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Influence of Diethyl Phthalate (DEP) on Fluorescence Emission Quenching of Poly Vinyl Chloride (PVC) in Solid Films

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Abstract

In this study, the effects of temperature on the absorption and emission spectra of polyvinyl chloride films were investigated in the presence of diethyl phthalate as a quencher. In this paper, diethyl phthalate (DEP) was used as a quencher at different concentrations to study its effect on the behavior of absorption and emission spectra in the wavelength range from 200 to 350 nm. The films have been treated thermally at 25, 40, 50 and 60^{o} C. The results showed that the absorption spectrum contains two absorption bands for all samples. The first absorption band appeared in the range of 200 to 220 nm. The maximum absorption band was shifted towards red wavelengths depending on the concentration and temperature.

The second absorption band appeared from 260 to 300 nm was weak, broad and unaffected by a concentration while showing a simple response to temperature without displacement in the maximum absorption ($\lambda_{max.}$). The changes in absorbance as a function of quencher concentration at room temperature (25^{o}C) are illustrated.

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The spectra do not show sharp differences by changing the concentration of the quencher. The fluorescence emission spectra showed a strong peak at 372 nm. The effect of quencher on the quantum efficiency of the fluorescence emission using the Stern-Volmer equation was discussed.

Keywords: absorption, fluorescence emission, plasticizers, poly vinyl chloride, diethyl Phthalate.

تأثير ثنائي إيثيل فثاليت (DEP) على كبت انبعاث الفلورة للبولي فينيل كلورايد (PVC) في حالة الاغشية الصلبة

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الخلاصة

في هذه الدراسة ، تم فحص تأثير درجة الحرارة على امتصاص وانبعاث أطياف أغشية كلوريد البوليفينيل في وجود المخمد ثنائي إيثيل فثاليت. استخدمنا ثنائي إيثيل الفثاليت (DEP) بتركيزات مختلفة لدراسة تأثيره على سلوك أطياف الامتصاص والانبعاثات في نطاق الطول الموجي من 200 إلى 350 نانومتر. تمت معالجة ألاغشية الصلبة حرارياً عند 25 و 40 و 50 و 60 درجة سيليزية .أظهرت النتائج أن طيف الامتصاص يحتوي على نطاقين من الامتصاص لجميع العينات. حزمة ألامتصاص الأول في حدود 200 إلى 220 نانومتر. تم إزاحة حزمة الامتصاص العظمى نحو الأطوال الموجية الحمراء حسب التركيز ودرجة الحرارة. ظهرت حزمة الامتصاص الثاني من 260 إلى 300 نانومتر وهي حزمة ضعيفة وعريضة وغير متأثرة بالتركيز بينما تظهر استجابة بسيطة لدرجة الحرارة دون ملاحظة اي إزاحة في حزمة الامتصاص العظمى (λ_{max}.).تم توضيح التغيرات في الامتصاص كدالة لتركيز الكابت في درجة حرارة الغرفة (25 درجة سيليزية). لم تظهر الاطياف اختلافات حادة عند تغيير تركيز المخمد. أظهرت أطياف أنبعاث الفلورة حزمة قوية عند الطول الموجي 372 نانومتر وتم مناقشة تأثيرالكابت على الكفاءة الكمية لانبعاث الفلورة باستخدام معادلة ستيرن – فولمر.

الكلمات المفتاحية : الامتصاص، انبعاث الفلورة، الملدنات، بولي فينيل كلوريد، ثنائي إيثيل فثاليت.

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Introduction

Fluorescence quenching is one of the most powerful techniques for obtaining information about energy transfer in macromolecules systems [1]. Generally, the quantum yield of fluorescence emission is described by two main processes. The radiative and non-radiative which involve all possible pathways of the fluorescence deactivation such as internal conversion, intersystem crossing, or other intra- and intermolecular quenching mechanisms. The mechanism of the quenching process includes energy transfer between fluorophore molecules (donor) in an electronically excited state to an adjacent quencher molecule (acceptor) [2-4]. When fluorophore molecule becomes excited, emits fluorescence, and a quencher will reduce that fluorescence by energy transfer from an excited species to another molecule [5]. Fluorescence quenching is observed because of the interaction between the fluorophore-quencher molecules and this quenching is directly dependent on the extent to which they can approach each other [6]. Quenching process happens in two ways either static or dynamic quenching [7]. Dynamic quenching or collisional quenching is a dominant process that occurs within molecular distances when the quencher diffuses to the fluorophore during the lifetime of the electronically excited state of the fluorophore molecule to cause a decrease in fluorescence intensity [8-11]. After collisions, the excited molecule returns to the ground state without emission of a photon. The effectiveness of dynamic quenching is limited due to the lifetime of the excited state of the fluorophore molecules and the quencher concentration [12]. Static quenching is non-fluorescent complex that occurs in the ground state between the quencher and the fluorophore molecule. Static quenching efficiency depends on the affinity of the fluorophore and quencher for each other.

