Available online at www.elixirpublishers.com (Elixir International Journal)

Applied Chemistry

Elixir Appl. Chem. 106 (2017) 46546-46551

ISSN: 2229-712X

Study of Some Recent Technologies of Azo Disperse Dyes on Polyester Fibers: Part (II). Thermodynamics and kinetics Parameters of Dyeing

M. S. Aboul-Fetouh[1], Rabie S. Farag [1], S .Shakra[2], Y. A. Youssef [2] and Ali.A.Ali[1]

[1]Chemistry Department , Faculty of Science, Al-Azhar University , Naser City, Cairo , Egypt.

[2]Textile Research Division, National Research Centre, Dokki, Cairo, Egypt.

ARTICLE INFO

Article history:

Received: 3 April 2017;

Received in revised form:

2 May 2017;

Accepted: 10 May 2017;

Keywords

Thiadiazole azo disperse dyes, Polyester, carrier and solvent-assisted dyeing, Kinetics and thermodynamic parameters.

ABSTRACT

This present work aims to investigate dyeing performance of some new azo disperse dyes belonging to diazotization of 1, 4-bis (2-amino-1, 3, 4-thiadiazolyl) benzene and coupling with different amines as to comparing and contrasting depth obtained of shade and levelness. Some new dyes, such, has been examined, and assessed. The study was concerned mainly with dye uptake, behavior and efficiency. Color measurements, kinetics and thermodynamic parameters were involved. Conventional dyeing, was considered as control for obtained results.

I. Introduction

Azo disperse dyes are a versatile class of colored organic dyes and receive a considerable attention, as a consequence of their exciting biological properties and their applications in various fields, e.g., textiles, leathers, papers, additives, and cosmetics.[1]

The azo disperse dyes based on thiadiazole result in brighter and deeper shades than their benzene analogues. The syntheses of different azo disperse dyes based on thiadiazole for polyester fabrics. Recently, other studies reported the application of synthesized azo dyes for dyeing and printing polyester fabrics.[1]

These techniques reduce the processing time and energy consumption and maintain or improve the product quality. Few of the technologies, which have been reported at laboratory scale, are listed below:

- Low temperature dyeing (at boil) is been carried out in presence of carriers. However, many of the carriers in use are found to be non-eco-friendly.
- Dyeing in presence of Infrared rays. No commercialization adopting this technology has been reported so far.
- Low temperature dyeing in presence solvent assisted to improvement in coverage increases very steadily with increased concentration of solvent.[2]

Thus, we have initiated a program of applying the synthesized dyes derived from thiadiazole to polyester as disperse dyes to study their color measurement, fastness properties.

II. Material and Experimental work.

All melting points were measured on a Gallenkamp melting point apparatus and automatic melting point SMP50. All wavelengths and absorbances were recorded on UV Visible spectrophotometer Jenway.

The infrared spectra were recorded on Agilent technologies Cary 630 or Shimadzu FT IR 8101 PC infrared spectrophotometers. Mass spectra were recorded on a Shimadzu GCMS-QP-1000EX mass spectrometer at 70 e.v.

II.1.Synthesis of 5,5'-(1, 4-phenylene) bis (1,3,4-thiadiazol-2-amine) (1):

A mixture of terphthalic acid (0.01mole), thiosemicarbazide (0.02mole), phosphorus oxychloride (5 ml) was refluxed gently for 3 hours. After cooling, ice water was added (50 ml). The mixture was then refluxed again for 4 hours and filtered. The filtrate was neutralized with potassium hydroxide. The precipitate was filtered and washed with distilled water and the resulting solid washed again with hot DMF, and the product was dried at room temperature.

II.2. Dye synthesis

The dyes (1 and 2) were synthesized by diazotization of the corresponding amine with nitrosylsulfuric acid and subsequent coupling with the chosen coupling agent. The nitrosylsulfuric acid, prepared by adding 0.76 g of sodium nitrite to 5ml of sulfuric acid, was cooled to 0^{o}C and 0.01 mole of the compound (1) were added portion wise under stirring. Then 10 ml of a propionic acetic acid mixture (1:4) were added to the diazonium salt keeping the temperature at 5^{o}C for 2h.

The clear diazonium solution obtained was added under stirring at 5 ^{o}C, to a solution of 0.02 mole of the chosen coupling agent, dissolved in 20 ml of a 1:4 mixture of propionic-acetic acid, at pH 4, by adding sodium acetate portion wise. After a short time the reaction mixture was poured into iced water and filtered. The dyes obtained were washed with water, dried and recrystallized.

