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## Synthesis and Study of Optical Properties for (4-Acetyl aminophenol –[2-(4-Azo)]-4-Aminodiphenyl Sulfonate) (AAS):Polyvinylpyrrolidone (PVP) by Film Preparation on Quartz Substrate

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### Abstract

New azo dye was prepared from 4,4-diaminodiphenyl sulfonate with 4-Acetyl aminophenol. The dye prepared by fox method, the azo dye were identified by IR–spectrophotometer and (CHN) analysis. Polyvinylpyrrolidone films of thickness  $32 \mu\text{m}$  was prepared onto quartz substrate. The optical constants of the film were investigated by spectrophotometric measurement. The refractive index, extinction coefficient and optical band gap ( $E_g$ ) are determined using the transmittance (T) and reflectance (R) in the spectra wavelength (340-700) nm.

**Keywords:** Optical azo dyes .

### Introduction:

Azo dye has received great attention due to its environmental stability, ease of preparation and its optical and electrical properties. Much work has been done on the molecular design, synthesis, and assembly of structures with desired properties [1-5]. The N=N group is called an azo or diimide functional group, and the R and R' groups of azo compounds are often aromatic or aliphatic. This helps to stabilize the N=N group by making it a part of an extended delocalized system. This also has the effect of making many azo compounds colored, as delocalized or conjugated systems often absorb visible frequencies. Due to its conjugated structure and richness in  $16\pi$  electrons azo dye received considerable

attention in many areas of modern chemistry and physics of the condensed matter owing to the electronic properties [6-7].

Optical tests giving transmittance and reflectance spectra provide the data to determine optical constants such as refractive index, extinction coefficient and dielectric constant [8]. It has been shown [9] that the analysis of optical absorption could provide useful information to the elucidation of electronic structure of material. Other analysis showed that optical absorption spectra could provide the necessary parameters to determine direct and indirect transition occurring in the band gaps of the materials [10]

The goal of the present work is the study of the optical properties of (4-Acetylaminophenol–[2-(4-Azo)]-4-

Aminodiphenyl sulfonate)(AAS): Polyvinylpyrrolidone (PVP) films in the wavelength range (340-700) nm.

## Experimental

### Chemical Material

Methanol, acetone, dimethylsulfoxide, 4,4-Diaminodiphenyl sulfonate, sodium hydroxide from (Fluka Co.), 4-Acetylaminophenol, sodium nitrite, hydrochloric acid from (Merck Co.), were purified before using [11]. IR spectrum were recorded on a Buck Scientific Model 500. IR spectrophotometer using a KBr disc in the range  $(500-4000)cm^{-1}$ . The melting point of the compound were determined with a 9300 Model – Electro thermal melting point. The spectrum of absorbance

(A), transmittance (T) and reflectance (R) of (AAS): PVP of the films were recorded by CE-3055 PC dual beam Reflectophotometer in the wavelength (340-700) nm. IR, UV-Visible spectrophotometer and melting point was performed by Chemistry Department – Education College – Basrah University. Elemental analysis (CHN) of the compounds were determined with Euro Vector EA 3000A Italy was performed by al-bayt University.

### Method

#### A- Synthesis of the Azo Dyes

The proposed azo dyes were prepared by a method similar to that described by Fox [12]. Step (1) (0.006mole, 1.4899g) of 4,4-Diaminodiphenyl sulfonate was dissolved in 2ml of concentration. HCl and then 10ml of D.water was added, the mixture was stirred and kept in ice bath. 0.456g of  $NaNO_2$  was dissolved in about 5ml of distilled water and kept in ice bath. Diazonium salt was prepared by adding sodium nitrite solution. In step (2) dropwise to the cold solution of amine in the step (1) with stirring and keeping the temperature  $(0-5) ^\circ C$ . Coupler was prepared by dissolving (0.006mole, 1.4355g) of 4-

Acetylaminophenol in 25% sodium hydroxide solution and keeping in ice bath. The diazonium salt was added drop wise to the couplers with constant stirring, keeping the temperature below  $5^\circ C$ ; the dyes were neutralized with dilute hydrochloric acid solution. The product dye was re-crystallized from acetone the purity of the azo dye is yellow and the yield is 2.266 g (92%) with melting point of  $272 ^\circ C$ . Azo dye have been characterized by IR spectra. The structure of the azo dye is shown in Figure ( 1).