The main purpose of this article is to study the effects of the quencher with temperature on the quantum efficiency of the fluorescence emission by using Stern-Volmer equation, which can be described as follows [13,14].

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$$\varphi_F = \frac{k_f}{K_f + K_{IC} + K_{ISC} + K_Q[Q]} = \frac{k_f}{\frac{1}{t_0} + k_Q[Q]} \quad (1)$$

in the presence of quencher

$$\varphi_{Fo} = k_f t_0 \quad (2)$$

in the absence of quencher

Where K_f, K_{IC}, K_{ISC} and K_Q are the rate constants for fluorescence, internal conversion, intersystem crossing, and bimolecular quenching constant processes respectively, furthermore [Q] represents the concentration of the quenching molecule in the ground state.

By dividing equations 1 and 2

$$\frac{\varphi_o}{\varphi} = \frac{I_o}{I} = \frac{k_f t_0}{\frac{k_f}{\frac{1}{t_0} + k_Q[Q]}} = k_f t_0 * \left(\frac{1 + k_Q t_0[Q]}{k_f t_0}\right) = 1 + k_Q t_0[Q] \quad (3)$$

$$\frac{\varphi_o}{\varphi} = \frac{I_o}{I} = 1 + k_{sv}[Q] \quad (4)$$

Stern–Volmer relation

Where KSV (= $k_Q \tau_o$) is the Stern-Volmer quenching constant, which tells about the efficiency of quenching [15]. KQ is the quenching rate constant *and* to is the excited-state lifetime of the fluorophore in the absence of quencher. φ_o and I_o are quantum yields and the fluorescence intensity in the absence of quencher respectively. According to equation (4), (Io / I) is the ratio of the fluorescence quantum efficiencies in the absence and presence of the quencher. When the intensity of the fluorescence emission is observed as a function of concentration of quencher a plot of (Io/I) vs. [Q] is a linear relationship according to Stern-Volmer relation. The slope shows the efficiency of the quenching of the fluorophore excited state [16]. The general kinetic scheme for photophysical and quenching processes in the polymer are [17, 18]:

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$1M + h\upsilon \xrightarrow{I_a} 1M\times$ Energy absorption

$1M\times \xrightarrow{K_F} 1M + h\upsilon_F$ Fluorescence

$1M\times \xrightarrow{K_{IC}} 1M$ Internal conversion

$1M\times \xrightarrow{K_{ISC}} 3M\times$ Intersystem crossing

$3M\times \xrightarrow{K_{FP}} 1M + h\upsilon_{FP}$ Phosphorescence

$3M\times \xrightarrow{K_{IC}} 1M$ Internal conversion

$1M\times + 1M \rightleftharpoons 1M + 1M\times$ Singlet migration

$1M\times + 1M \xrightarrow{K_{DM}} 1D\times$ Singlet excimer formation in solution

In solid films:

$M\times + (M\text{--------}M) \xrightarrow{K_{DM}} 1D\times$ Singlet excimer formation

$1D\times \xrightarrow{K_{FD}} 1M + 1M + h\upsilon_{FD}$ Excimer formation

$1D\times \xrightarrow{K_{DM}} 1M\times + 1M$ Excimer dissociation

$1D\times \xrightarrow{K_{ISC}} 3D\times$ Intersystem crossing

$1D\times \rightarrow 1M\times + 1M$ Dissociation internal conversion

The rate constants are presented according to particular processes as shown in Table 1

Table 1: Rate constants presented according to particular processes

Rate constants	Description
KF	Fluorescence Emission
KIC	Internal conversion
KISC	Intersystem crossing
KFP	Phosphorescence
KFD	Excimer formation
KDM	Excimer dissociation