II.3. Fabrics

Scoured and bleached 100% polyester fabric. The fabrics were scoured in aqueous solution having a liquor ratio of 1:50 and containing 2 g/L of nonionic detergent solution

Tele: 00201155011735

E-mail address: dr_ali055@yahoo.com

supplied by Egyptian Turkish Co. (Cairo, Egypt) and 2 g/L of Na_2CO_3 at 50 °C for 30 min to remove waxes and impurities, then rinsed thoroughly in cold tap water, and dried at room temperature.

II.4. Carrier and/or solvent-assisted Dyeing Process:

Dyes were used as pure powder in the same form as prepared without milling. Fabric samples (2 g) were introduced into a flask containing a dye bath of 4% (o.w.f) dye shade and Avolan as dispersing agent, commercial HC carrier (Liquid) supplied by Egyptian Turkish Co. (Cairo, Egypt) for auxiliaries with ratio 4% (o.w.f) and/or *n*-butanol with ratio 6% at dyeing temperature 100°C with a 1:50 liquor ratio. During dye bath preparation, the dye was mixed with 10 drops of DMF and then mixed with dispersing agent, and water was added to prepare a homogeneous dispersion of the dye. The pH was adjusted to 4.5 by using acetic acid. At the end of the dyeing process after 1 h, the dyed samples were removed, rinsed in warm water, and subjected to reduction clearing in a solution comprising 2 g/L of sodium hydrosulphite and 2 g/L of sodium hydroxide (caustic soda) for 10 min at 60°C, with a liquor ratio of 1:40, This was aimed at removing unfixed dye and carrier residues that may be left on the fabric after dyeing and the reduction-cleared sample was rinsed thoroughly in water. The dyed samples were removed, rinsed in tap water, and allowed to dry in the open air.[3]

II.5. High temperature dyeing method (HT)

A dispersion of the dye was produced by dissolving the appropriate amount of dye (2% shade) in 1 mL dimethylformamide (DMF) and then added drop wise with stirring to the dye bath (Liquor ration 50:1) containing 4% a volane as dispersing agent. The ratio of dispersing agent to dyestuff is 1:1. The pH of the dye bath was adjusted to 4.5 using aqueous acetic acid and the wetted-out polyester fabrics were added. Dyeing was performed by raising the dye bath temperature to 130°C and high pressure (24–30 psi) for 60 min under pressure in an infra-red dyeing machine.

After dyeing, the fabrics were thoroughly washed and subjected to surface reduction clearing (2 g NaOH + 2 g sodium hydrosulphite)/L, and soaped with 2% nonionic detergent to improve washing fastness). The samples were heated in this solution for 45 min at 80 °C. Rinse well in cold water and neutralize with 1g/L acetic acid for 5 min at 40°C, the dyed samples were removed, rinsed in tap water and allowed to dry in the open air.[1]

II.6. Exhaustion Isotherms

The rate of exhaustion of the dyestuffs on polyester fiber was measured at equilibrium at 100°C, according to previous methods. The rate of exhaustion was assessed by taking samples from the dyebath at different times during the dyeing process. The optical density of the dye bath samples was then measured using a UV-visible spectrophotometer.

II.7. Thermodynamics and kinetics parameters [4]

II .7.1. Partition coefficient and standard dyeing affinity

The partition coefficient, K, of the dye concentration between the fiber and the dyeing solution was obtained from the adsorption isotherm. The standard affinity of the dye was calculated using the following equation.

$$K = [D]_f / [D]_s \quad \text{---------- (1)}$$

$$-\Delta\mu^\circ = RT\ln K \quad \text{---------- (2)}$$

K, The partition coefficient. $-\Delta\mu^\circ$, standard dyeing affinity ;$[D]_f$,dye concentration in fiber on adsorption isotherms [mol/kg]; $[D]_s$, dye concentration in solution on adsorption isotherms [mol/kg]; T, absolute temperature [K]; R, gas constant [1.9872cal/mol.K].

II.7.2. Heat of dyeing ΔH^0 and entropy change ΔS^0

ΔH^0 and ΔS^0 can obtained from the empirical plot between Lin k and 1/T using Eq.2 and 3.

$$\Delta H = \Delta G_{100} + T_{100}\Delta S \quad \text{---------- (3)}$$

ΔH ,heat of dyeing[cal/mol]; ΔS change of entropy[cal/mol.K]; T, absolute temperature [K]; R, gas constant [1.9872cal/mol K].

