Electron Transport in solids, Vol. 14 Pergamon Press.
- 6- Elliot ,S.R., *Advance in Physics*, 1987, **36**(2).
- 7- Kittle, C. (2005). Introduction to Solid State Physics, 8<sup>th</sup> Edition, J.S. John Wiley and Sons Inc., Canada.
- 8- Michael ,B.B. (1986). Encyclopedia of Materials Science and Engineering, Vol. 2, Institute of Technology, USA.
- 9- Rodriguez , F. (1970). Principles of Polymer Systems, McGraw-Hill Book Company, New York, ch. (10).
- 10- Al-Uquily , A.O.M. (2005). Ph.D.Thesis, department of physics, college of science, Al-Mustansiriyah University, Iraq.
- 11- Gutmann,F.and Lyons, L.E. (1976). Organic Semiconductors, John Wiley and Sons Inc., Canada.
- 12- Yaseen ,M.T. (2003). Ph.D. Thesis, department of physics, college of science, Al-Mustansiriyah University, Iraq.
- 13- Lai ,J.H. (1989). Polymers for Electronic applications, CRC Press Inc., Florida, ch. (4).
- 14- Omar ,M.A. (1975). Elementary Solid State Physics, 2<sup>nd</sup>. Edition, John Wiley and Sons Inc., New York.
- 15- Okamoto ,Y. and Brenner, W. (1964). Organic Semiconductors, Chapman and Hall Ltd., London.
- 16- Miller,M. (1966). The Structure of Polymers, Reinhold Publishing Corporation, New York.
- 17- Orton , J. and Cold Smith, B.J., *J. Appl. Phys.*, 1982, **53**( 3).
- 18- Nicodemo,L., Nicolais, L., Romeo, G. and Scafora ,E. (1978). Polymer Engineering and Science, Academic Press, New York, ch. (3).