Experimental

The molecular weight of the polymer was calculated by using the Mark-Houwink equation [19, 20]**:**

$$[\eta] = kM^{a} \quad (5)$$

Where M is average molecular weight, K and a are the Mark-Houwink constants. There is a specific set of Mark-Houwink constants for every polymer-solvent combination. The experimental calculations showed that the molecular weight of the polymer was 9.3 × 104 g mol-1. A stock solution of the polymer (1× 10-3 M) was prepared by dissolving the appropriate amount of PVC into 20 mL of Tetrahydrofuran as a solvent. The solvent did not find any absorption band in the range of 200-350 nm. The thin films of pure polymer were prepared by solution casting in Tetrahydrofuran solvent (THF). The PVC-DEP films at different concentrations of plasticizer were prepared by solution casting technique in THF solvent. The thin films were left for six hours for the slow evaporation of the solvent at room temperature to ensure that solid films are free of solvent residues. Optical absorption spectra for the samples were recorded in the range 200-350 nm using spectrophotometer device by Lasany company model LI-295. Fluorescence spectrophotometer model RF-5301PC was used to measure the fluorescence spectra. Fluorescent spectra of solid samples were made by supporting the rigid test piece at an angle of 45° to the incident radiation. The quencher diethyl terephthalate used

in this work has a high purity (99.8%) and it has no absorption band in the range of study wavelengths.

Results and discussion

In this project, the thermal effects on the absorption and fluorescence emission spectra of the polymer PVC were studied after the addition of different concentrations of the quencher DEP. Figure 1-A illustrates the behavior of the absorption spectra of the polymer using different concentrations at 25°C. Two absorption bands were detected; the first band exists at the range from 200 - 210 nm attributed to the transition $\pi - \pi^*$, which is shifted toward the red wavelengths with increasing the concentration of the polymer. It is clear from the figure that at the high molar concentration the maximum absorption band was shifted to 212 nm. Figure 1-B shows the linear dependence of absorbance on the concentration of the polymer according to Lambert Bear's law. The second absorption band appears weak and broad band in the range 260-290 nm which is attributed to the transition $n - \pi^*$. The intensities of this peak vary slightly with increasing concentration of the polymer.

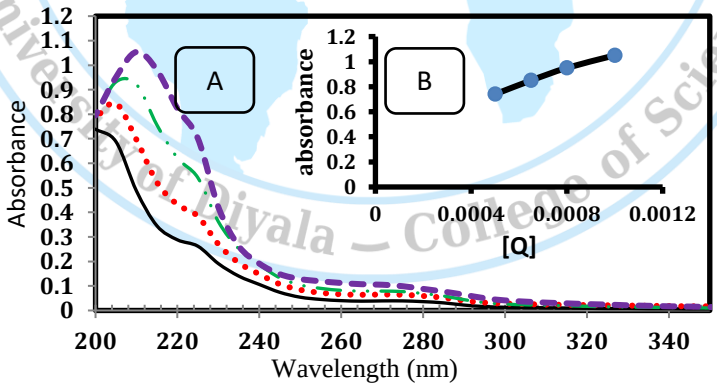

Figure 1: (a) Absorption spectra of PVC solid film at 25° C with 5×10-4M, 6.5×10-4M, 8×10-4M, 1×10-3 M. (b) Relationship between absorbance and polymer concentration at 25°C

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Figures 2 and 3 show the fluctuation of absorption spectra of all samples investigated as a function of concentration at 40 and 50°C. Figure 2 indicates that the absorption spectra at temperature 40°C have a behavior that is not very different from the first situation. Figure 3 indicates that the absorption spectra at 50°C have become wider with a significant increase in the intensity of adsorption, particularly at high concentrations. In addition, the maximum absorption beam is displaced to appear at 215 nm for high concentrations.

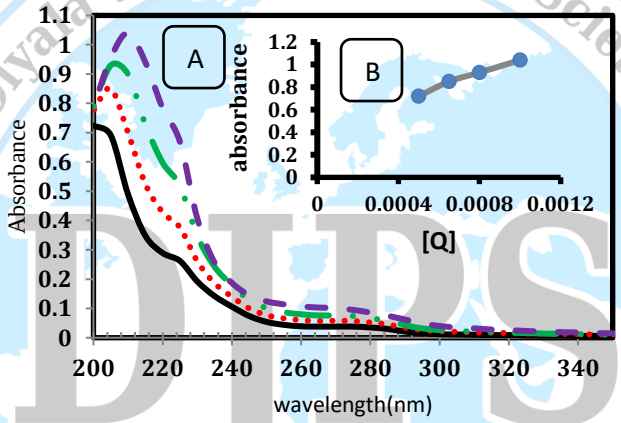

Figure 2: (a)Absorption spectrum of PVC solid film at 40oC with 5×10-4M, 6.5×10-4M, 8×10-4M, 1×10-3M. (b) relationship between absorbance and polymer concentration at 40°C

