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Preparation and Characterization of Two Azo Dyes For Dibenzothiophen by The Diazotization Reaction and Studying Their action as Acid-Base Indicators.

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Abstract:

This research describes the preparation of two dyes , by nitration of dibenzothiophen to form p-nitro dibenzothiophen and reduction to form p-amino dibenzothiophen , and creating by the diazonium salt that is reacted with (1&2-naphthol) to form azo dyes . Their FT.IR spectra and melting points were measured . One of these preparation dyes with orange color had been studied as an acid- base indicator by its effects in Titrimetric analysis by using methods of acid – base titration . Which was changed its color from colorless to orange in basic media , and from orange to colorless in acidic media . Dye (p- dibenzothiophen azo-8-naphthol) was an active acid-base indicator .The color difference between two spaces was clear, and the pH range of color change was (6-10).

Key word: Dibenzothiophen, Azo dyes , Indicator, Titrations.

Introduction:

Aromatic azo dyes are the largest group of organic dyes for their widespread applications in many areas of textile and medicine [1]. Azo dyes are characterized by the presence of at least one ($R_1-N=N-R_2$) functional group. The azo group often helps to stabilize the dyes and form a conjugated system, which very often absorbs visible frequencies of light yielding colored compounds [2] . Dyes are normally very large aromatic molecules consisting of many linked rings [3]; The more stable derivatives contain two aryl groups [4]. Although Azo dyes are a separate class of dyestuff mainly used in the dyeing of cotton (cellulose) fibers [5]. As a consequence of π -delocalization, aryl azo compounds have vivid colors, especially reds, oranges, and yellows. Therefore, they are used as dyes, some azo compounds, methyl orange, are used as acid-base indicators (Azo couplings) due to the different colors of their acid and salt forms ; Azo pigments are important in a variety of paints including artist's paints. They have excellent coloring properties, again mainly in the yellow to red range, as well as light fastness [6,7] . Many azo pigments are non-toxic, although some it has been reported that several bacteria and fungi are capable of catabolizing and mineralizing azo dyes [8] . Prontosil and other sulfa drugs are also produced using this reaction [9,10].

Experimental:

Instrumentation:

FT.IR (NICOLETFT.IR-100- Infrared Spectrophometer) was used to record the spectra by KBr disc as diffuse reflectance mode on a Chem. Dept. College. Of Education For Women, ANBAR UNIV; Melting points were determined by an electric heated block apparatus (Gallen Kamp.).

Materials:

Dibenzothiophen was supplied from (Riedel Dehaen) Chemicals ,The conc. Hydrochloric acid was supplied by (Fluka) Chemicals, Ethanol absolute , sodium hydroxide ,acetic acid, sulfuric acid, nitric acid , zinc , ether , sodium nitrite, 1-naphthol , and 2-naphthol , oxalic acid and sodium carbonate were supplied by BDH Chemicals .

The organic part & preparation (General Procedures) [11,12]: p-Nitro dibenzothiophen:

Dibenzothiophen (3 g, 16.2 mmole) was added to glacial acetic acid (10 mL) in a 50 mL Erlenmeyer flask with stirring ; conc. sulfuric acid (10 mL) was poured into the solution until the dibenzothiophen had dissolved. The flask was placed into an ice-salt bath and cooled to 5°C. A solution of concentrated nitric acid (4 mL) and concentrated sulfuric acid (2.6 mL) was prepared . While stirring the dibenzothiophen solution, The nitric/sulfuric solution was added drop wise at a rate such that the temperature did not rise over 20°C. The mixture was

allowed to stand at room temp for 20 minutes. The reaction mixture was poured into cold water (50 mL) and ice (30 g) and the solid that formed was collected by vacuum filtration. The solid was washed by a three portions of cold water (30mL). The solid was recrystallized by ethanol, producing a pale yellow solid. A small amount was saved for analysis (FT.IR and mp).

p-Amino dibenzothiophen [13]: p-Amino dibenzothiophen (2g) was added to a 25 mL round bottom flask. With stirring. A concentrated hydrochloric acid (5 mL) was slowly added. Zinc powder (2g) was added and all the contain was removed to beaker containing ice –salt as bath with stirring. The reaction mixture was warmed in water bath for (10 mint) until dissolving all the mixture. A solution (24% , 6M) of sodium hydroxide was slowly added. Approximately (20-30 mL) was formed. The mixture was separated by extraction from alkaloid compound by ether. The organic layer was vaporated by vacuum filtration. Producing brown solid, A small amount was saved for analysis (FT.IR).

