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Synthesis, Characterization and Analytical Study of New Azo Dye

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ABSTRACT

The azo dye ((E)-4-((4-aminophenyl) diazenyl) naphthalen-1-ol) was prepared by diazotization and coupling reaction with 1-naphthol. The azo dye was diagnosed by FT-IR, 1H-NMR, mass spectra and visible spectrometry. The acid and basic properties were studied by the visible absorption spectra of the dye at different pH values and appearance of a clear isobestic point and a high absorption peak at the maximum wavelength (595nm) which is due to the absorption of the negative formula of the dye in the basic medium and an absorption peak at the wavelength (477nm) that is due to the absorption of the proton formula of the dye in the acidic medium. The ionization and protonation constants were calculated and the extent of the indicator within pH (7.4 - 9.4). The effect of the solvents on the visible absorption spectra of the dye was studied, and a clear red shift of the dye spectra was observed in the polar solvents.

1. Introduction

Dyes are complex unsaturated organic substances that absorb electromagnetic energy and give color to the visible region (~350-700 nm) [1]. In fact, a dye is a body capable of absorbing certain luminous radiations and then reflecting the complementary colors. The absorption of electromagnetic waves by the chromophore is due to the excitation of the electrons of a molecule [2]. Azo dyes represent the largest production volume of dye chemistry today, and their relative importance may even increase in the future. Out of more than 900,000 tons of dyes produced annually, 70% of them are belongs to azo group based dyes. These compounds are characterized by the functional group (-N=N-) uniting two symmetrical and/or asymmetrical identical or non-azo alkyl or aryl radicals [3]. Among the various dyes classifications, aromatic azo dyes are non-biodegradable, and more stable due to the electrons conjugated system which lead to the various shades in dyes. The molecular structure of dye possess both chromophores (responsible about the color), which is the azo group (-N=N-) and auxochromes (intensifies color), which is the electron withdrawing groups or donating such as (–NH2, -COOH, -SO3H, –OH, etc.) [4, 5]. The synthesis of most azo dyes involves converting a mono-aromatic amine to a diazonium salt compound. This process is known as "diazotization" followed by coupling this compound with one or more electron-rich nucleophiles groups such as phenol or an aromatic amine to produce the corresponding azo dye [6, 7]. Azo compounds have been extensively studied due to their different applications in various fields such as dying textile fibres, food, pesticidal, cosmetics, paper printing, biomedicinal studies, the textile

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industry the largest consumer of dyes [8]. It’s also widely used for various therapeutic applications, technological applications, optical signal processing, solar cells, photo-switches, biomedical sensors, in the field of electronics as storage components, holography, biological studies, as acid-base indicators [9-11], as inhibitors of corrosion [12]. The color changes occur due to the presence of different compensated groups on the aromatic rings, which leads to changes in the extent of the delocalization of electrons. Increase in the electrons conjugated system lead to shifts the max absorption to longer wave lengths (bathochromic) and it makes the absorbed light redder, while decrease in the electrons conjugated system lead to shifts the max absorption to shorter wave lengths (hypsochromic) and it makes the absorbed light less redder [2, 7].

