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SPECTRAL STUDY FOR THE EFFECT OF SOLVENT DIELECTRIC CONSTANT ON THE OPTICAL BAND GAP FOR (4-OXOTHIAZOLIDIN-2-YLIDENE) ACETONITRILE.

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ABSTRACT:-

Heterocyclic compound of (4-oxothiazolidin-2-ylidene) acetonitrile was prepared in powder form. The crystalline nature of the prepared sample was checked by X- ray diffraction (XRD). IR absorption spectra were recorded on a Shimadzu 440 infrared spectrophotometer (cm^{-1}) using the KBr technique (Shimadzu, Japan). Reflection spectra of the powder sample were obtained in the wavelength range (200-2500 nm) at room temperature using spectrophotometer. Absorption and transmission spectra of the prepared sample were obtained in different solvents in the wavelength range (190-1100nm).The solvent used are acetone, dimethyformamid (D.M.F.) and glycerol. The measurements were carried out at room temperature using (JENWAY 6405 UV/VIS) spectrophotometer. The optical energy gap which is the difference between lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) was estimated. The effect of the solvent dielectric constant on optical band gap was discussed. Keywords:- Optical band gap, FT-IR absorption and X-ray diffraction.

1- INTRODUCTION

Sulfur containing heterocyclic compounds finds enhanced interest for a long time because of their important medical applications [1]. Among this class of molecules (4-oxothiazolidin-2-ylidene) acetonitrile has been shown to have various important biological activities such as antimicrobial [2],antifungal [3], antiviral [4], antituberculostatic [5], anti-Hiv [6], cardio-protective [7], anticancer[8], anticonvulsant[9], anti-inflammatory[10] and analgesic properties[11]. The chemical formula of the compound is shown in Fig.(1).

The aim of the present work are to investigate the optical behavior of (4-oxothiazolidin-2-ylidene) acetonitrile system in crystalline and solution in three different solvents. The effect of dielectric constant of the solvents was considered by X-ray diffraction and IR absorption. The absorbance of the prepared system was also measured to study the effect of the solvent dielectric constant on the optical band gap. The solvent is used are acetone, dimethyformamid (D.M.F.) and glycerol.

2- EXPERIMENTAL TECHNIQUES

Yellow crystals, yield 72 % (melting point around 180-82ºC), from ethanol was added to a solution of malononitile (0.01 mol) in acetic acid (20 mL) (0.5 mL) thioglycolic acid (0.01 mol). The reaction mixture was heated under reflux for 3 h. The solid product formed was collected by filtration. IR absorption spectra was recorded in the frequency range (400-4000 Cm^{-1}). The optical reflection spectra of the obtained powder samples were accorded. The optical absorption of (4-Oxothiazolidin-2-ylidene) acetonitrile solved in acetone, dimethylformamid (D.M.F.) and glycerol were recorded in the wavelength range (190-1100 nm). The optical energy gap between HOMO and LUMO was determined and the effect of solvent on the optical band gap width was discussed**.**

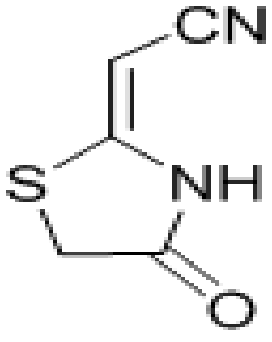


Fig. 1: The chemical formula of (4-oxothiazolidin-2-ylidene) acetonitrile.

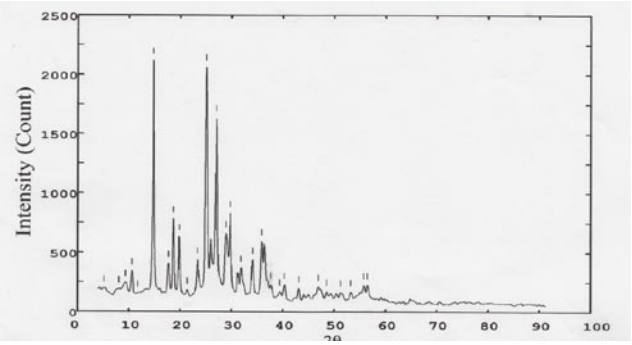


Fig. (2):- X-ray diffraction of (4-oxothizolidin-2-ylidene) acetonitrile.

3- RESULTS AND DISCUSSION:-

3-1-:X-Ray Diffraction (XRD)

The XRD pattern obtained for (4-oxothiazolidine-2-ylidene) acetonitrile at room temperature is given in Fig.(2). As shown, a,sharpe peaks centered at 2θ=14.7, 25.05 and 27.02 θ are observed indicating the polycrystalline nature of the prepared sample.