Preparation of dye (1) (p-dibenzothiophen azo 4- naphthol) [14] : A solutions of concentrated hydrochloric acid (4 mL) and water (10 mL) were placed in a 50 mL Erlenmeyer flask. The solution was stirred while p-amino Dibenzothiophen (1g) was added. The mixture was cooled to 5°C in an ice bath. While stirring, a solution of sodium nitrite (0.5 g) in water (2 mL) was slowly added. The temperature was kept under 10°C. A solution of 1-naphthol (1 g, 6.94 mmole) in (10% , 2.5M) sodium hydroxide (10 mL) was prepared and cooled to a temperature of 10°C and poured into the mixture ,which was then stirred vigorously for a few minutes and then acidified with (1M) sulfuric acid .The pink precipitate that formed was filtered by vacuum and washed with water, producing a pink solid (% yield; mp 210-212 °C). A small amount was saved for analysis (FT.IR, mp).

Preparation of dye (2) (p-dibenzothiophen azo 8-naphthol) : Dye (2) was prepared by the same above method , but a solution of (2-naphthol) was used in the reaction instead of (1-naphthol) . The orange precipitate that formed was filtered by vacuum and washed with water, producing a pink solid (75% yield; mp 260-262 °C)[15] .

The titrimetric analysis part :

Effect of prepared dye (2) (p-dibenzothiophen azo 8-naphthol) as acid –base indicator :

0.1g Of the prepared dye (2) was dissolved in 100mL of absolute ethanol in the volumetric flask , and by same method a

solutions of methyl red and methyl orange and pheolphthalein was prepared.

The perparated dye can be using as acid-base indicator because it is containing phenols rings [16] , azo and thios as functional groups , azo is the largest group that have absorb visible frequencies of light using .

By the dye (p-dibenzothiophen azo 8-naphthol) we recorded data procedure pH titration curve to use it as indicator , because the color of dye was changed the solution was colorless to orange in the acidic medium , and from orange to colorless in the basic medium . In this titration HCl was used as strong acid ,also acetic acid and oxalic acid as weak acids to titrate with solution of NaOH and Na₂CO₃. [17] , Results are summarized in Tables (1) [18].

Results and Discussion:

The organic part:

p-Nitro Dibenzothiophen: Dibenzothiophen (97-100°C) was nitrated to p-nitroDibenzothiophen employing conc. nitric acid, glacial acetic acid, conc. sulfuric acid and an ice bath . The FT.IR for p- Nitro Dibenzothiophen gives bands[19,20] (fig1) at: 14310 cm⁻¹ for a sym NO₂ and 1521 cm⁻¹ for N-NO stretch; 1595 cm⁻¹ that signify C=C stretch (aromatic ring) ,and C-H aromatic at 3086 cm⁻¹, N-O at peak at 1170 cm⁻¹ that signifies .

p-Amino dibenzothiophen [21] . The FT.IR of p-amino dibenzothiophen (fig 2) gave the bands at: 3421-3000 cm⁻¹ signifying both and N-H stretch (2° amide), C-H stretch (aromatic); 2964 cm⁻¹ C=C stretch (aromatic); and C-H aromatic at 3086 cm⁻¹; 861-807 cm⁻¹N-H oop bend (amide).

The protecting group of p-amino dibenzothiophen was removed from p-Nitro dibenzothiophen using conc. hydrochloric acid, (24%) 6M sodium hydroxide and zinc powder by ether to give the diazonium salt.

Preparation of Dye (1)(p-Dibenzothiophen azo 4-naphthol) [22] : 1-Naphthol was added to the diazonium salt by way of a diazocoupling to form dye (1)(p-dibenzothiophen azo 4-naphthol) (m.p, 260-262°C) in 76.8% yield . The FT.IR of Dye (1) (fig. 3) Spectra with bands at: 30702 cm⁻¹ for a C-H stretch (aromatic) ; 1577-1510 cm⁻¹ for a C=C stretch (aromatic ring); 1625 cm⁻¹ for N=N stretch; 3427 cm⁻¹ for OH alcohol.