2. Experimental

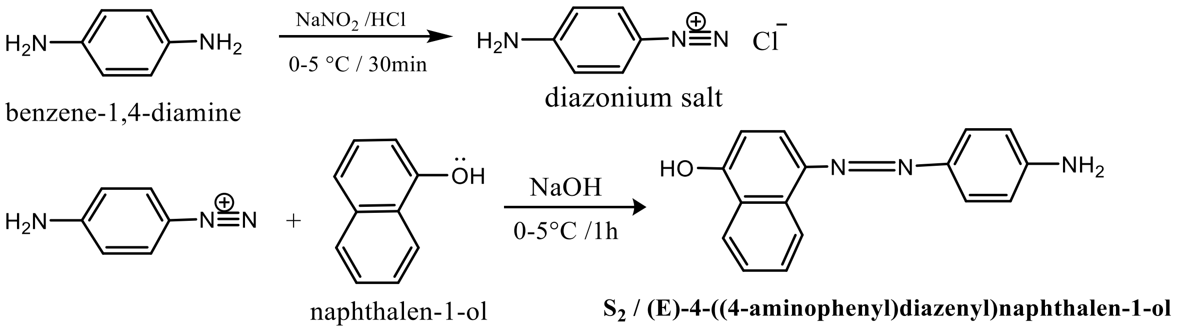
2.1. Used Devices

The melting point was determined on the M. P. apparatus (BüCHT 510), infrared spectrum was scored on FT-IR-8400S Shimadzu)using KBr disc(for the prepared azo dye, the pH measurements were scored by using pH meter (OAKTON) pH 2100 (pH /mV/ION/°F/°C meter with RS232C communication) and UV-Vis Absorption spectra were recorded by using 1800 UV.VIS-Spectrophotometer (Shimadzu, Japan) in the laboratories of the Department of Chemistry, College of Education for Pure Sciences, University of Basrah. 1H-NMR spectrum was recorded using a Bruker (400MHz) spectrometer, (DMSO-d6) was used as a solvent and TMS as an internal reference, As well as mass spectrum was recorded by using modems at 5975c VL MSD (EI) 70 eV at Tehran University (Iran).

2.2. Preparation of Azo Dye

The azo dye was prepared by dissolving (0.541 gm, 0.005 mol.) of 4-amino aniline in 10 ml of distilled water and 1.7 ml of concentrated hydrochloric acid, then cooled in an ice-bath at a temperature lower than 5°C. The sodium nitrite solution was added dropwise (0.38 gm, 0.005 mol. in 5 ml of distilled water) and left until complete formation of the diazonium salt after 30 min. The solution of diazonium salt was added to the coupling agent solution prepared by dissolving (0.005mol, 0.721 gm) of 1-naphthol in l00 ml of (0.005 mol, 1.5 gm) sodium hydroxide solution. The component was stirred for 1 hour and left in the refrigerator for the whole day. Then, diluted hydrochloric acid was added until it equalized the solution of the dye. The precipitate was collected and recrystallized from chloroform [5, 13]. Table 1 shows the physical characteristics of prepared azo dye.

2.3. The interaction equations:



2.4. Procedure:

- To determine the ionization and protonation constants and the isobestic point, a series of buffer solutions with different pH values for the pH range (1–12) were prepared using universal buffer solution and acetate buffer solution with addition of the dye with a concentration (1.25×10-4 M) for each different pH solutions. The absorption spectra of these solutions were recorded within a range of wavelengths (375-725) nm and a cell length of 1 cm. Using the buffer solution as a blank solution. By aid of the half-height method the constants were calculated [14].

- The solvent effect on the visible absorption spectra of dye (S2) was studied by preparing the dye solution with a concentration (1.25×10-4 M) in different polar solvents, including (acetone, chloroform, DMF, DMSO, ethanol, and methanol), and absorption spectra were recorded in the visible region with a range of wavelengths (375-725) nm using cell of 1cm length, at room temperature and using the solvent as a blank solution [15].

3. Results and Discussion

The table below shows the molecular formula, molecular weight, the Color and Melting Point (The physical properties) of the prepared azo dye.

Table 1. The physical properties of the prepared azo dye.

Symbol of Dyes	Molecular Formula	Molecular Weight (g/mol)	The Color	Melting Point (°C)
S_2	$C_{16}H_{13}N_3O$	263.30	Blue	287-288

FT-IR spectroscopy of the azo dye is show in Fig. 1. The broad and medium peak at position 3427 cm^{-1} belong to the stretching vibrations of O-H bond, the weak peak at position 3072 cm^{-1} belong to the stretching vibrations of C-H bond, the medium and weak peaks in the range 1502-1595 cm^{-1} belong to the Stretching vibrations of C=C bond, the weak peak at the position 1411 cm^{-1} belong to the stretching vibrations of N=N bond, the weak peak at the position 800 cm^{-1} belong to the bending vibrations C-H bond, the medium peak at the position 3269 cm^{-1} belong to the stretching vibration of NH_2 group. the strong peak at the position 1550 cm^{-1} belong to the bending vibration of NH_2 group [16].