3.2- FT-IR STUDIED

For getting information about the structural units, FT-IR absorption spectrum in the frequency range (400-4000 Cm^{-1}) has been recorded for the (4-oxothiazolidin-2-ylidene) acetonitrile as shown in Fig.(3). The main absorption bands of the structural units are given in table (1).

Table (1):- IR absorption spectrum of (4-oxothiazolidin-2-ylidene) acetonitrile.

Structural Unit	NH	CH. Aleph	CN	CO
Wave number (Cm^{-1})	3414	2945	2221	1722

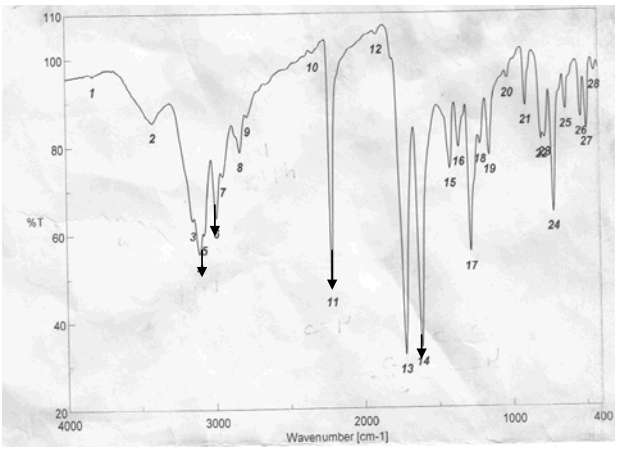


Fig. (3):- The FT-IR Spectrum data of (4-oxothiazolidin-2-yliddene) acetonitrile

The spectrum reveals clearly the formation of NH, CH, CN and CO functional groups. This confirms that the prepared samples are (4-oxothiazolidin-2-ylidene) acetonitrile.

3- Band gap

Effect of Solvent Dielectric Constant on the Optical

3-1:- Optical Band Gap Determination

The transmission T was measured in the wavelength range (190-1100 nm) using three different solvents acetone, D.M.F. and glycerol. Figs. (4 -a,b,c) show the transmission spectrum as a function of wavelength for three different solvents; the former two solvents are non polar i.e. of low dielectric constant. On contrary the third (glycerol) is a polar solvent because of high dielectric constant. The dielectric constants, the onset wavelength and the maximum values of transmission of the studied system for the three solvents are listed in table (2) [12].

Table (2):-dielectric constant, their onset wavelength and maximum values of T for (4-oxothiazolidin-2-ylidene) acetonitrile.

Solvent	Dielectric Constant at 25°C	Onset Wavelength at 400 nm	Maximum Values of (T)
Acetone	20	390	70%(900 nm)
D.M.F.	36.5	730	85% (1100 nm)
Glycerol	47	740	65 % (1070 nm)

Many remarks can be extracted; first, the onset of the transmission depends on the type of solvent as given in table (2). Second, the degree of absorption depends on the solvent. Inspection of table (2) reveals that the onset wavelength increases by increasing dielectric constant of the solvent. Such results are expected. On the other hand, the degree of transmission T tends to increases with increasing wavelength. Table (2) gives the maximum values attended for each solvent and the corresponding wavelength.

The obtained data of transmission T were used to calculate the absorption coefficient α through the well known relation:- $\alpha = -\frac{1}{t} Ln\, T$, where t is the thickness of the sample [13].

Figs. (5- a,b,c) show the relation between absorption coefficient α and wavelength λ using

the three different solvents. It can be seen that, all absorption coefficient spectrum follow a one common pattern where α increases with increasing wavelength λ. In case of acetone α =1.29 cm^{-1} at wavelength λ = 380 nm, then it increases up to 4 Cm^{-1} at λ = 469 nm and finally it remains almost constant with increasing wavelength (in the high investigated wavelength range). In case of glycerol α = 0.4 cm^{-1} at λ = 424 nm then, it increases with increasing wavelength. Finally, the variation of α with λ of D.M.F. follow the same trend where α= 0.1 cm^{-1}at λ = 660 nm and it increases with increasing wavelength. From the above results we can say that, the dielectric constant of the solvent plays an important role on the absorption coefficient value.