Preparation of dye (2)(p-dibenzothiophen azo 8- naphthol):

2-Naphthol was added to the diazonium salt by way of a diazocoupling to form Dye (2)(name) (mp, 260-262°C) in 76.8% yield. The FT.IR of Dye (2) (fig 4) Spectra bands at: 3052 cm⁻¹ for a C-H stretch (aromatic); 1596,

1510 cm^{-1} for a C=C stretch (aromatic ring); 1629 cm^{-1} for N=N stretch; 3373 cm^{-1} for OH alcohol. In the Azo couplings reaction the diazonium salt is an electrophile and the activated arene is a nucleophile in an electrophilic aromatic substitution [23].

Action of prepared dye(2) as indicator :

In table -1- the results of titration of the solution of HCl ,oxalic acid and acetic acid with different concentrations that calibrated with with solutions of NaOH and Na_2CO_3 that prepared and calibrated by presence methyl orange , methyl red and prepared dye (2) as indicators .

In the dilution of solutions of HCl ,oxalic acid , acetic acid , NaOH , and Na_2CO_3 to 10^{-1} and 10^{-2} the results it were similar to titration in concentrated of solutions and that the dilution was not influenced of clearness of end points. But the dilution was taken more clarity

to change color in the equivalent points , in spite of separate some of value. In this case, the weak acid is colorless and its ion is bright orange . Adding extra hydrogen ions shifts the position of equilibrium to the left, and turns the indicator colorless. Adding hydroxide ions removes the hydrogen ions from the equilibrium which tips to the right to replace them - turning the indicator orange, The Calibration of various of acids with difference bases solutions by changing color of indicators by changing of volume(mL) can be shown in table-1 and-2 .The (fig.5) their showed surprising change of pH values at equivalence point. The pH at the equivalence point falls within the pH range (6-10) in which the prepared dye (2) change color .