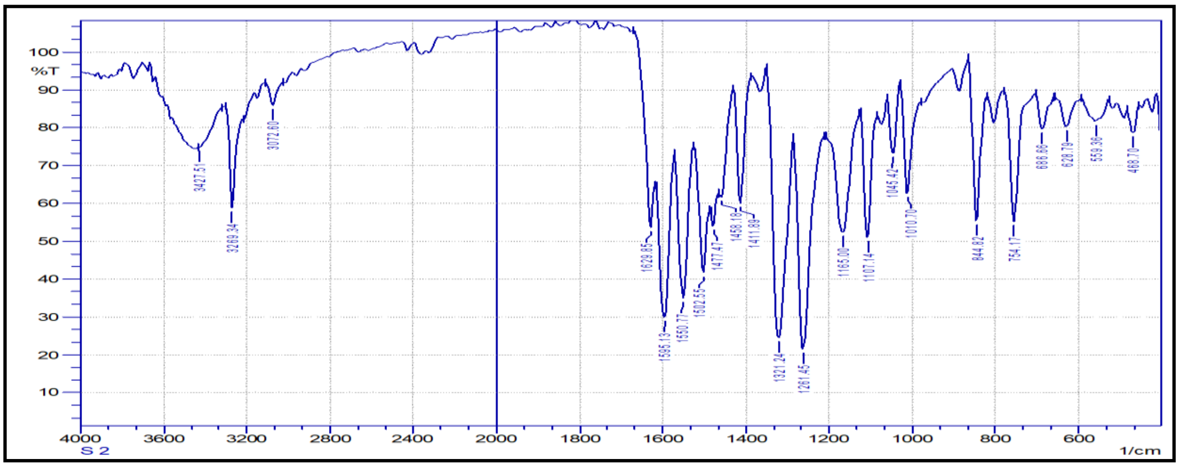


Fig. 1. FT-IR spectrum of azo dye (S_2).

The ^{1}H-NMR spectrum of the azo dye is shown in Fig. 2. The dye spectrum gives a collection of double and triple peaks that have a chemical shift (δ) within the range (7.08–8.49) ppm belonging to the eight protons of the aromatic rings, the single peak that has a chemical shift (δ) at site 12.24 ppm belonging to the proton of the OH group and the single peak that has a chemical shift (δ) at site 6.77 ppm belonging to the two protons of the NH_2 group [17, 18].

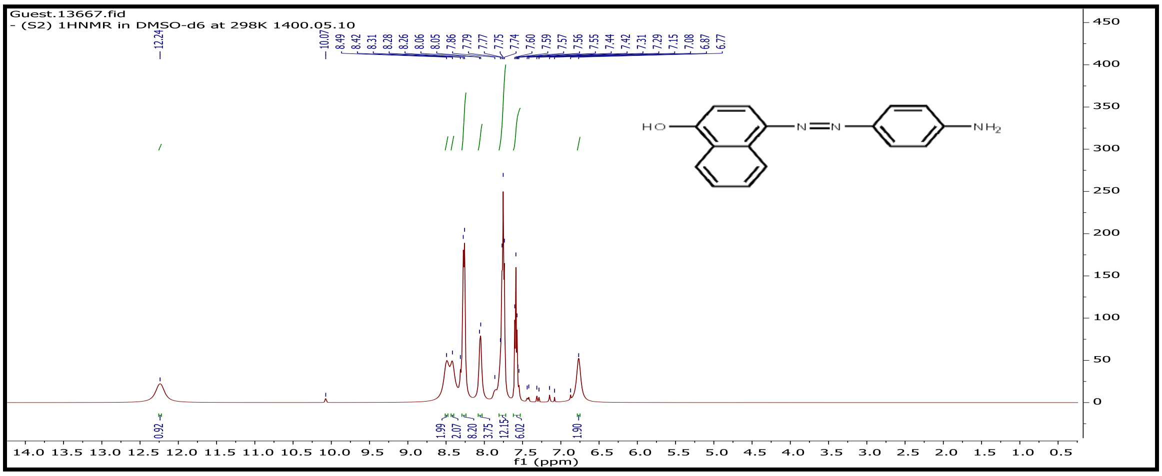


Fig. 2. ^{1}H-NMR spectrum of azo dye (S_2).