III. Results and Discussion

(Cpd 1): Yield 22 %, m.p 343-344 °C, yellow crystals, IR bands (KBr pellets cm^{-1}): 3280 and 1505 ν (NH) and δ (NH), 3085 ν(C-H, ar.), 1689 ν(C=N), 1424 ν(C=C ar.), 1070 ν (=N-N=), 731 δ(C-S-C). Mass spectra of compound 1 gave molecular ion peak at m/z 276 (M^{+1}) corresponding to molecular formula$C_{10}H_8N_6S_2$.

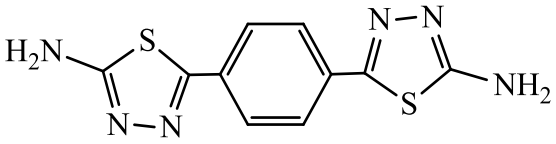
(Dye 1): Yield 83 %, m.p 284°C, reddish orange crystals, λ_{max} in DMF/H_2O 361 and IR bands (KBr pellets cm^{-1}): 3379 and 1503 ν (NH) and δ (NH), 3063 ν(C-H, ar.), 1620 ν(C=N), 1414 ν(C=C ar.), 1015 ν (=N-N=), 690 δ(C-S-C). The molecular formula is $C_{22}H_{14}N_8S_2O_2$ (484) and the elemental analysis is C (54.53), H (3.33), N (28.91), S (13.23) and also good agreement with structure data.

Dye 2: Yield 81 %, m.p>300°C, Dark red crystals, λ_{max} in DMF/H_2O 552, and IR bands (KBr) ν_{max}/cm^{-1}: 3380 and 1510 (NH), 3052 (C-H, ar.), 1686 (C=N), 1420 (C=C ar.), 1014 (=N-N=), 732 (C-S-C). Molecular formula $C_{30}H_{20}N_{10}S_2$ (584) and the elemental analysis is C (61.63), H (3.45), N (23.96), S (10.97) and also good agreement with structure data.

III.1. Dyestuffs Synthesis

Thiadiazole is an important five membered heterocyclic ring containing two nitrogen atoms for synthesis sulphur dyes. The target 5, 5'-(1,4-phenylene)bis(1,3,4-thiadiazol-2-amine) (1) was synthesized by the reaction of terphthalic acid with thiosemicarbazide in the presence of phosphorus oxychloride

The disappearance of C=O stretching in IR spectra was good indication of conversion of terphthalic acid to heterocyclic ring, in addition to the following frequencies: NH_2, 3280, 1505 cm^{-1} due to NH stretching, 1689 cm^{-1} for C=N and 731 cm^{-1} for C-S ring stretching, Fig. (1).



(1)

Fig 1. Structure of compound (1).

The dyes 1 and 2 were diazotized and coupling with different amines to form disperse dyes used for the dyeing of polyester fibre; Fig. 2. The structural identification of synthesized dyes 1 and 2 have been confirmed from both spectral and elemental analysis.

III.2. Application of prepared dyes on textile fiber

Disperse dyes (2-5) were applied to polyester fabrics at 4% (shade), using

- high Temperature dyeing method (HT) at 130°C
- HC carrier with ratio 4% (o.w.f) at dyeing temperature 100°C
- Solvent –assisted dyeing using 6% high molecular soluble solvent (*n*-butanol)

Above techniques are assist in comparison against conventional dyeing at the boiling (100°C).

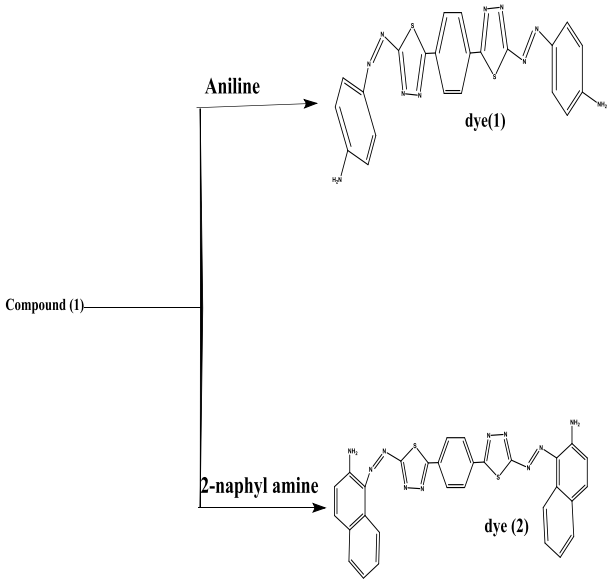


Figure 2. Reaction scheme.