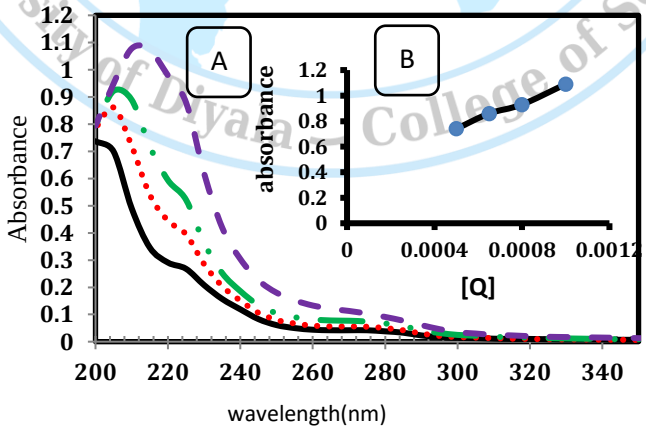

Figure 3: (a) Absorption spectrum of PVC solid film at 50oC 5×10-4M, 6.5×10- 4 M,8×10-4M,1×10-3M. (b) Relationship between absorbance and polymer concentration at 50°C

From figure 4, it can be seen that the absorption band becomes wider and the spectral peak of the maximum absorption was considerably shifted to the red shift at 60°C. When examining the behavior of the absorption spectra of all samples, the results showed that the effects of temperature were more obvious than that of concentration. Table 2 summarizes the differences in absorption ranges observed when the temperature changes

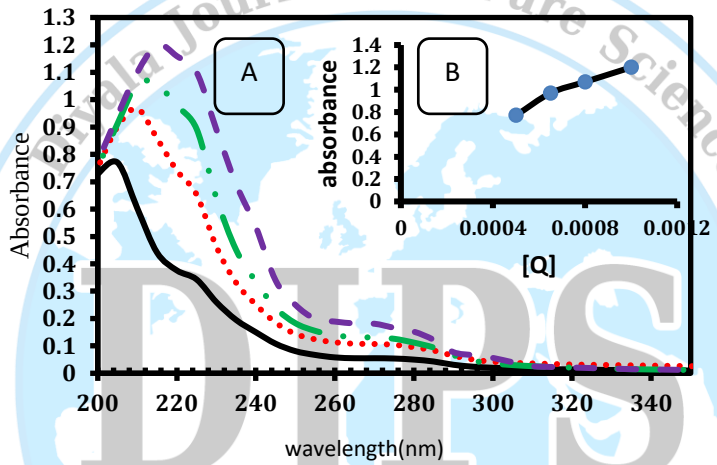

Figure 4: A(a) Absorption spectrum of PVC solid film at 60oC with 5×10-4M, 6.5×10-4M,8×10-4M,1×10-3M. (b) Relationship between absorbance and polymer concentration at 60°C.

Table 2: Variation of maximum absorption bands as a function of temperature

Concentration [M]	Temperature			
	25°C	40°C	50°C	60°C
1×10^{-3}	212nm	212nm	215nm	218nm
8×10^{-4}	208nm	208nm	208nm	216nm
6.5×10^{-4}	206nm	207nm	206nm	212nm
5×10^{-4}	200nm	200nm	200nm	206nm

Figure 5 shows the dependence of the absorption band on the temperature at different concentrations of the polymer. The peak of the absorbance band (λmax.) was shown to be affected linearly when the temperature of the polymer films was increased especially at high

concentrations. All samples showed no difference in absorption intensity values between 25°C and 40°C.

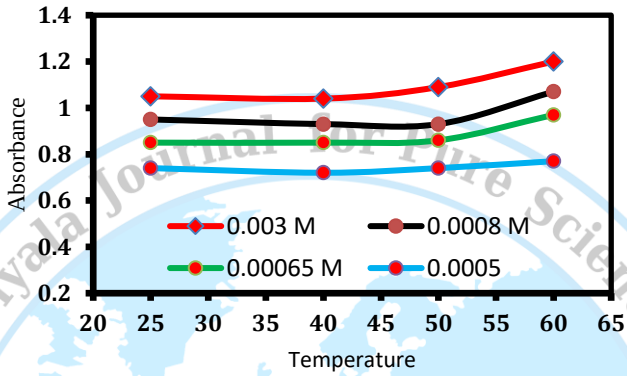

Figure 5: Absorbance and temperature °C relationship at different concentrations of PVC

