Study The Effect of Molecular Weight, Viscosity and Temperature on Relaxation Times for the Liquid Crystal Material

$CH_3OC_6H_4CH:NC_6H_4(CH_2)_3CH_3$

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Abstract

The research aim is the study of the effect of the molecular weight, viscosity and temperature on the relaxation times for liquid crystal material(p-Methoxybenzylidene-p-Butylaniline) (MBBA) $CH_3OC_6H_4CH:NC_6H_4(CH_2)_3CH_3$ the liquid crystal material-Schiff bases-(MBBA) has been selected as a sample of study since if shows nematic behavior at room temperature in addition to being are of the major compounds that shows the effect of following dynamic scattering mode. Four samples and its ions of metallic complexes (Cu^{+2}, Ni^{+2}, Co^{+2}, Cr^{+3}) of different molecular weights had been used.

The logarithmic of molecular weights for five samples are calculated and study the dynamic electro-optic properties, measurements are performed at wavelength (632.8nm). It has been found that the relaxation times (τ^N) are depends on the heating temperature, and functions of viscosity. The voltage needed to produce complete orientation in the molecules of the liquid crystals material and four complexes, are found that the increased by the increases of the molecular weight.

* **Keywords: Liquid crystal; $CH_3OC_6H_4CH:NC_6H_4(CH_2)_3CH_3$; Schiff base; Viscosity; Relaxation time.**

الخلاصة

يهدف موضوع البحث إلى دراسة تأثير الوزن الجزيئي واللزوجة ودرجة الحرارة على أزمان الاستجابة للمادة البلورية السائلة (MBBA) $CH_3OC_6H_4CH:NC_6H_4(CH_2)_3CH_3$ وقد تم اختيار هذه المادة كونها إحدى المركبات التي تظهر السلوك النيماتي عند درجة حرارة الغرفة فضلا" عن كونها من المركبات الرئيسة التي تظهر تأثير التشتت الديناميكي. استخدمت أربع نماذج بشكل معقدات من هذه المادة بأوزان جزيئية مختلفة مع ايونات النحاس والنيكل والكوبالات الثنائية التكافؤ والكروم الثلاثي التكافؤ.

تم حساب الأوزان الجزيئية ولوغاريتماتها للنماذج الخمسة ودراسة الخواص الديناميكية الكهروبصرية، وقد وجد أن أزمان الاستجابة (τ^N) تعتمد على درجة الحرارة وهي دالة إلى اللزوجة، كما وجد كذلك أن الفولتية اللازمة لإحداث توجيه تام في جزيئات المادة البلورية السائلة ومعقداتها الأربعة تزداد مع زيادة الوزن الجزيئي.

1- Introduction

The term liquid crystal signifies a state of aggregation that is intermediate between the crystalline solid and the amorphous liquid. As a rule, a substance in this state is strongly anisotropic in some of its properties and yet exhibits a certain degree of fluidity, which in some cases may be comparable to that of an ordinary liquid. The first observations of liquid crystalline or mesomorphic behaviour were made towards the end of the last century by Reinitzer and Lehmann. Several thousands of organic compounds are now know to form liquid crystals. An essential requirement for mesomorphism to occur is that the molecule must be highly geometrically anisotropic, usually long and relatively narrow. Depending on the detailed molecular geometry, the system may pass through one or more mesophases before it is transformed into the isotropic liquid. The transitions to these intermediate states may be brought about by purely thermal processes (thermotropic mesomorphism) or by the influence of solvents (lyotropic mesomorphism) (Dietrich and Demus, 1973).

2- Theoretical part

The nematic liquid crystal differs from a normal liquid in that it is composed of rod-like molecules with the long axes of neighbouring molecules a ligand approximately parallel to one another. To allow for this anisotropic structure, we introduce a vector $(\hat{n})$ to represent the direction of preferred orientation of the molecules in the neighborhood of any point. This vector is called the director. Its orientation can change continuously and in a systematic manner from point to point in the medium. Thus external forces and fields acting on the liquid crystal can be a result in a translational motion of the fluid as also in an orientation motion of the director (Frank, 1958).