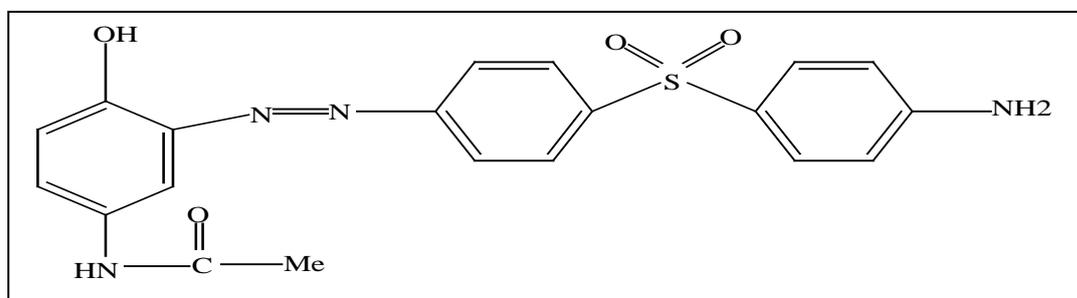


Figure (1): The chemical of structure of the prepared azo dye

### B- Film preparation

The azo dye polymer film was prepared by dissolving 0.2 g azo dye was dissolved in 1 ml of DMSO and then diluted the solution to 20 ml of distilled water and 0.1 g PVP was dissolved in 20 ml of distilled water and then mixed the azo dye solution in the ratio of (1:1) V/ V. Then the mixture

was stirred at 70 C° for 1h, then the mixture was filtered by the filter paper of 0.2 μm. We attended the quartz and used spray method to cast film with thickness of 32 μm. Finally, the prepared film was heated from room temperature to 50 C° for 4 hrs to evaporate the solvent used.

### Result and Discussion

The azo dye was identified by IR spectroscopy in the range (500–4000) $cm^{-1}$  as KBr discs (Figure 2). The stretching vibration of the OH groups which appeared in the region of (3450-3460)  $cm^{-1}$ . The band shows broad appearance due to its relatively low frequency. It can be concluded that the (-OH) groups may form a hydrogen bond with nitrogen atom. Also azo dye show two absorption band (3430-3440)  $cm^{-1}$  which may be attributed to the  $\nu$  (-NH<sub>2</sub>) group, which overlap with the

stretching vibration of the OH groups. The band shows broad appearance due to its relatively low frequency.. The band corresponding to (-N=N-) stretching vibration usually lies around (1440)  $cm^{-1}$  [13], the (-C=C-) stretching vibration of the aromatic ring appeared at (1580-1600)  $cm^{-1}$ . Stretching vibration of the (-C-H-) aromatic appears at (3085)  $cm^{-1}$  [14,15] The all mentioned bands were shown in table (1).

**Table 1: IR, C.H.N data for azo dye compound**  
(br:broad,s:sharp,m:medium,w:weak)

Compound	Wave numbers ( $cm^{-1}$ )					Calculated (Found)(%)		
	$\nu$ O-H m	$\nu$ N-H br	$\nu$ C=C m	$\nu$ N=N s	$\nu$ C-H m	C	H	N
Azo dys	3450-3460	3430-3440	1600-1580	1440	3085	57.27 (57.23)	4.55 (4.34)	14.06 (13.98)