The mass spectrum of the azo dye is show in Fig. 3. The molecular ion peak ($C_{16}H_{13}N_3O^{+\cdot}$**)** to the dye at m/z 263.1 it's relative abundance 2.5%. The base peak ($C_{10}H_7O^+$) to the dye at m/z 143 it's relative abundance 100% [19].

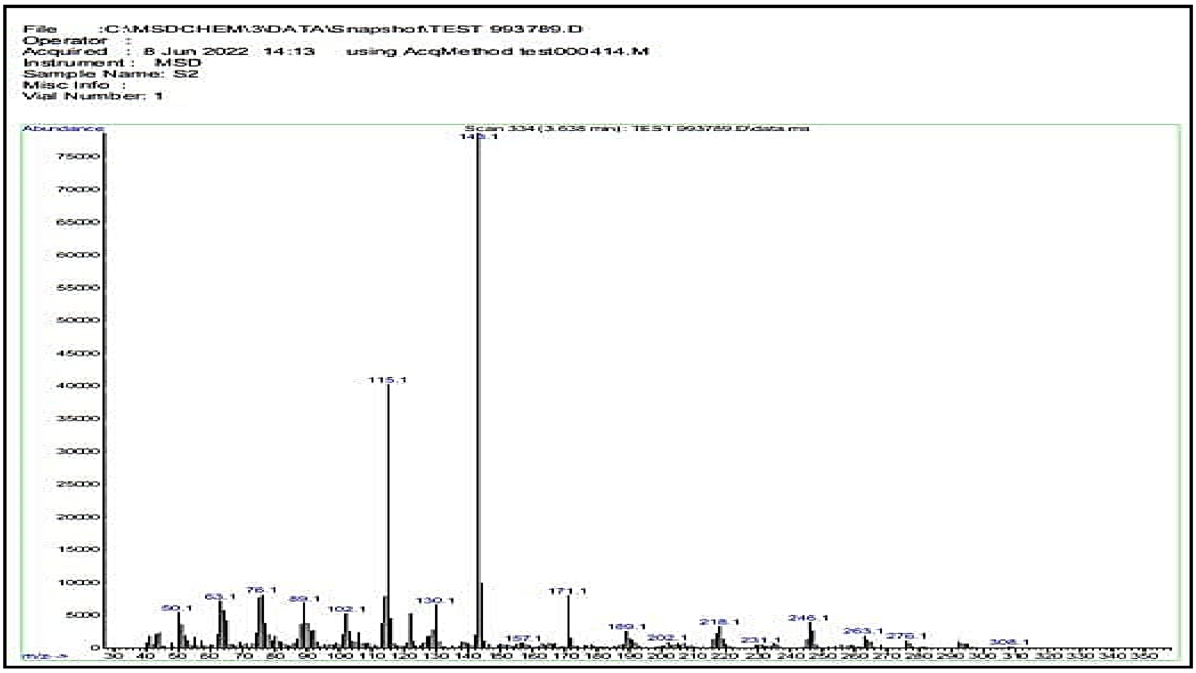

File :C:\MSDCHEM\3\DATA\Snapshot\TEST 993789.D
Operator :
Acquired : 6 Jun 2022 14:13 using AcqMethod test000414.M
Instrument : MSD
Sample Name: S2
Misc Info :
Vial Number: 1

Fig. 3. Mass spectrum of azo dye (S_2).

3.1. Acid-Base Properties:

The visible absorption spectra of dye solutions at a concentration of (1.25×10^{-4} M) with different pH values for the pH range (1–12) measured using buffer solutions within a wavelength range of (375–725) nm to know the effect of acidity and basicity on the dye and to calculate the ionization and proton constants of the dye as shown in Fig. 4. The spectra were characterized by the appearance of absorption peaks at wavelength (477nm), which is attributed to the absorption of the cationic formula (protonation of the dye in acidic solutions) and a high absorption peak at the maximum wavelength (595nm), which is attributed to the absorption of the anionic formula (ionization of the dye in basic solutions and the abundance of the electron pairs). It was observed that a distinct isobestic point at the wavelength appeared between the peaks at the wavelength (494 nm) [20, 21].