The effects of temperature and concentration on the optical properties of the PVC solutions were studied [21]. The obtained results showed that the energy gap of the PVC solutions decreased with increased concentration and temperature. In this work, the effects of plasticizer diethyl phthalate (DEP) as a quencher on the absorption and fluorescence spectra of the polymer solid films are examined. Generally, plasticizers are organic liquids or solids which are added to a polymer to increase its flexibility, decreasing tensile strength and lowering the glass transition temperature [22-24]. However, the main point in all of these is that plasticizers reduce polymer-polymer chain attractions, and provide greater mobility to the polymeric chains. In this paper, absorption spectra of PVC in solid films as a function of quencher concentration [Q] are taken at 25°C as shown in figure 6. Except for the difference in the absorption intensity, the figure does not show sharp differences between the absorption spectra by changing the concentration of the quencher. The main reason for this result is due to the interaction between the polymer and quencher by charge transfer process [25].

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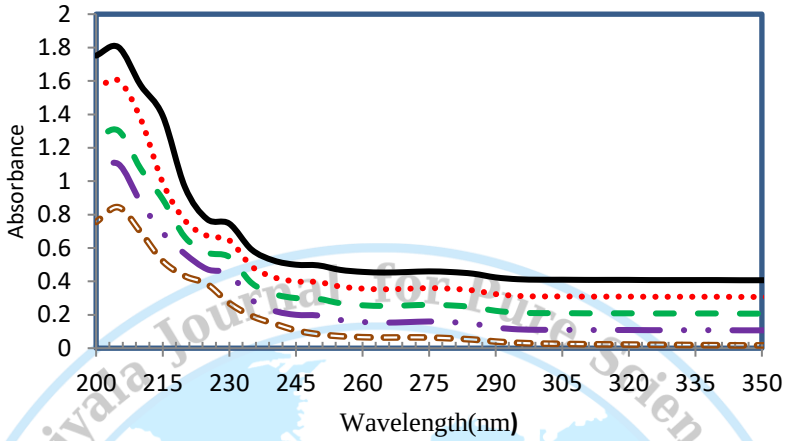

Figure 6: The absorption spectrum of plasticized PVC film at R.T 6.5×10-4 M (PVC) +0M (DEP), 6.5×10-4M (PVC)+2×10-5M (DEP) 6.5×10-4 M(PVC)+4×10-5M (DEP),6.5×10-4M (PVC)+6×10-5M (DEP), 6.5×10-4 M (PVC) + 8×10-5M (DEP)

Figure 7 shows fluorescence emission spectra of PVC films with varying polymer concentrations at room temperature. Obviously, the spectrum has a significant emission band at 372 nm which is due to the first excited state of the monomer where excitation was at 210 nm. An increase in the concentration of the polymer will reduce the intensity of the fluorescence monomer due to the self-absorption emission without any shift of emission maximum during quenching processes .

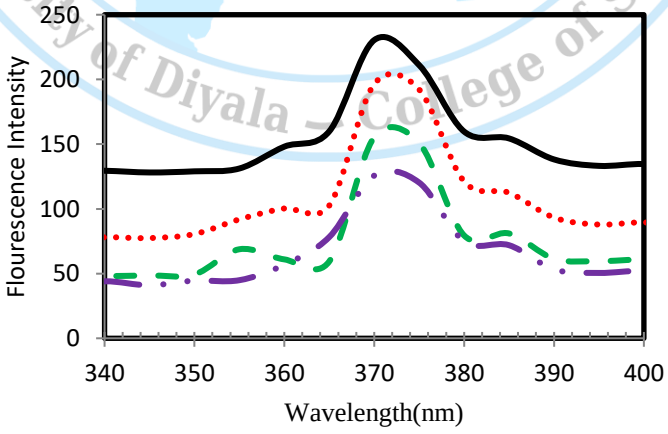

Figure 7: The fluorescence spectrum of PVC in R. T. (1)5×10-4M, (2)6.5×10-4 M, (3)8×10-4M, (4)1×10-3M