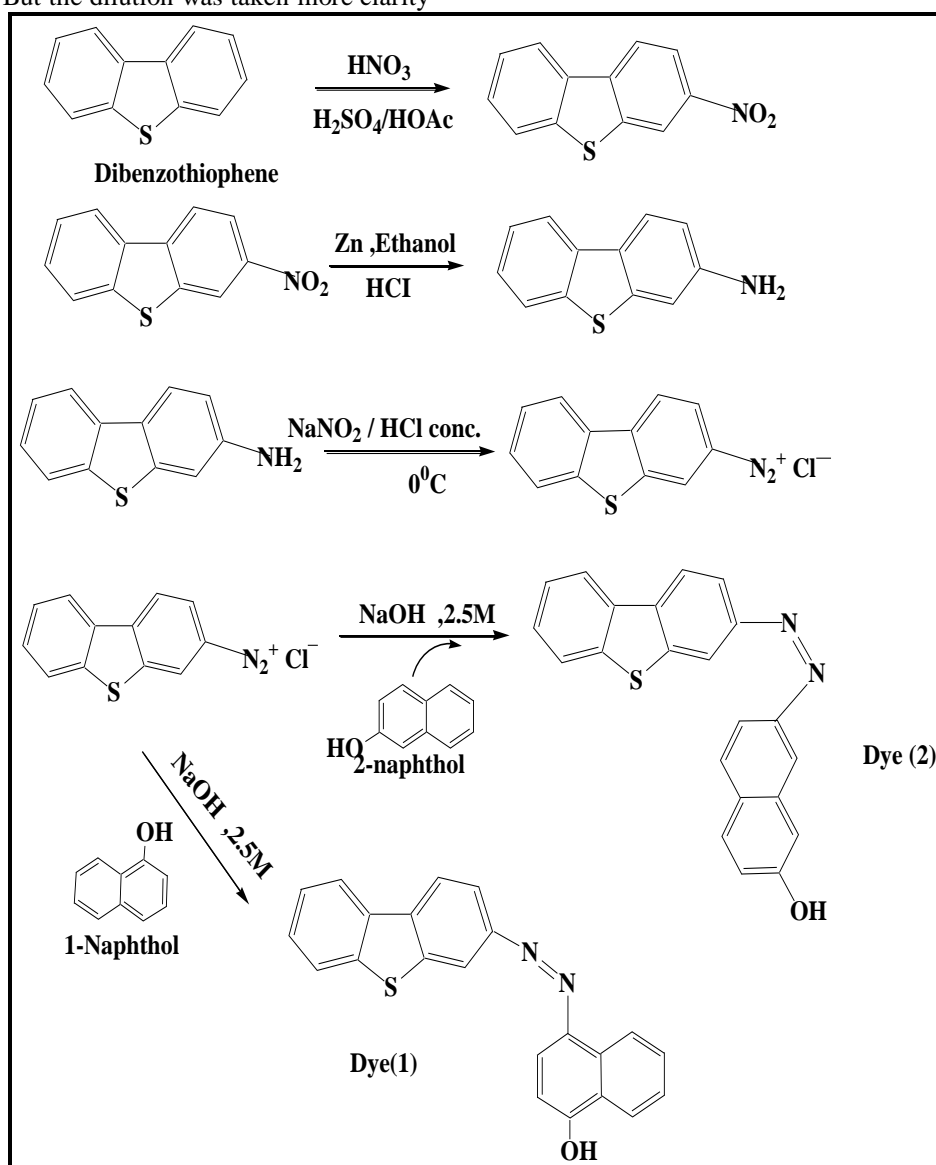


Table-1- Calibration of various of acids with difference bases by changing color of indicators by changing of volume(mL) of solutions .

	Volume of NaOH (mL) NaOH (0.144N)with HCl (0.16 N).	An indicators	Color at equivalence point	color of indicator in solution
1	V av : 9.03 ± 0.1	Methyl red	yellow	pink
2	V av : 9.03 ± 0.1	methyl orange	yellow	pink
3	V av : 9.03 ± 0.1	dye 1	yellow	orange
	Volume of Na ₂ CO ₃	titration Na ₂ CO ₃ (0.144N)with of HCl(0.101 N).		
1	V av : 9.8 ± 0.1	Methyl red	yellow	pink
2	V av : 9.9 ± 0.1	methyl orange	yellow	pink
3	V av : 9.9 ± 0.1	dye 1	yellow	orange
	Volume of HCl	titration HCl (0.0861 N) with NaOH (0.0817N).		
1	V av : 9.13 ± 0.1	Methyl red	pink	yellow
2	V av : 9.16 ± 0.1	methyl orange	pink	yellow
3	V av : 9.2 ± 0.2	dye 1	orange	yellow
	Volume of NaOH	titration Oxalic acid (0.08 N) with NaOH (0.142N).		
1	V av : 10.3 ± 0.2	phenolphthalein	pink	colorless
2	V av : 10.4 ± 0.1	Prepared dye 1	orange	colorless
	Volume of NaOH	titration Acetic acid(0.2N) with NaOH (0.14N).		
1	V av : 22.4 ± 0.2	phenolphthalein	pink	colorless
2	V av : 19.2 ± 0.1	Prepared dye 1	orange	yellow
	Volume of NaOH	titration HCl (0.011 N) with NaOH (0.15N).		
1	V av : 9.03 ± 0.1	Methyl red	yellow	pink
2	V av : 9.03 ± 0.1	methyl orange	yellow	pink
3	V av : 9.03 ± 0.1	Prepared dye 1	yellow	orange
	Volume of Na ₂ CO ₃	titration (Na ₂ CO ₃ (0.144) with HCl(0.101 N).		
1	V av : 9.4 ± 0.1	Methyl red	yellow	pink
2	V av : 9.1 ± 0.1	methyl orange	yellow	pink
3	V av : 9.5 ± 0.1	Prepared dye 1	yellow	orange
	Volume of NaOH	titration (NaOH (0.01N)with oxalic acid(0.01 N).		
1	V av : 26.3 ± 0.2	phenolphthalein	colorless	pink
2	V av : 25.7 ± 0.1	Prepared dye 1	colorless	orange
	Volume of NaOH	titration (NaOH (0.14N)with (0.2 N) of acetic acid)		
1	V av : 18.2 ± 0.2	phenolphthalein	colorless	pink
2	V av : 18.2 ± 0.2	Prepared dye 1	yellow	orange
	Volume of NaOH ,	titration (NaOH (0.00144)with HCl (0.0016 N).		
1	V av : 6.4 ± 0.2	Methyl red	pink	yellow
2	V av : 6.2 ± 0.2	methyl orange	pink	yellow
3	V av : 6.4 ± 0.2	dye 1	orange	yellow
	Volume of NaOH	titration NaOH (0.0014N)with oxalic acid(0.001N).		
1	V av : 25.4 ± 0.2	phenolphthalein	colorless	pink
2	V av : 25.5 ± 0.2	dye 1	colorless	orange
	Volume of Na ₂ CO ₃ ,	titration (Na ₂ CO ₃ (0.00144) with HCl(0.00101 N).		
1	V av : 9.3 ± 0.2	indicators	pink	yellow
2	V av : 9.1 ± 0.1	Methyl red	pink	yellow
3	V av : 9.5 ± 0.2	methyl orange	orange	yellow
	Volume of Na ₂ CO ₃	titration Na ₂ CO ₃ (0.00144) with Acetic acid(0.0010N).		
1	V av : 10.4 ± 0.1	indicators	pink	yellow
2	V av : 9.9 ± 0.2	Methyl red	pink	yellow
3	V av : 9.6 ± 0.3	methyl orange	orange	yellow

