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Effect of Temperature and Concentration on the Optical Properties of PVC Solutions

Abstract- *In this paper, effects of temperature and concentration on the absorption spectra for Polyvinyl chloride solutions are studied at wavelengths from 200 to 400 nm and with the range of temperature 20, 30, 40, 50, and 60 degrees (C^o). Electronic absorption spectra were examined over the wavelength range 200-400 nm by different concentrations ($1x10^{-3}$, $8x10^{-4}$, 6.5x10-4, 5x10-4 and 3x10-4)[M]. The UV spectra shifted slightly towards large wavelength with increasing the temperature. The values of the energy gap of polyvinyl chloride are decreasing as concentration and temperature increased. The data shows that the refractive index of the polymer decreases with increasing the wavelength and temperature. The relationship between the absorption coefficient and photon energy of the PVC solutions are calculated.*

Keywords- *photophysical processes, absorption, polyvinyl chloride, refractive index, absorption coefficient, thermal effect.*

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1.Introduction

The absorption spectrum was widely proved to be an important and efficient tool in exploring and interpreting the various phenomena of electronic structures and processes in the materials subjected to radiation. The optical properties of molecules depend on the interaction between the molecule and the incident light. When light passes through it, the absorption process occurs in a way that makes absorption of a photon creates a free electron and a free hole in the conduction band and the valence band respectively[1] . But in indirect optical energy gap , the energy will be lost as heat during the recombination for most molecules, the lowest-energy occupied molecular orbitals are the σ orbitals, which correspond to σ bonds. The π orbitals are located at somewhat higher energy levels, and orbitals that carry unshared pairs, the non-binding (n) orbitals, lie at even higher energies. The unoccupied, or anti-bonding orbitals (π* and σ*), are the orbitals of highest energy. Figure (1) shows typical electronic energy levels

There are several factors that affect the energy gap; the temperature of the substrate, the amount of impurities present and type of the material. Any change in the above factors causes a variation in the value of the energy gap.

The heat treatment effect on the optical properties of PVC was a good technique used to obtain the modified properties of the polymer. The polymer is solid materials relent by raising the temperature and then returning to its hardness without the change in chemical structure if the temperature does not reach to the extent that it leads to destroying the molecules of the polymer

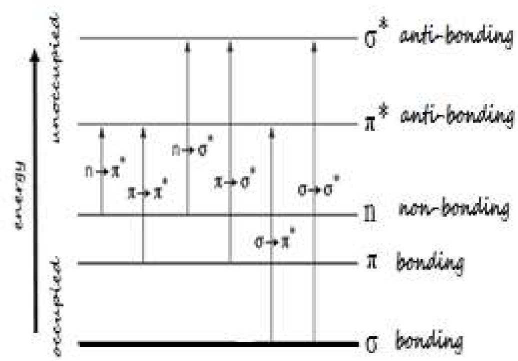

Figure (1) Electronic energy levels and transitions

2.Experimental Method

I.Materials used and preparation of samples

PVC sample is weight power supplied by Hyundai Company, Korea used without further purification as a solute sample. Measurements of absorption in solution were made by spectroscopic grade THF, which does not show any absorption band at the range from (200-400)nm nm. We prepared an amount of the polymer in 50 ml to get a primary solution with 1×10^{-3}M, different concentrations were prepared 3×10^{-4} [M], 5×10^{-4}[M], 6.5×10^{-4} [M] and 8×10^{-4} [M]. Furthermore, In the same way as above, we attended different concentrations of DEP solution within range (2×10^{-5} to 8×10^{-5}[M]).

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II.Experimental measurements

The absorbance measurements of the PVC in THF solvent were received by UV/Vis spectrophotometer in the range (200-400) nm before and after thermal treatment. To determine the effects of thermal treatments on the optical characteristics of the PVC, absorption coefficient, refractive index, and the optical energy gap were displayed at different concentrations.

III.Molecular weight measurement:

Viscometer method was used to determine the molecular weight of polymer. The intrinsic viscosity [η] can be determined by using the Mark Houwink relation [2].

$$[\eta] = K(M_v)^{\alpha} \qquad ---- (1)$$

Where K and α explain constants depends on the polymer-solvent interactions at a certain temperature [3]. We used Ostwald U-tube viscometer to identify the intrinsic viscosity of the polymer. Relative viscosity (η_{rel}) and Specific viscosity (η_{sp}) were calculated by:- .

$$\eta_{rel} = t/ t_o \qquad ---- (2)$$

$$\eta_{sp} = \eta_{rel} - 1 \qquad ----- (3)$$

Where **t, t$_o$** represent the flow time of the polymer and the flow time of the solvent which is used in this work. The intrinsic viscosity can be defined: [4].