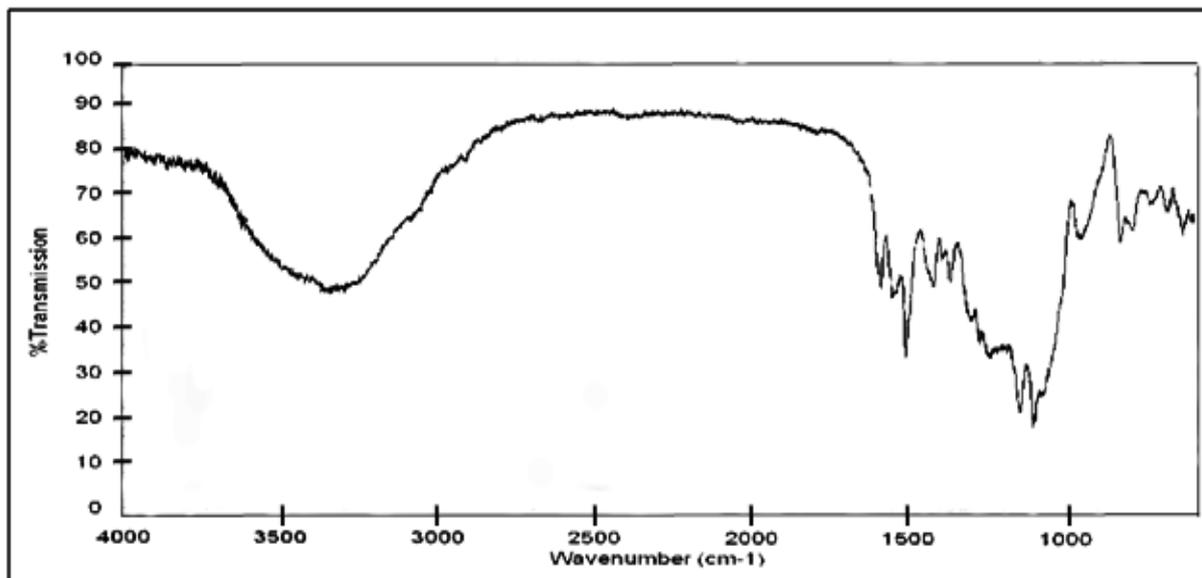


Figure ( 2): IR-spectrum of azo dye

The optical Absorption, Transmittance and Reflectance spectral is measured at (340–700)nm to the (AAS):PVP film prepared on the quartz substrates are depicted in the figure (3a) and (3b) . Figure (3a) show the absorbance(A) spectrum in the UV range, the maximum absorption observed at wavelength reign (340-380 nm) and then it decreases to zero at wavelength > 550 nm, the absorption edges of the films occurs at wavelength

region (500-550 nm) corresponding to photon energy (2.25-2.48 eV) ,while the figure (3b) show the transmittance spectrum increase in the wavelength range (340-550 nm) and the curves reach's saturation above 550 nm and the average transmittance of the films is 80% and show the reflectance spectrum and it has maximum value at region (340-355 nm) and its decreasing in the wavelength region (355-550 nm).