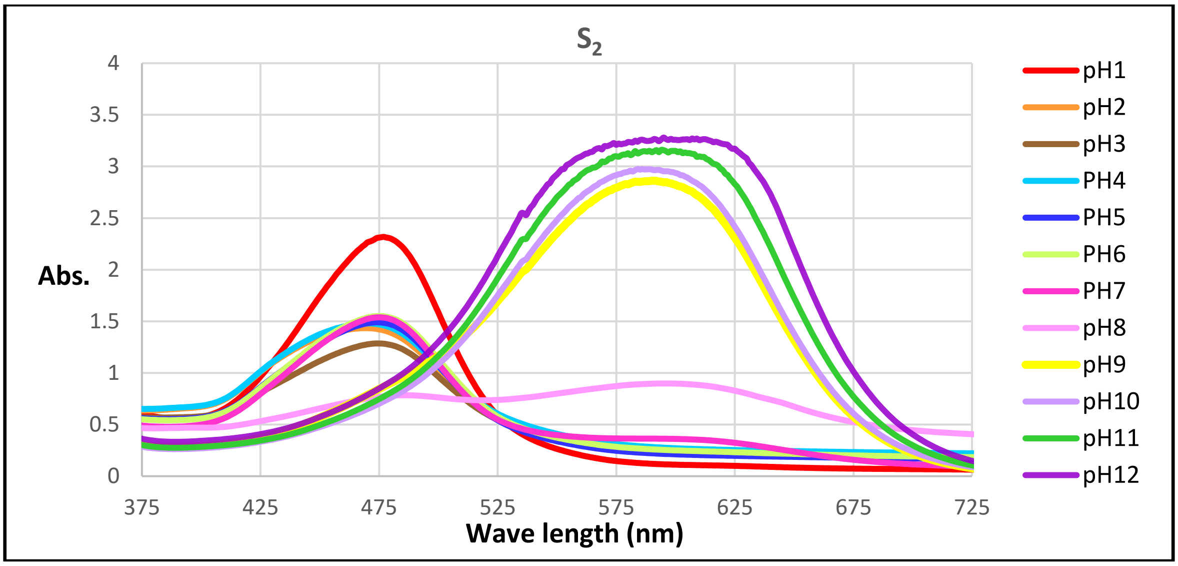


Fig. 4. The visible absorption spectra of the dye in different pH solutions.

The ionization and protonation constants of the dye were calculated as shown in Table 2 based on the data obtained in Fig. 4 and the suggested mechanism as shown in Fig. 5. Using the half-height curve method, the absorption values of the dye were taken at the maximum wavelength (595nm) versus the different pH values, the absorption curve of the dye was drawn as shown in Fig. 6, and the pK values were obtained by the subsequent equations:

$$pK = pH\left(\text{at } A_{1/2}\right) \tag{1}$$

$$A_{1/2} = (A_{max} + A_{min})/2 \tag{2}$$

A_{max} : maximum absorption, A_{min} : minimum absorption [22, 23]. The Fig. 7 shows the color of the dye in the acidic, neutral and basic medium.