Let the material volume to be (V) bounded by a surface (A). The conservation laws take the following form, conservation of mass (Ericksen,1961):

$$\frac{d}{dt}\int_V \rho dV = 0 \qquad \text{......... (1)}$$

where (ρ) is the density.

Conservation of linear momentum is:

$$\frac{d}{dt}\int_V \rho v_i dV = \int_V f_i dV + \int_A t_{ji} dA_j \qquad \text{......... (2)}$$

where (f_i) is the body force per unit volume and (t_{ji}) the stress tensor.

Conservation of energy is:

$$\frac{d}{dt}\int_V \left(\frac{1}{2}\rho v_i v_i + U + \frac{1}{2}\rho_1 \dot{n}_i \dot{n}_i\right) dV = \int_V \left(f_i v_i + G_i \dot{n}_i\right) dV + \int_A \left(t_i v_i + s_i \dot{n}_i\right) dA \qquad \text{......... (3)}$$

where (ρ_1) is a material constant having the dimensions of moment of inertia per unit volume, (U) is the internal energy per unit volume, (G_i) is the external director body force (which has the dimensions of torque per unit volume since n_i has been chosen to be dimensionless), ($t_i = t_{ji}\, \nu_i$) is the surface force per unit area acting across the plane whose unit normal is (ν_i) and ($s_i = \pi_{ji}\, \nu_i$) is the director surface force (which has the dimensions of torque per unit area).

Conservation of angular momentum is:

$$\begin{aligned} &\frac{d}{dt}\int_V \left(\rho e_{ijk} \chi_j v_k + \rho_1 e_{ijk} n_j \dot{n}_k\right) dV \\ &= \int_V \left(e_{ijk} \chi_j f_k + e_{ijk} n_j G_k\right) dV + \int_A \left(e_{ijk} \chi_j t_k + e_{ijk} n_j S_k\right) dA \end{aligned} \qquad \text{.............. (4)}$$

Finally, we have Oseen's equation as the following:

$$\int_V \rho_1 \ddot{n}_i dV = \int_V \left(G_i + g_i\right) dV + \int_A \pi_{ji} dA_j \qquad \text{.............. (5)}$$

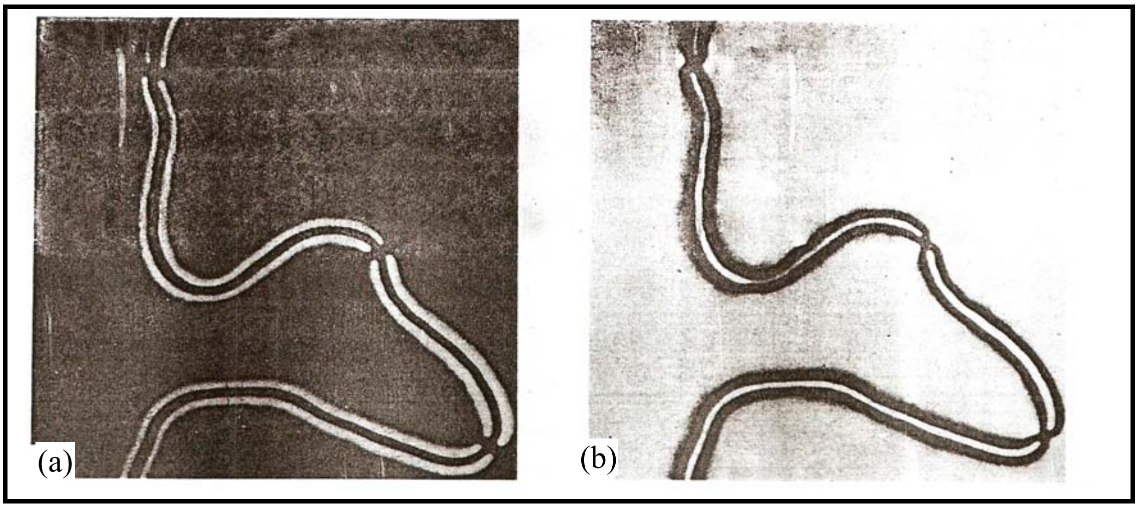
where (g_i) is the intrinsic director body force, which has the dimensions of torque per unit volume and whose existence is independent of (G_i).