$$|\eta| = \left(\sqrt{2}/c\right)(\eta_{sp} - \ln\eta_{rel})^{1/2} \qquad --- (6)$$

where **c** represents the concentration of polymer solution. We found from calculations that the molecular weight value of polyvinyl chloride in the tetrahydrofuran solvent was equal to 9.3 x10^4 g/mol. [5]

3.Results and Discussion

I.Absorbance measurements (Thermal Treatment and concentration):

(We studied the effect of thermal behavior of poly (vinyl chloride) with or without plasticizer solutions over the temperature range 20-50˚C. Electronic absorption spectra were recorded over the range (200-400) nm under different concentrations (1x10^{-3}, 8x10^{-4}, 6.5x10^{-4}, 5x10^{-4} and 3x10^{-4}) [M]. Figure (2) shows the effect of the thermal treatment on the absorbance spectra after two hours, which led to an increase of the maximum intensity bands.The UV spectra shifted slightly towards large wavelength with increasing the temperature, especially for the sample with high concentration 1x10^{-3}M, the intensity of the second band 285nm was more sensitive to the temperature change.

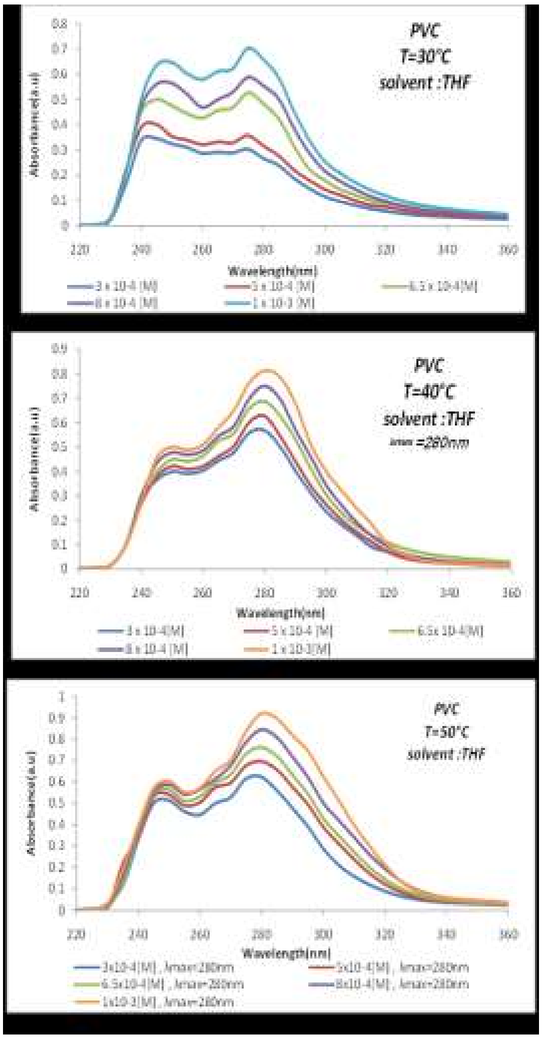

Figure (2) Absorbance spectra of pvc solutions at different temperatures

The dependence of absorption intensity upon the polymer concentration at different temperatures can be clearly seen in figure (3). The absorption is directly proportional to the polymer concentration. The absorption spectrum of the samples consists of two bands centered at 245 nm and 285nm which are attributed to $\pi \rightarrow \pi$ *electronic transition. The absorbance of the dissolved sample depends on the molar concentration c, optical path length l (in cm) and on the molar absorptivity (ϵ) [6]:

$$A_{\lambda} = \epsilon\, cl \ldots\ldots (7)$$

$$\text{if } l = 1cm$$

$$\text{then } A_{\lambda} = \epsilon\, c \ldots\ldots (8)$$

We observed from the last equation that absorption at a certain wavelength is proportional to the molar concentration of the polymer.

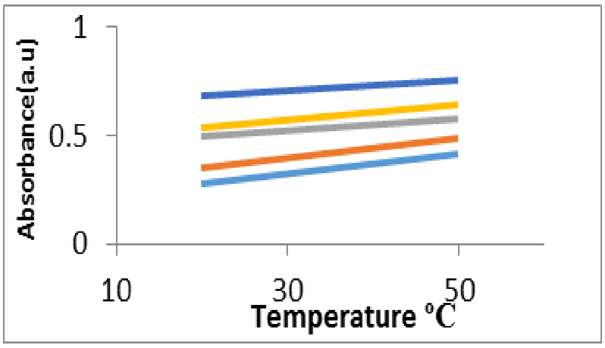

Figure (3) linear relation between absorbance and temperatures

Figure (4) gives an idea of the nature of the relationship between the intensity of absorption of polymer and its concentration.