III.3. Solvent – assisted against carrier dyeing of polyester

The use of *n*-butanol at about 60 ml/l in the dye bath considerably accelerates the diffusion rates of disperse dyes in polyester, and is capable of improving the levelling properties of the dyes and shortening the time required at top temperature to give full yields. In all these respects, however, its performance is similar to that of conventional carriers used at much lower concentrations - about 2 g/l. Without solvent recovery, the cost of the solvent assisted dyeing method would be much greater than that of methods using conventional carriers, with no increase in performance. Solvent recovery is, therefore, crucial if the solvent assisted process is to be commercially viable. It might then show advantages over the use of carriers on a throw-away basis, both in cost and in reducing the problems of effluent disposal, from which most conventional carriers are likely to suffer increasingly in the future.

It is apparent that the improvement in coverage increases very steadily with increased concentration of butanol, up to the region of 5% by weight in the dye bath. In subsequent work, therefore, this concentration of solvent was used in most cases.[5]

III.4. Dyeing characterization on polyester fabric

For some time an effort has been made to replace certain anthraquinone disperse dyes by new dyes often derived from hetero compounds to improve the properties. Useful dyes in this respect are derived from 2-amino-1, 3, 4-thiadiazole derivatives as diazonium components and amines or phenols as coupling components. Thus dyes were synthesized to assess their dyeing properties and performance. All these dyes were used for dyeing polyester fabric at 4% (w/w) shades as dispersed dyes.

Variation in the shades of the dyed fabric results from both the nature and position of the substituent present on the diazo component. A remarkable degree of levelness and brightness after washing indicates good penetration and excellent affinity of these dyes to the fabric. [6]

III.5. Kinetic and thermodynamic behavior of some extracted dye on polyester

III.5.1. Exhaustion Isotherm

Dye solutions (4%) were prepared from the crude extract by maintaining material-to-liquor (MLR) ratio at 1:50.

The absorbance of the dye solution was recorded before and after dyeing process with UV-Visible spectrophotometer. The per cent dye uptake was calculated using the following formula. [7]

$$\text{dye uptake} = \frac{(\text{Absorbance before dyeing} - \text{Absorbance after dyeing})}{\text{Absorbance before dyeing}}$$

Table 1. Comparative study of efficiency for dye (1) on polyester by different dyeing method.

Dyeing Condition	Temperature of dyeing (^{o}C)	dye take up %	Half-time of dyeing $t_{1/2}$
Conventional	100	55.6	21
High temp	130	91.44	17
Carrier dyeing	100	60.4	18
Solvent-assisted	100	73.7	19
80 °C dyeing	80	51.1	21

Table 2.Comparative study of efficiency for dye (2) on polyester by different dyeing method.

Dyeing Condition	Temperature of dyeing (^{o}C)	dye take up %	Half-time of dyeing $t_{1/2}$
Conventional	100	69.74	26
High temp	130	83.14	11
Carrier dyeing	100	75	19
Solvent-assisted	100	71.26	18
80 °C dyeing	80	63.5	18

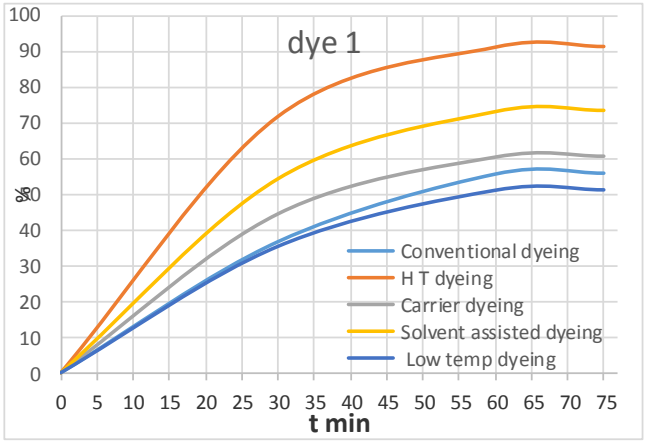


Figure 3. Dyeing performance of dye (1) on polyester by different methods.