We can use the simple hydrodynamic model of Stokes-Einstein-Debye, which links the relaxation time (τ) and the viscosity (η) of isotropic liquids (Ginovska et al.,2001).

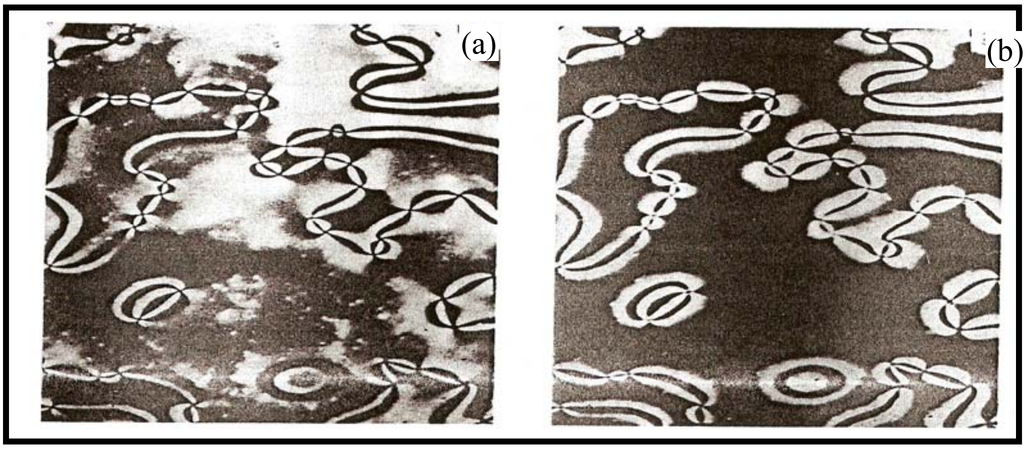
$$\tau^{\text{iso}} = \frac{\pi \ell^3 \eta^{\text{iso}}}{2KT} \qquad \text{.............. (6)}$$

where (T) is the absolute temperature and (K) is the Boltzmann constant. In the model, the sphere of a diameter (ℓ) represents a dipolar, rigid and axially symmetric rotating molecule.

For special orientations of the crossed polarizers, all point singularities are connected by sharp black lines and at the same time large areas of the sample appear black, see figures (1) and (2) (Nehring and Saupe,1972).



Figure(1):Narrow inversion line of the first kind in an uncovered sample of nematic (MBBA)*T. Crossed polarizers rotated by(45º) on going from (a) to (b).



Figure(2): Inversion lines of the first kind in nematic(MBBA)* .Crossed polarizers rotated clockwise by (67.5º) on going from (a) to (b).

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3- Experimental Part and Materials

A Schiff base may be defined as an organic compound which contains a characteristic functional group of carbon-nitrogen double bond $(R'R''C=NR''')$, a linkage called azomethine or imine linkage. If the group ($R'=H, R''$ and R''' = aromatic groups) the compounds are called anils, benzanils, or the widely used benzylidene anilines. Most of the work has been done on the latter type of Schiff bases as well as on the substituted derivatives. Much work has been made on Schiff bases complexes, their stability, spectra, and other properties that can be readily determined (Irving, *et al.*, 1954).

A novel Schiff base ligand from liquid crystal material para-methoxybenzylidene para-n-butylaniline (MBBA) and its transition metal complexes with $(CH_3COO)_2Cu.H_2O$, $Ni(NO_3)_2.6H_2O$, $CO(NO_3)_2.6H_2O$ and $Cr(NO_3)_3.9H_2O$ have been preparation (Al-Uquily, 2005). A Schiff bases have the ability of coordination with transition metal ions to prepare of stable complexes of copper (II), cobalt (II), nickel (II) and chromium (III).