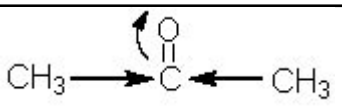
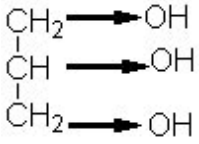
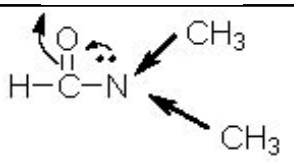
3-4:- Reflection Spectrum

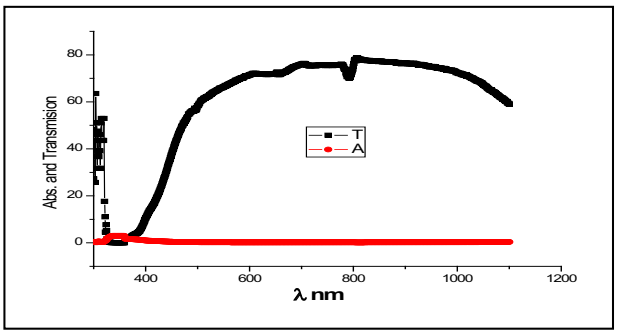
The reflection spectrum R of the (4-oxothiazolidin-2-ylidene) acetonitrile powder sample was measured in the wavelength range (200-2500 nm) using spectrophotometer at room temperature. Fig.(6) show the relation between absorbance A (where A=100- R) with wavelength λ. Extrapolating the curve gives the gap E_g, which lies between HOMO and LUMO width. The obtained value of E_g was listed in table (3). The dependence of A on wavelength λ is shown in Figs. (7- a,b,c) solvent in acetone, D.M.F. and glycerol. The obtained values of E_g are given in table (3). It can be seen that, the optical energy gap E_g of the powder sample (1.31 eV) is lower than that of the solutions. This can be accounted for by the fact that in the powder form the intermolecular interaction is smaller than that of the interaction between molecules [14]. For solution case the E_g value has 1.59eV for D.M.F. For acetone and glycerol E_g values increases This behavior can be attributed to the greater positive charge on carbon atom in case of acetone and glycerol with respect to that of dimethylformamide [15]. In the present case (molecular species) the absorption is due to the electron transition from HOMO to LUMO width. It is expected that dielectric constant of the solvent should change the position of both i.e. change the optical absorption. The higher value of E_g is not expected due to the fact that acetone and glycerol exhibit less polarity with respect to D.M.F. This is most likely due to the internal hydrogen bonds in the glycerol molecule.

4:- Conclusion

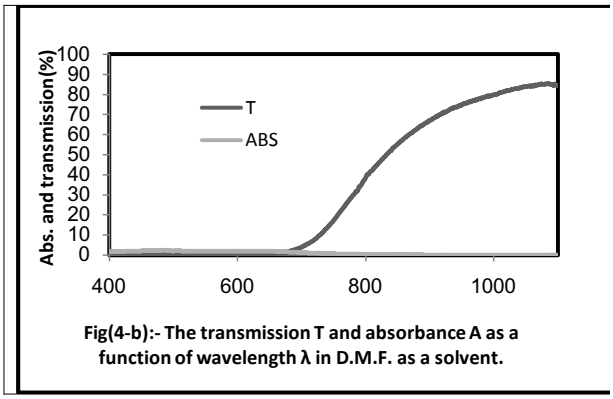
Crystalline of (4-oxothiazolidin-2-ylidene) acetonitrile system was prepared. The crystalline nature of the prepared system was checked by X-ray diffraction which revealed in polycrystalline form. IR absorption spectrum was recorded on a Shimadzu 440 infrared spectrophotometer using the KBr technique (Shimadzu, Japan). The spectrum reveals clearly the formation of NH, CH, CN and CO functional groups. The obtained data confirmed the formation of the (4-oxothiazolidin-2-ylidene) acetonitrile. The optical energy gap

Table (3):- Effect of solvent on the optical gap Eg of (4-oxothiazolidin-2-ylidene). acetonitrile.

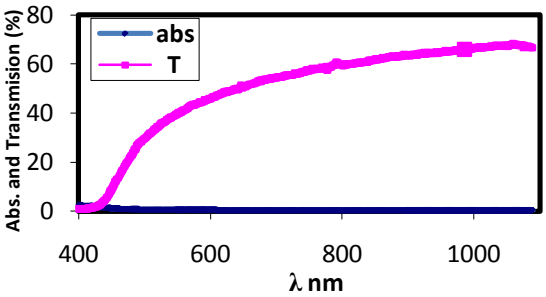
Solvent	Structure	Eg (eV)
Acetone		3.55
Dimethylformamide		1.59
Glycerol		3.30
1.31		Powder sample



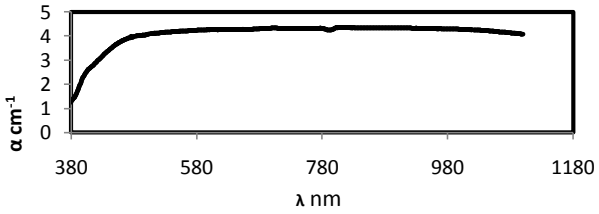
Fig(4-a):- The transmission T and the absorbance A as a function of wavelength λ in acetone as a. solvent



Fig(4-b):- The transmission T and absorbance A as a function of wavelength λ in D.M.F. as a solvent.