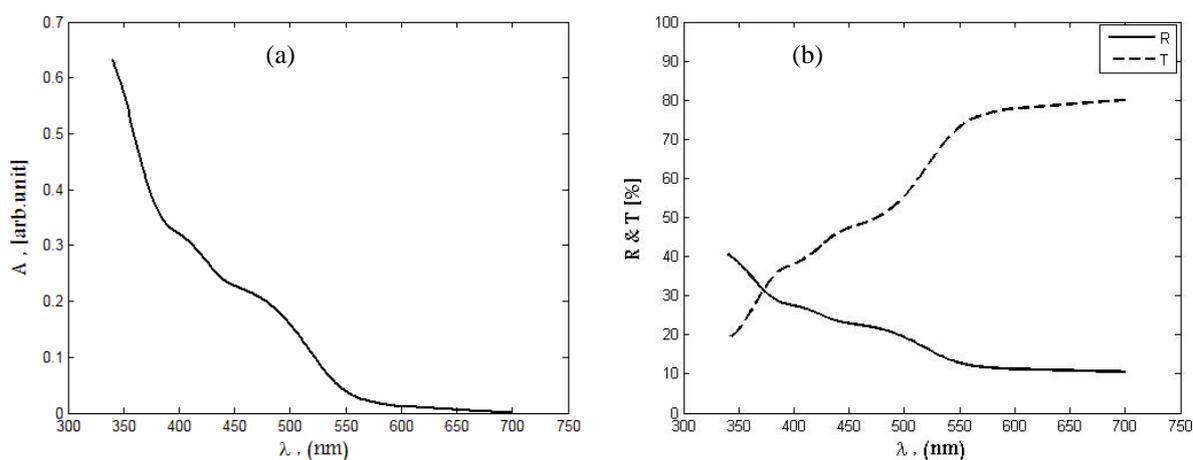
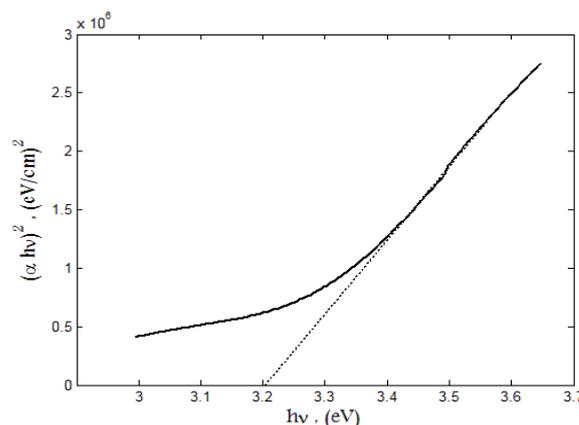
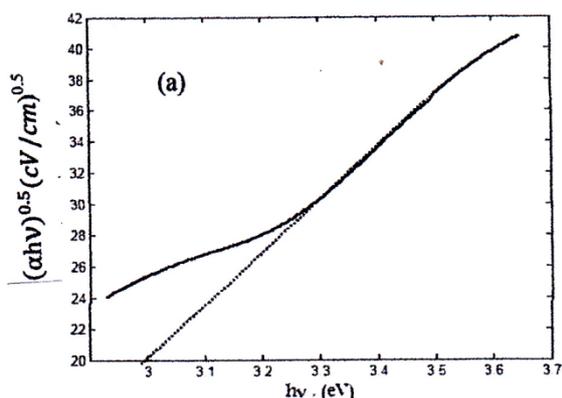


Figure.(3) (a) The optical absorbance spectra and (b) Transmittance and Reflectance spectral vs. wavelength of the (AAS):PVP film .

The optical band gap and the nature of optical transitions can be obtained from the dependence of the absorption coefficient on the photon energy. The optical absorption coefficient of the film was calculated from the relationship  $(\alpha = \frac{1}{d} \ln(\frac{I_0}{I_T}))$  [16] where  $(I_0)$  is the transmittance of the film and  $(d)$  is its thickness. The optical absorption edge was analyzed by the Tauc power law [17] for the direct optical transition according to the value of  $r$  as follows in equation (1).

$$\alpha h\nu = B(h\nu - E_g)^r \tag{1}$$

Where  $B$  is a constant (the edge width parameter representing the film quality),  $r$  is an index that characterizes the optical absorption process and is theoretically equal to 1/2 and 2, for the direct allowed and indirect allowed transitions respectively,  $E_g$  is the optical energy gap [18]. We plotted  $(\alpha h\nu)^{0.5}$  and  $(\alpha h\nu)^2$  as functions of photon energy, as shown in Figure (6a, 6b). Thus, the direct and indirect optical band gap was determined by the intercept on the energy by extrapolating the linear part of the curve to zero absorption value and we found values of direct and indirect energy gap ( $E_g^d, E_g^{ind}$ ) equal to 2.8, 3.2 respectively



Figure(6) (a) plot  $(\alpha h\nu)^{0.5}$  as a function to photon energy of the prepared film (b) Plot  $(\alpha h\nu)^2$  as a function to photon energy of the prepared film.