The liquid crystal material (MBBA)-Schiff bases- has been selected as a sample of study since if shows nematic behaviour at room temperature [phase transitions and the textures of the mesomorphic phases were observed with a Leitz Laborlux (12) Pol equipped with a Leitz hot-stage (350) and a Vario-orthomat camera] (Al-Hamadani, 2004), in addition to is being are of the major compounds that shows the effect of following dynamic scattering mode.

Four samples and its ions of metallic complexes (Cu^{+2}, Ni^{+2}, Co^{+2}, Cr^{+3}) of different molecular weights [see Table (1)] are preparation, the shear viscosity was measured with a Haake Viscometer Rotovisco RV20 (serial no. BS3154).**

Nematic liquid crystals are rod-like molecules and they exhibit orientated order (on average) along a common direction known as director $(\hat{n})$. If the polarization axis of the laser is tilted (45^o) with respect to the director axis of the liquid crystals molecules, then the polarized laser light propagating along the liquid crystals experiences a phase difference (δ) between the ordinary and extraordinary components of the propagating light. The fundamental principle of birefringence measurement is to measure this phase difference (δ) and an accurate way of determining (δ) is to measure the $(I_\perp / I_{//})$ ratio, where $(I_\perp)$ and $(I_{//})$ are the filtered intensity values of perpendicular and parallel polarized laser beams, respectively. Details of the optical configuration is depicted in Figure (3)*.

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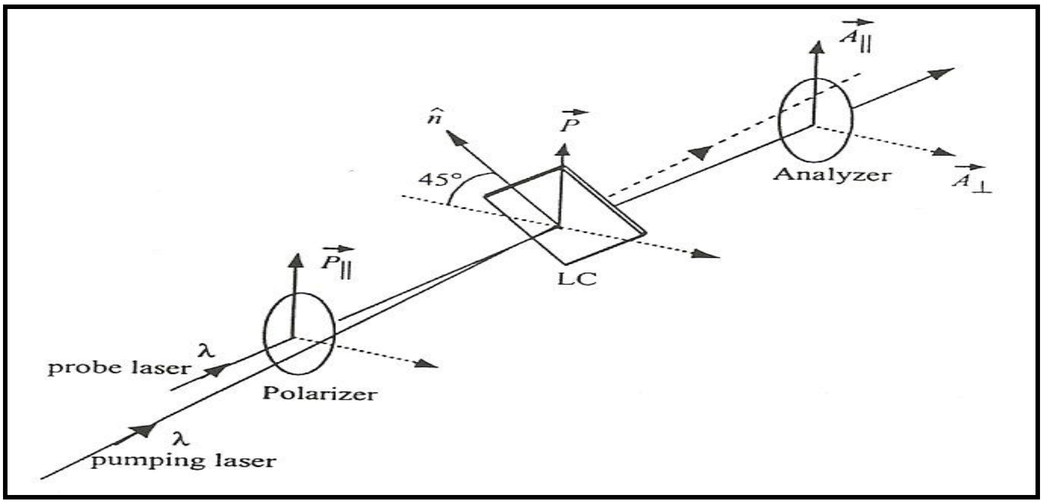


Figure (3): Optical configuration of birefringence measurements.

where: p: Polarizer, A: Analyzer, $\hat{n}$: Director, λ: Wavelength of the incident laser beams.

We calculated the logarithmic of molecular weights for five samples and study the dynamic electro-optic properties, measurements are performed at wavelength (632.8 nm), it has been found that the relaxation times (τ^N) for different temperatures are depends on the heating temperature. The color of the resultant mixture changed immediately, which is indicated that the complex is formed. Table (1) listed the physical and chemical properties of prepared bases of compounds study in this research.