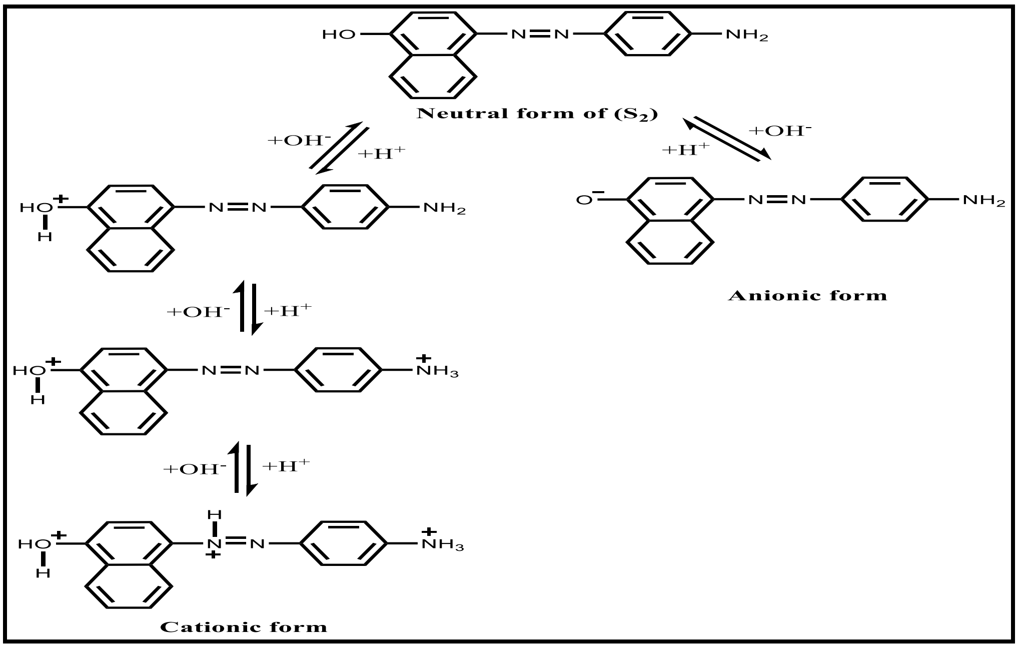


Fig. 5. The suggested mechanism for ionization and protonation of the dye.

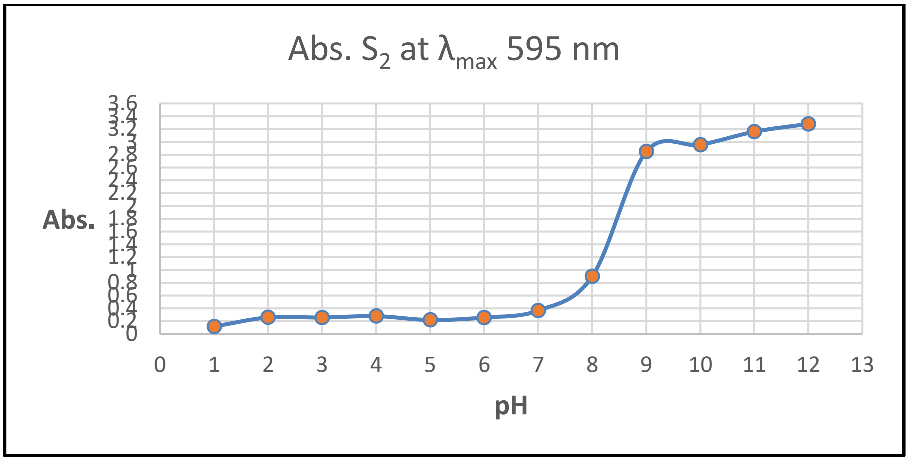


Fig. 6. The absorption curve of the dye at the maximum wavelength (595 nm).

Table 2. Evalution the ionization (pKa) and protonation (pKp) constants and the indicator range for azo dye.

Dye	**λ max (nm)**	**Abs. at (pH 9 – pH 7)**		**Abs. at (pH 7 – pH 5)**		**Abs. at (pH 4 – pH 3)**		**Abs. at (pH 2 – pH 1)**		**Indicator range**
		$A_{1/2}$	**pKa_1**	**$A_{1/2}$**	**pKp_1**	**$A_{1/2}$**	**pKp_2**	**$A_{1/2}$**	**pKp_3**	**(pK_a-1 , pK_a +1)**
S_2	595	1.605	8.4	0.289	6.7	0.265	3.2	0.185	1.5	(7.4 - 9.4)

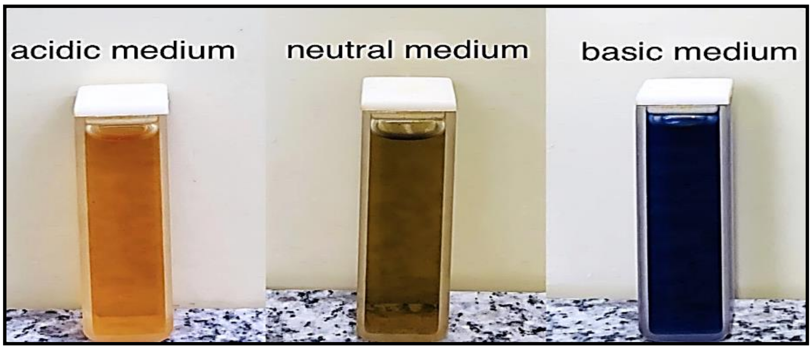


Fig. 7. The colors of the azo dye are in the acidic, neutral and basic medium.