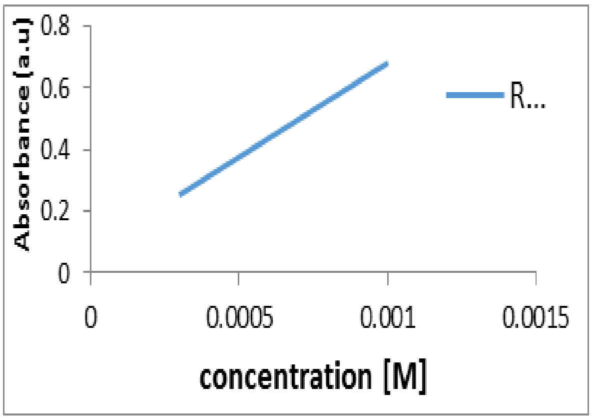

Figure (4) The relation between absorbance intensity and concentration at room temperature.

4.Refractive Index Measurements

The variations of refractive indices with temperature are evaluated at different concentrations. Figure (5) shows the refractive index as a function of temperature. It is clear that the refractive index of the polymer decreases with increasing temperature, and the results showed linear relationship between refractive index and temperature of the polymer within the ranges of temperature, this behavior is due to the temperature effect to activate of the kinetic atoms of the polymer. Results showed that there is a good agreement with the finding Sultanova and et al [7], Michel and et al [8].

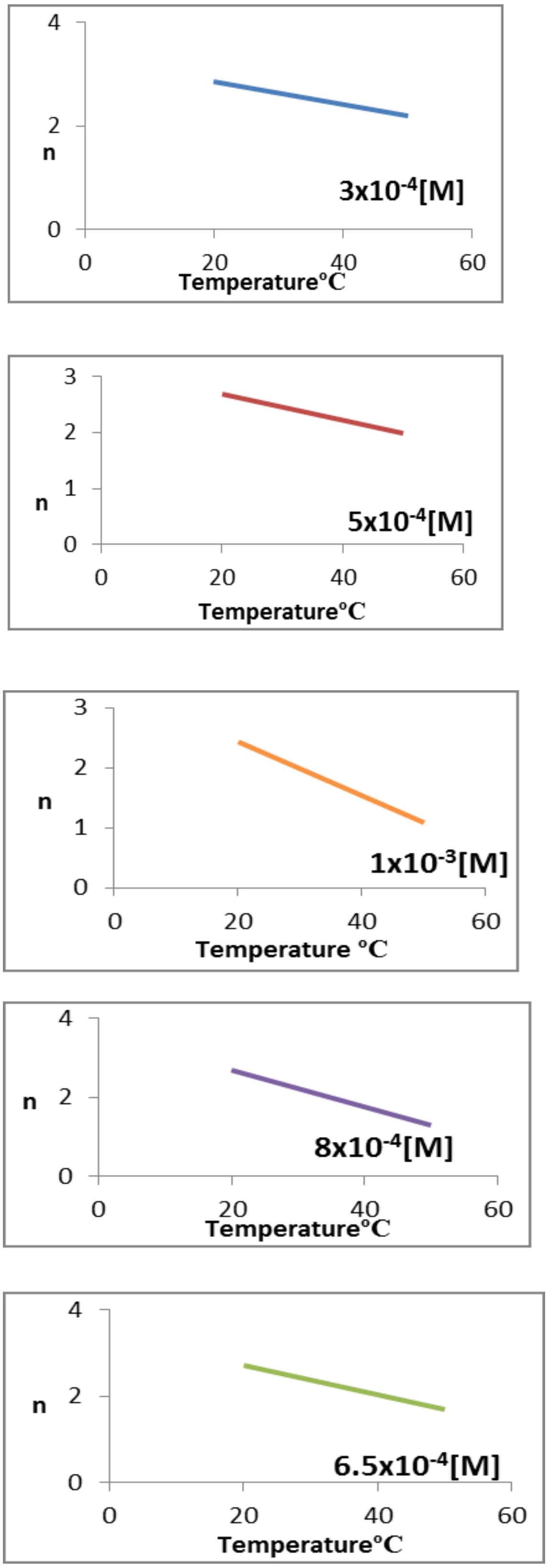

Figure (5) The variation of refractive index and temperature at different concentrations

5.Energy Band Gap Calculations

Optical energy gap is the minimum energy between the lowest level of the construction band and the highest level of the valance, which depends on certain circumstances such as temperature, rate of impurity, and defect of the material. Any change in such parameters causes blue or red shift in the absorption spectra. The relation between (αhυ) 2 versus hυ was shown in Figure (6), the value of the energy gap of poly vinyl chloride is decreasing as concentration and temperature increased as indicated in table(1)

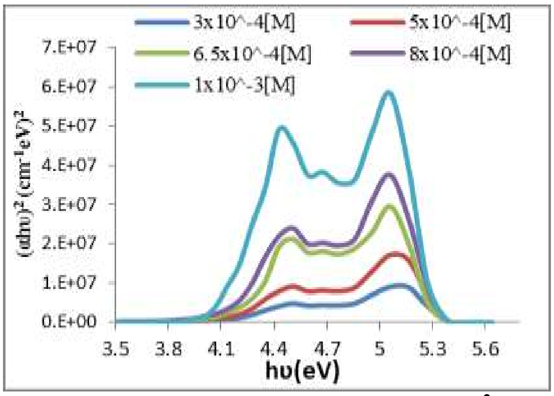

Figure (6) The relationship between (∝hν) ^{2} and (hν) at different concentrations.