Table (1) Physical and chemical properties of the prepared poly (Schiff bases) with complexes

Compounds	Color	η Viscosity (poise)	$\mathrm{M.W_t}$ ($\mathrm{gm.mol^{-1}}$)	Log ($\mathrm{M.W_t}$)	Voltage (Volt)	τ^N (seconds)		
						50ºC	70ºC	90ºC
MBBA	White	22	273.37	2.437	220	$(6.92)^{*}$	$(5.22)^{**}$	$(4.00)^{***}$
MBBA-$\mathrm{Cu^{+2}}$	Dark	23.5	693.28	2.841	240	15.1	5.66	4.24
MBBA-$\mathrm{Ni^{+2}}$	Dark	25.2	753.45	2.877	260	18.2	7.11	4.45
MBBA-$\mathrm{Co^{+2}}$	Dark brown	27	770.67	2.887	280	22.5	7.88	4.66
MBBA-$\mathrm{Cr^{+3}}$	Dark green	28.3	826.74	2.917	300	26.3	9.4	6.38

* at T = 25ºC ** at T = 30ºC *** at T = 35ºC

4- Results and Discussions

In general, organic macromolecular materials have been considered in term of a good electrical insulators, but it has been known for along time. Most polymers become highly electrical conductive or semiconductive when doped or blended with certain amount of metals or the polymer repeating units are coordinated with metal ions or metal salts (Gutmann and Lyons, 1976).

The problem is that the viscosity of nematic liquid crystal is an anisotropic quantity and at least three different viscosity coefficients have to be taken into account, as proposed by Miesowicz (Ginovska *et al.*, 2001).

The experiment shows that in the absence of external forces, the flow of a nematic liquid crystal (consisting of elongated molecules) causes a molecular orientation, very similar to that presented in Figure (4), where (η_1, η_2 and η_3) are the viscosity coefficients of (MBBA) and (T_N) is the twisted nematic phase.

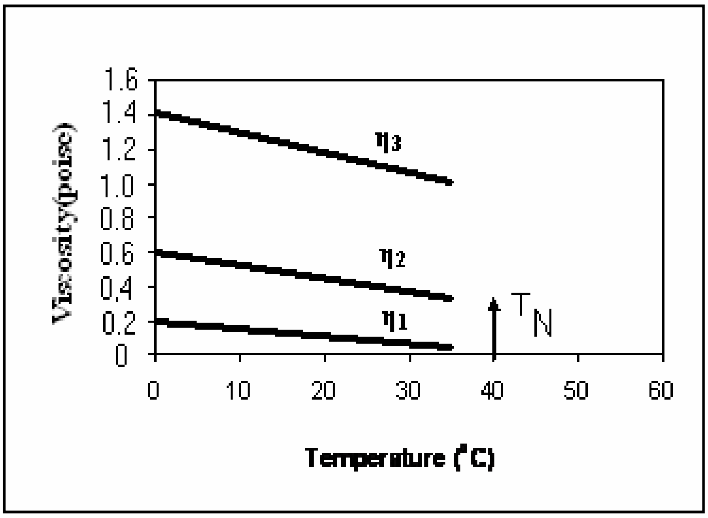


Figure (4): The viscosity coefficients (η_1, η_2 and η_3) of (MBBA) as functions of temperature.

By using eqn. (6) we can calculate and plot that the linear relation isotropic between (τ^{iso}/η^{iso}) and (T^{-1}), is quite good fulfilled in the case of (MBBA). The slope of the linear dependence is proportional to the effective length (ℓ) of the rotating molecule. Figure (5) presents the results of the shear viscosity measurements for freely flowing (MBBA) in the isotropic and nematic phases.

Figure (6) presents the Arrhenius plots for the dielectric relaxation time and the viscosity of (7CB). The important observation concerns the viscosity: both in the isotropic and nematic phases the values of the activation energy are practically the same.

By using the values from table(1),we can plots the relation between the relaxation time (in second) and temperature (in ºC) , see figure(7a), and the other between the relaxation time and reciprocal temperature (in K^{-1}) , see figure (7b),and plot that the linear relation between viscosity and voltage needed to produce complete orientation in the molecules of the liquid crystals material put in figure(8), of poly (Schiff bases) and their complexes with Cu(П),Co(П),Ni(П) and Cr(Ш).