The refraction index of the (AAS): PVP films is given by the following equation (2) [16].

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\left(\frac{4R}{(1-R)^2} - k^2\right)} \tag{2}$$

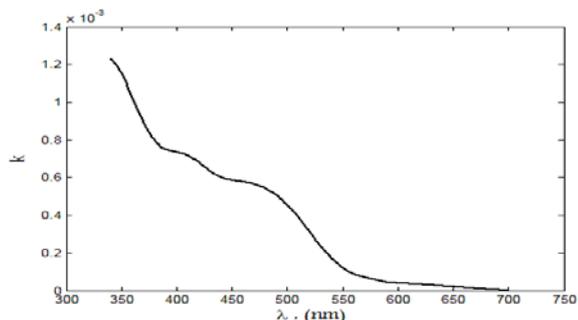


Figure (7) Plot of  $k$  as a function of wavelength for of the (AAS): PVP film

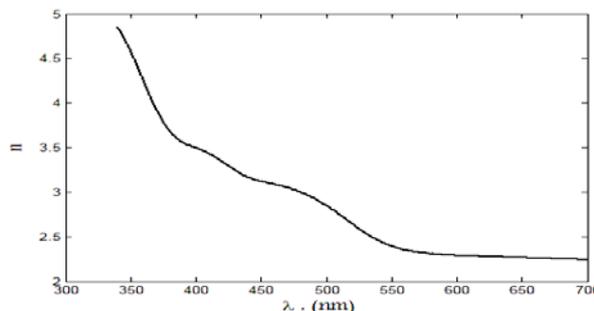


Figure (8) Refraction index (n) as a function of wavelength of the (AAS): PVP film

Where  $k = \frac{2\pi}{\lambda}$  is the extinction coefficient which show in the Figure (7) and we notes that the refractive index decreases with increasing the wavelength as shown in the Figure(8), the decrease in the value of refractive index is due to that some interactions takes place between photons and electrons. The refractive index changes

### Conclusions

The optical properties of the (AAS): PVP film prepared on the quartz substrate were investigated. The direct and indirect energy gaps of the film changes found to be 3.2 and 2.8 (eV) respectively for (AAS):

with the variation of the wavelength of the incident light beam due to these interactions, in another word, one is the optical loss caused by absorption and scattering, which decreases the amplitudes of the transmission intensity oscillations at shorter wavelengths.

PVP. The film prepared on quartz substrate exhibit strong interaction between photons and electron so this reflects high optical response.

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تحضير ودراسة الخصائص البصرية لفلم رقيق من (4- اسيتايل أمينو فينول - [2- (4- أزو) ]-4-امينو ثنائي فينايل سلفونيت (AAS) مع بولي فينايل بيروليدون (PVP) محضرة على قاعدة من الكوارتز

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### المستخلص

تم تحضير صبغة ازوية جديدة مشتقة من 4,4 ثنائي أمينو ثنائي فينايل سلفونيت مع 4- اسيتايل أمينو فينول بطريقة فوكس. شخّصت الصبغة المحضرة باستخدام طيف الأشعة تحت الحمراء والتحليل الدقيق للعناصر. درست الخصائص البصرية لفلم رقيق من هذه الصبغة الازوية مع بولي فينيل بيروليدون محضرة على قاعدة من الكوارتز . جميع الثوابت البصرية تم حسابها بالاعتماد على القياسات الطيفية للنفاذية الانعكاسية . النتائج العملية أظهرت أن هذه الصبغة ذات فجوة طاقة عالية نسبيا تقع ضمن حدود فجوات الطاقة للمواد شبه الموصلة.