Table (1) Energy gap values of poly vinyl chloride solution at different temperatures.

Concentration [M]	Eg at R.T	Eg at 30° C	Eg at 40° C	Eg at 50° C
$3x10^{-4}$	4.3eV	4.25 eV	4.19 eV	4.15eV
$5x10^{-4}$	4.26 eV	4.2 eV	4.14 eV	4.09 eV
$6.5x10^{-4}$	4.23 eV	4.19 eV	4.1 eV	4.05 eV
$8x10^{-4}$	4.19 eV	4.14 eV	4.09 eV	4 eV
$1x10^{-3}$	4.18 eV	4.1 eV	4.04 eV	3.9 eV

6.Absorption Coefficient Measurements

Absorption coefficient is the most important optical constant for photodetectors. It is the amount of penetration of the light at a certain wavelength before they are absorbed by the material. The study of absorption coefficient of polymer PVC solutions gives notes about the validity of the absorption in solutions. Figure (7) shows the relationship between the absorption coefficient and photon energy of the PVC solutions. The variation of the absorption coefficient is seen from high energy to low energy. It means that the probability of electron transition is little, because the energy is not sufficient to move the electron from the valence band to the conduction band (hυ < Eg). The absorption of incident light is characterized by the relation. [10-12]

$$I = I_0 exp(-\alpha x) \quad \ldots\ldots (8)$$

$$or\ \alpha = \frac{1}{x}\ lin(\frac{I_0}{I}) \quad \ldots\ldots (9)$$

Where I_0 and I are the intensity of incident and absorbed light during a certain time respectively. α is the absorption coefficient measured in(1/length). Figure(7)(a)-(c), represents the experimental data of the absorption coefficient as a function of photon energy $(h\vartheta)$ at different temperatures. it is Clearly from the results that α is direct proportional to the concentration of the polymer at different temperatures.

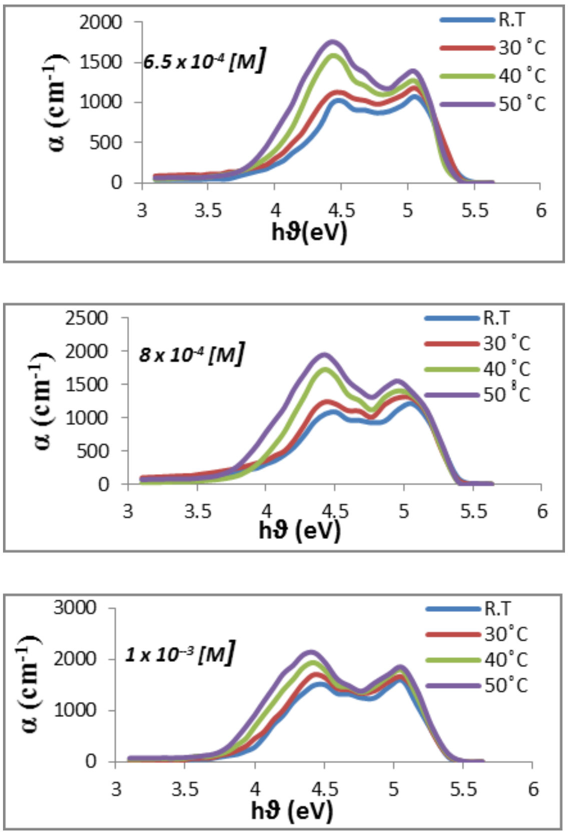

Figure (7) Values of absorption coefficient of the samples for different energies.

Conclusions:

1.The absorption spectrum of Polyvinyl chloride solutions was affected by increasing concentration, the maximum absorption intensity in solution was at wavelength (240-270)nm at room temperature .

2.The absorption peak position of polyvinyl chloride has a small red shifted about 5 nm by increasing temperature.

3.The absorption coefficient at room temperature was found to increase as increasing in concentration.

4.The refractive index at room temperature was found to increase as increasing in concentration for solution

5.The energy gap of polyvinyl chloride in solution was reduced by increasing the concentration and temperatures of polyvinyl chloride.

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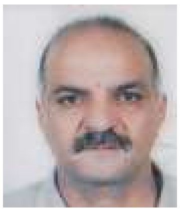

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