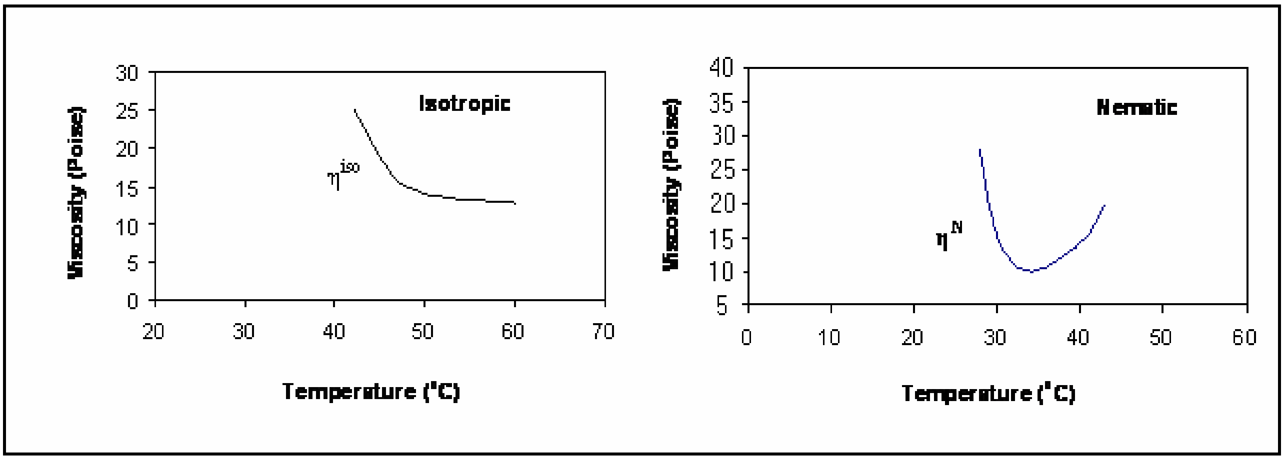


Figure (5): Temperature dependence of the shear viscosity of freely flowing (MBBA) in isotropic and nematic phases.

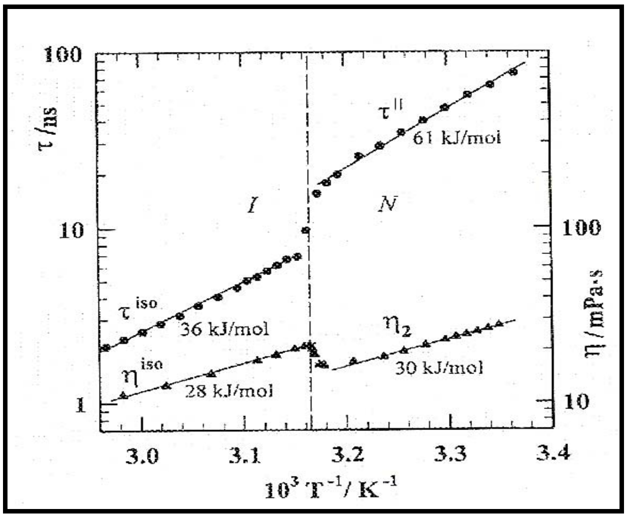
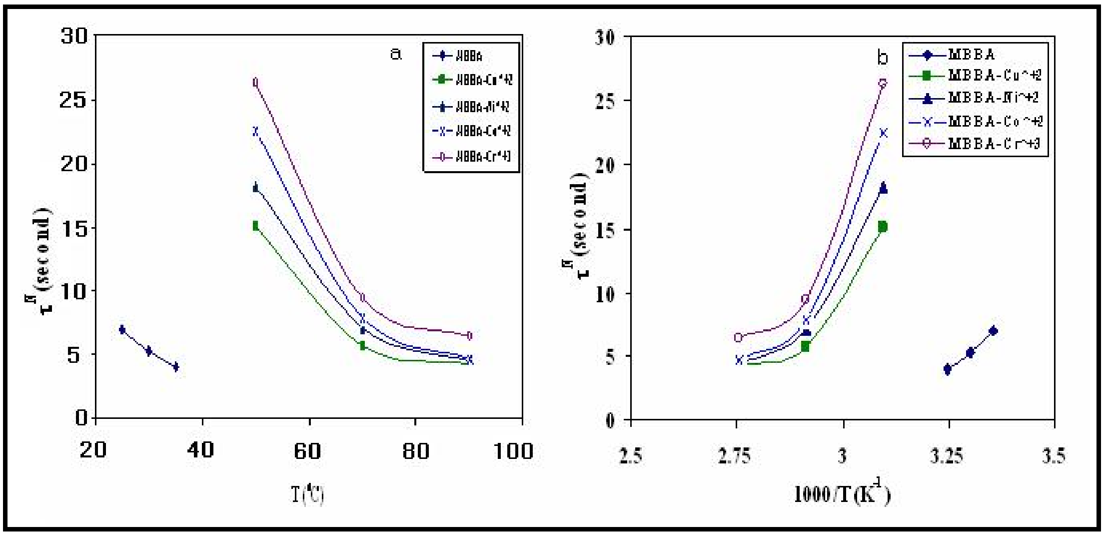
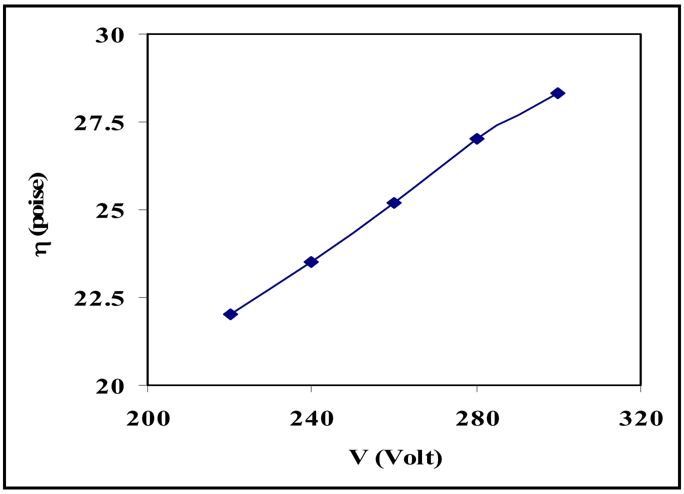