Fig(4-c) :- The transmission T and absorbance A as a f unction of wavelength λ in glycerol as a solvent.



Fig(5-a):- The absorption coefficientα with wavelength λ in acetone as a solvent.

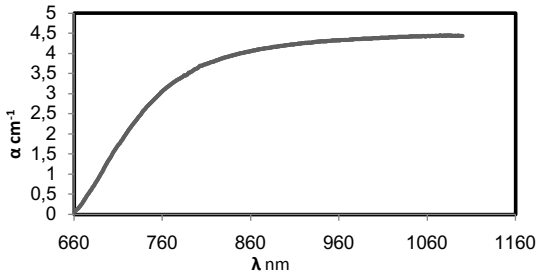
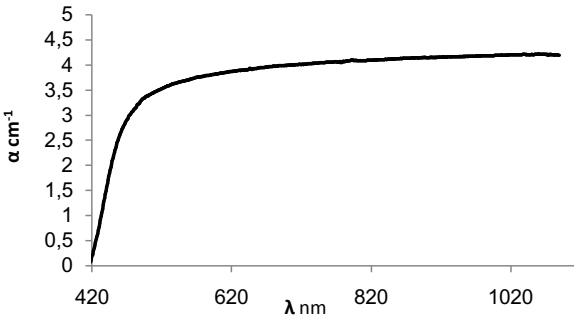


Fig (5-b):- The apsotption coefficient α with wavelength λ in D.M.F. as a solvent.



Fig(5-c):- The absorption coefficient α with wavelength λ in glycerol as a solvent.

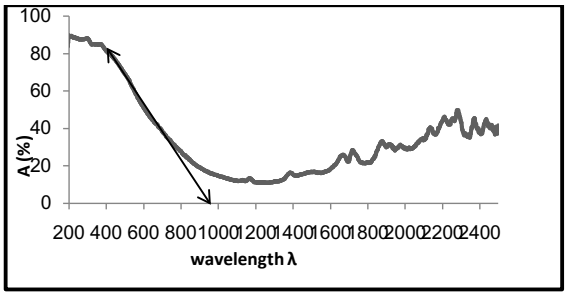
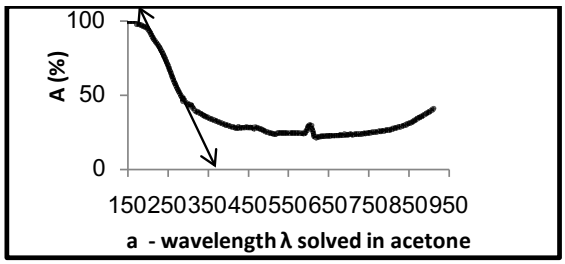
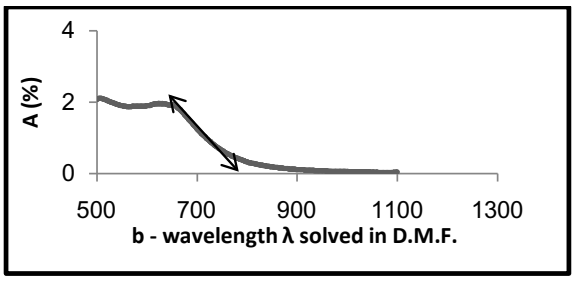


Fig. (6): - Relation between absorbance A and wavelength λ for powder sample.





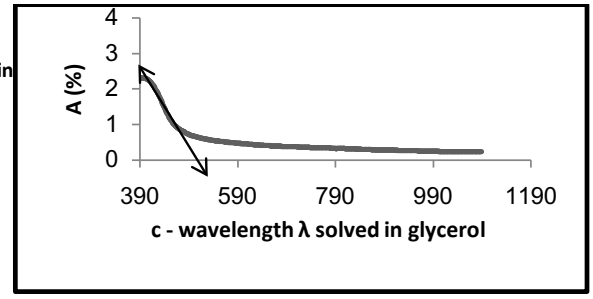


Fig. (7a,b.c): - Relation between absorbance A and wavelength λ for(4-oxothiaxolidine-2-ylidene) acetonitrile.

of the powder sample was determined and found to smaller than that of the solutions. The optical absorption of the prepared sample was studied in different three solvents. The solvents used are acetone, dimethylformamid (D.M.F.) and glycerol. It can be seen that, optical energy gap Eg has a value of 1.31 eV in powder form. The value of Eg (1.59eV) was obtained for D.M.F. However in cases of acetone and glycerol Eg values are higher. The effect of the solvent dielectric constant on optical band gap was discussed.

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