3.2. Solvent Effect

Fig. 8 shows the absorption spectra in different polar solvents. In the polar proton solvents, ethanol, methanol, and acetone, absorption peaks were observed in the range (450–460) nm. The absorption peak was shifted to a longer wavelength at 460 nm in the DMF solvent, while the absorption peak was shifted to 635 nm in the DMSO solvent. Fig. 9 shows the linear relationship or close to it in the case of the solvents used, and this linear relationship confirms that the dielectric constant of the solvent is the main factor that controls the displacement of the dye absorption band (S2), and the deviation from this relationship in the case of the solvent (DMSO) is due to the formation of a strong hydrogen bond between the molecules of the solvent and the solute, which leads to a state of dissolution and its effect overcomes the effect of the dielectric constant. The solubility or the effect of the dielectric constant is expressed by applying the (Gati and Szaly) relationship as in the following equation:

$$\Delta\tilde{v} = [(a-b)(n^2 - 1/2n^2 + 1)] + b(D - 1/D + 1) \quad (3)$$

Where n and D are refractive index and dielectric constant of the medium, a and b are constants. More precisely, the dielectric constant function (D-1) (D+1) leads to a linear relationship when the dielectric constant is the only influence of the beam displacement. Table 3 show the dielectric constant values of the solvents and the maximum wavelengths and the molar absorption coefficient of the dye (S_2) in different polar solvents.

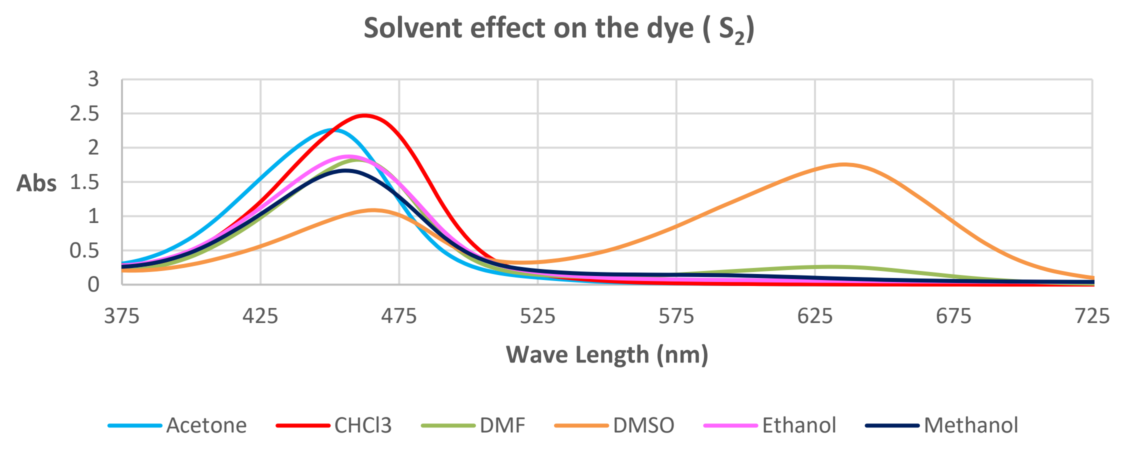


Fig. 8. The visible absorption spectra of the dye in different polar solvents.

Table 3. The dielectric constant values of the solvents and the maximum wavelengths and the molar absorption coefficient of the dye (S_2) in different polar solvents.