Figure (6): Arrhenius plots for the relaxation time corresponding to the molecular rotation around the short axis and for the shear viscosity of freely flowing(7CB) (Böttcher and Bordewijk, 1978).



Figure(7):The relaxation time as a function of temperature of these poly (Schiff bases) with complexes Cu(П),Co(П),Ni(П) and Cr(Ш).



Figure(8): Relation between viscosity and voltage of liquid crystal material (MBBA) and their complexes with Cu(Π), Co(Π), Ni(Π) and Cr(Ш).

5- Conclusions

The values of activation energy (Ea_1) in the poly (Schiff bases) studied ranged from (0.343 – 0.711)eV and the values of (Ea_2)vary between (1.834 – 2.727)eV, these results for (Ea_1) and (Ea_2) are expected for organic semiconductors.

On the basis of temperature dependences of the relaxation time and the shear viscosity of (MBBA), the strength of the nematic potential and the effective length of the rotating (MBBA) molecule were estimated.

The result allows one to conclude that the difference in the activation energies for the dielectric relaxation time in the nematic and isotropic phases of (MBBA) is connected mainly to the existence of the nematic potential.

In principle, the difference in the activation energy for the rotation of mesogenic molecules around the short axis in the isotropic and nematic phases can be a measure of the nematic potential strength, provided the viscosity effect is not too different in both phases.

We calculate and determine the viscosity coefficients (η_1, η_2 and η_3) of liquid crystal material in study (MBBA) as functions of temperature, and found the temperature scale in linear in (T^{-1}) see figures (4) and (5), and in general, the values of the relaxation time agree with the data obtained previously for (MBBA) by (Ginovska *et al.*, 2001),see figure(7). As seen in Figure (6), the strength of the (7CB) nematic potential estimated in this way equals (25 KJ/mol).

The shape in figure (8) refer to linear relation between viscosity and voltage needed to produce complete orientation in the molecules of the liquid crystals material and four complexes ,are found that the increased by the increases of the molecular weight .

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