Table-2- measurement the calibration of acetic acid with NaOH by sequence changing of pH .

NaOH (mL)	pH	NaOH (mL)	pH	NaOH (mL)	pH
0	2.2	4.4	5.99	6.5	10.39
0.5	3.4	4.5	6.3	7	10.53
1	4.05	4.6	6.55	7.5	10.55
1.5	4.29	4.8	7.21	8	10.63
2	4.6	4.9	8.04	8.5	10.74
2.5	4.73	4.4	5.99	9	10.92
3	4.94	5	8.53	9.5	10.99
3.5	4.98	5.5	9.46	10	11.4
4	5.23	5.9	9.52		
4.3	5.61	6	10.04		

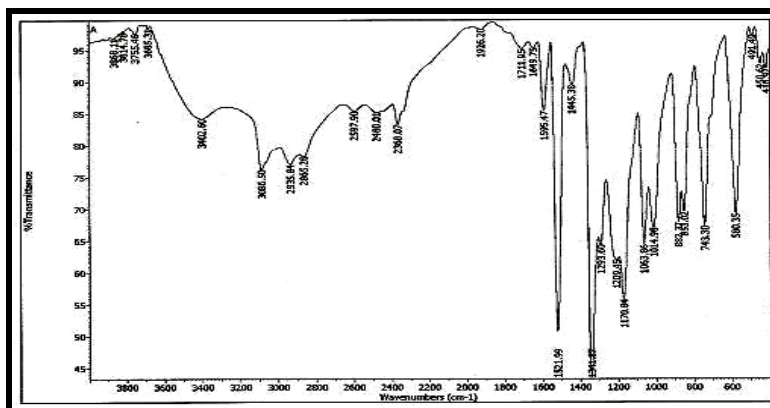


Figure (1) : FT-IR spectra of p-NitroDibenzothiophen .

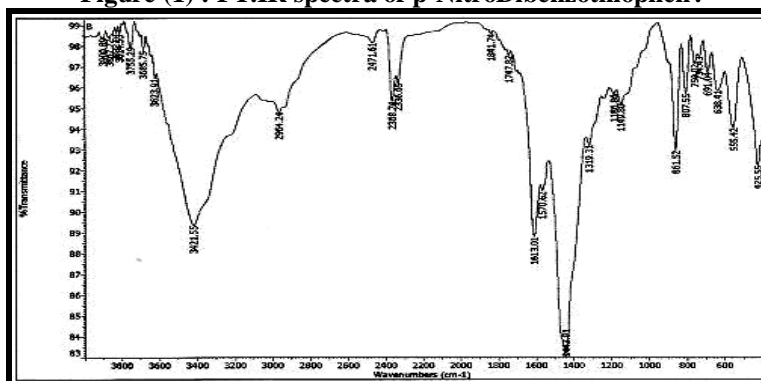


Figure (2) : FT-IR spectra of p-amino Dibenzothiophen.