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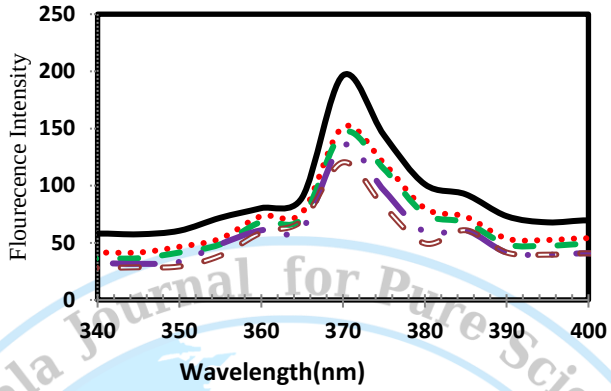

Figure 8: Fluorescence quenching of PVC / DEP at 25oC 6.5×10-4 M (PVC) +0M (DEP), 6.5×10-4M(PVC)+2×10-5M(DEP) 6.5×10-4 M(PVC)+4×10-5M(DEP),6.5×10-4M(PVC)+6×10-5M(DEP) 6.5×10-4 M(PVC) + 8×10-5M(DEP)

In this paper, the effects of adding DEP on the fluorescence emission spectra at 25^{o}C are given by preparing a series of solid films containing a fixed concentration of the polymer PVC to the different concentrations of the quencher [DEP]. The quenching of fluorescence emission spectra of 6.5×10^{-4}M polyvinylchloride (PVC) by adding Diethyl Phthalate DEP from 2×10^{-5}M to 8×10^{-5}M solid films as shown in figure 8. The maximum emission intensity band at 370 nm is found to be quenched by mixing of DEP. Mixing of 2×10^{-5}M of DEP caused 23.6% quenching of polymer emission intensity. While the quenching rate reaches 40% when the concentration of DEP increases to 2×10^{-8}M.

The Stern–Volmer relationship (eq.4), between the ratio of the fluorescence intensity with and without the quencher, was used to examine the quenching efficiencies as shown in figure 9. The linearity of Stern -Volmer plot indicates that the dynamic quenching is responsible for the process of the quenching in the system. The value of the Ksv obtained from the slope is equal 8333.33 M-1 indicating an interaction between the polymer molecules and the quencher molecule.

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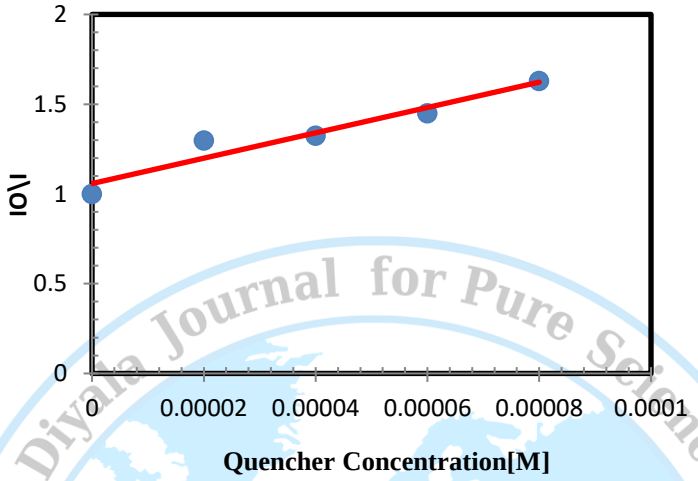

Figure 9: Stern-Volmer plot for fluorescence quenching of PVC by DEP in different concentrations at 25°C

Conclusions

From the data of absorption and emission spectra for plasticized and not- plasticized PVC solid films, the following notes are marked:

1. The absorption characteristics of PVC thin films prepared on quartz slides from tetrahydrofuran solutions by casting technique are sensitive to their concentrations. The absorption intensity bands of PVC solid films increases with increasing the polymer concentration with a significant displacement at the position of the maximum absorption peaks towards the red wavelengths.
2. The results indicated that the first absorption band is clearly affected by temperature and concentration more than the second absorption band
3. Quenching tests of the fluorescence emission for the PVC thin films were executed at room temperature. The fluorescence intensities decreased with increasing the concentration of DEP without any shift in the maximum fluorescence emission. The quenching efficiencies were possible because donor energy was effectively available over the polymer chain and the DEP molecules were able to quench the excited polymer by the energy transfer process

where a part of energy occurs as heat (non-radiative process) and part is emitted via fluorescence emission from excited polymer molecules. The quantitative measurement (ksv) of fluorescence quenching was calculated from the slope of a plot of (Io/I) against the quencher concentration [Q] and this constant was equal to 8333.33M-1

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