Symbol	Solvent	D	(D-1)/(D+1)	S_2			
				Azo		**Hydrazo**	
				λ_{max}	ε_{max}	λ_{max}	ε_{max}
A	Acetone	21.00	0.909	450	18056	—	—
C	$CHCl_3$	4.80	0.655	465	19680	—	—
D	DMF	36.71	0.947	460	14608	—	—
S	DMSO	46.68	0.958	635	14048	465	8704
E	Ethanol	24.55	0.940	460	14872	—	—
M	Methanol	32.70	0.920	455	13328	—	—

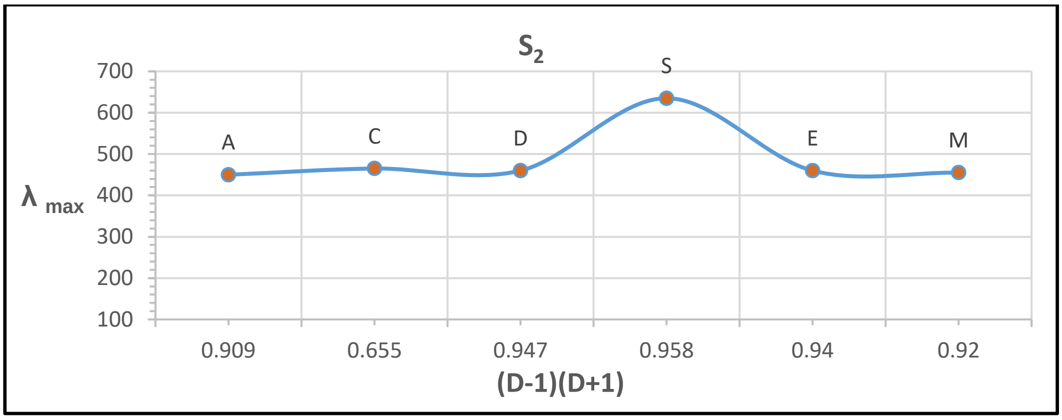


Fig. 9. The relationship between the maximum wavelengths of azo dye and the dielectric constant function in different polar solvents.

4. Conclusion

The azo dye was prepared through the reaction of diazotization and conjugation. The dye molecule was characterization using FT-IR Infrared spectroscopy, proton nuclear magnetic resonance (^{1}HNMR) and mass spectrometry.The visible absorption spectra of the dye was measured in different pH solution in the range (1-12), and it was noted that an absorption peak at wavelength (477 nm) of the appeared in acidic solutions, a maximum absorption peak at wavelength (595 nm) in basic solution, and an isobestic point at wavelength (494 nm).The ionization and protonation constants were calculated using the half-height curve method and the indicator range was calculated, where it was found (7.4-9.4).The effect of the solvent on the dye was studied and it was found that the absorption spectra shifted to longer wavelength 460 nm and 635 nm when using polar solvents DMF and DMSO, respectively.

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تحضير وتشخيص ودراسة تحليلية لصبغة أزو جديدة كدليل حامض- قاعدة

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معلومات البحث

الاستلام ١٤ نيسان ٢٠٢٢
القبول ٢٦ مايو ٢٠٢٢
النشر ٣١ تموز ٢٠٢٢

الكلمات المفتاحية

أصباغ الأزو، دلائل ، ثوابت التأين والبرتنة، تأثير المذيب.

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الملخص

تم تحضير صبغة الأزو ٤-((٤- أمينو فنيل) أزو) ١-نفثول) عن طريق الدستزة وتفاعل الأقتران مع ١-نفثول. تم تشخيص صبغة الأزو بواسطة ، FT-IR، ^{1}H-NMR طيف الكتلة ومطيافية الأشعة المرئية. تم دراسة الخصائص الحامضية والقاعدية بواسطة أطياف الأمتصاص المرئي للصبغة عند قيم pH مختلفة وظهور نقطة أيزوبستية واضحة وقمة أمتصاص عالية عند الطول الموجي الأعظم (595) nm تعزى لأمتصاص الصيغة السالبة للصبغة في الوسط القاعدي وقمة الأمتصاص عند الطول الموجي (٤٧٧) nm التي تعزى لأمتصاص الصيغة المبرتنة للصبغة في الوسط الحامضي. تم حساب ثوابت التأين والبرتنة ومدى الدليل ضمن (9.4 - 7.4) pH. تم دراسة تأثير المذيب على أطياف الأمتصاص المرئي للصبغة ولوحظ أزاحة حمراء واضحة لأطياف الصبغة في المذيبات القطبية.

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