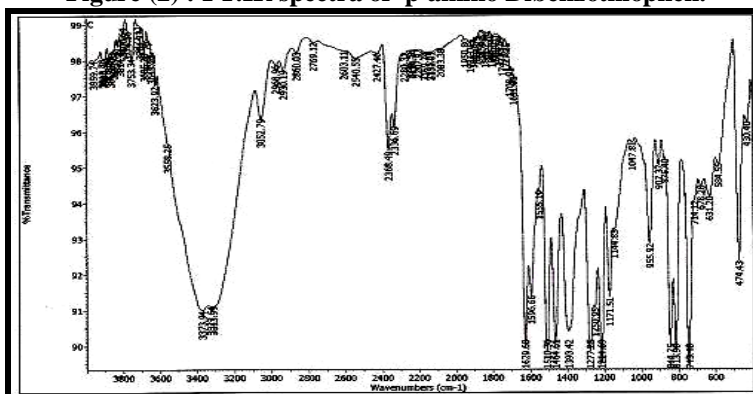


Figure (3) : FT-IR spectra of Dye (1)(p- Dibenzothiophen azo 4- naphthol).

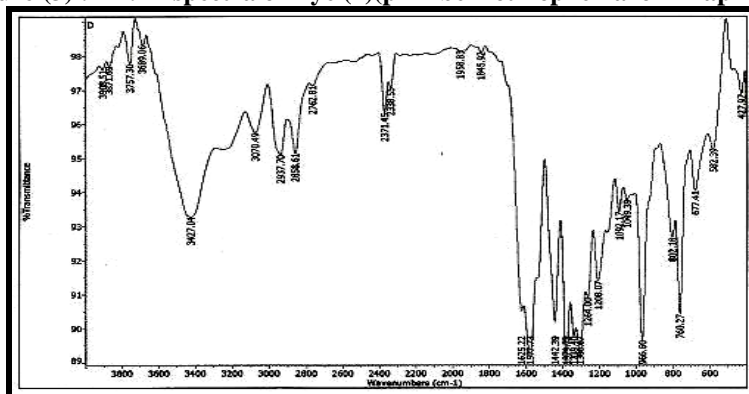


Figure (4) : FT-IR spectra of Dye (2)(p-Dibenzothiophen azo 8-naphthol).

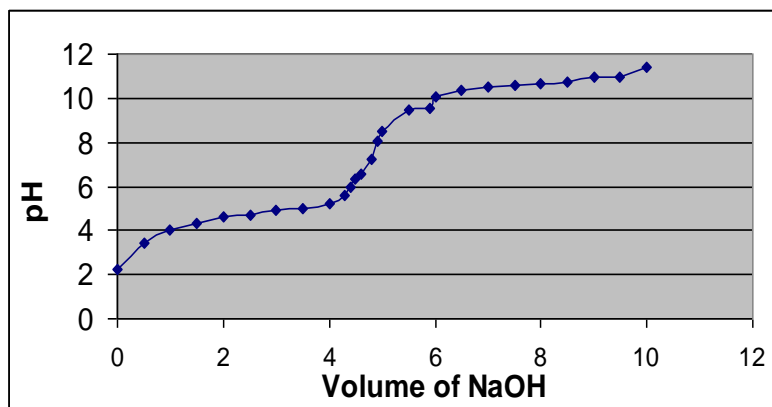


Figure (5) : A surprising change of pH values at equivalence point.

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تحضير وتشخيص صبغتي أزو لمركب ثنائي بنزو ثايوفين بتفاعل الدايزونيوم ودراسة فعلها كدلائل حامض - قاعدة .

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الخلاصة:

تم في هذا البحث تحضير صبغتي أزو بتفاعل ننترة لمركب (ثنائي بنزو ثايوفين) ثم اختزال مجموعة النايترو الى مجموعة الامينو لتحضير الصبغتين باملاح الدايازونيوم بتفاعل الناتج مع محلولي (الفا وبيتا نفثول) , وقد شخصت جميع المركبات الوسيطة والنهائية بنقاط الانصهار وطيف الاشعة تحت الحمراء, ثم تمت دراسة صبغة بيتا نفثول ذات اللون البرتقالي كدليل حامض قاعدة بتفاعلات تسحيحات حامض - قاعدة , وقد اثبتت النتائج فعالية الصبغة (بارا- بنزو ثايوفين -8 - نفثول) كدليل , وذلك بتغير اللون من البرتقالي الى عديم اللون في المحيط الحامضي وبالعكس في المحيط القاعدي واستعمالها بمدى حموضة من (6-10) .