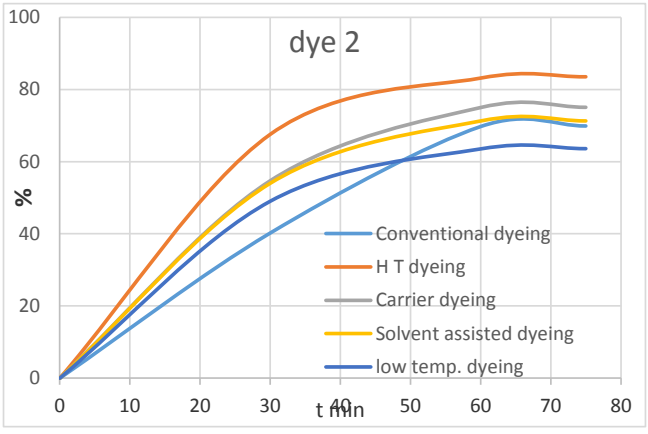


Figure 4. dyeing performance of dye (2) on polyester by different methods.

The obtained results for synthetic dyes on polyester fiber from Tables (1 and 2) indicate that:

In case of dye (1) in Table (1) and fig, (3), the maximum dye uptake (51.1, 73.7,60,4 and 91. 4 %) for low temperature (80 ^{O}C), solvent assisted, carrier and high temperature dyeing, respectively, and this indicates that excellent dye uptake by the fiber, while the maximum dye

uptake (55.6) for Conventional dyeing and this indicate that good dye uptake by fiber.

In case of dye (2) in Table (2) and fig, (4), the maximum dye uptake (63.5, 71.26, 75, 75 and 83.14 %) for low temperature (80 ^{O}C), solvent assisted, carrier and high temperature dyeing, respectively, and this indicates that excellent dye uptake by the fiber, while the maximum dye uptake (69.74) for Conventional dyeing and this indicate that good dye uptake by fiber.

III.5.2. Time of half dyeing ($t_{½}$)

The rate of dyeing of polyester fiber when dyed with dyes (1 and 2) was calculated and expressed as time of half dyeing ($t_{½}$). Time of half-dyeing ($t_{½}$) was calculated from the plot of amount of dye exhausted in the fiber expressed as g/kg at different intervals of time during dyeing ranging from 10 minutes to 75 minute. The exhaustion of dye in the fiber (dye uptake) was estimated in each case calorimetrically. [8]

- The $t_{1/2}$ min for dye (1) in Table (1) range from (17-21) for high temperature, carrier, solvent, conventional dyeing and low temperature dyeing, respectively, and this indicates that good dyeing process on fiber and medium rate of dyeing.
- The $t_{1/2}$ min for dye (2) in Table (2) range from (11-26) for high temperature, carrier, low temperature dyeing, solvent and conventional dyeing, respectively, and this indicates that good dyeing process on fiber and medium rate of dyeing.

III.5.3. Partition coefficient and dyeing standard affinity

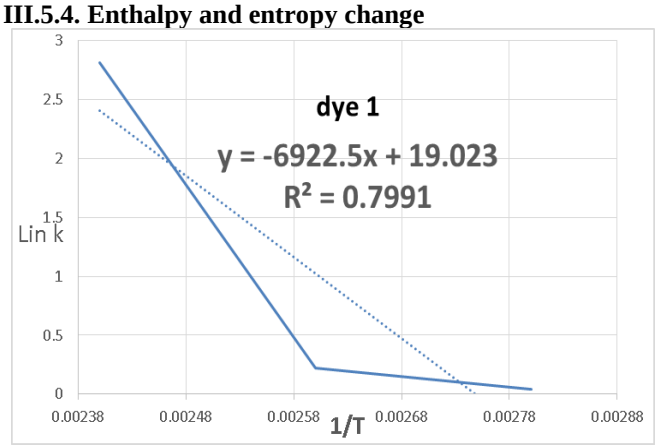
The adsorption isotherms of dyes (1 and 2) on PET in different temperatures are show in Table 3 from Eq.1 and Eq.2, the standard affinity and partition coefficient can be calculated and shown on Table 3.

Table 3. the partition coefficient and the standard affinity of dyes (2, 5,6and 8) on PET.

Dye No	Temperature [℃]	Partition coefficient *K* [g/ml]	Standard affinity -Δμ	Lin k
	80	1.042	28.85	0.041
Dye(1)	100	1.25	165.38	0.223
	130	16.62	2250.62	2.81
	80	1.77	398.06	0.57
Dye(2)	100	2.32	623.7	0.84
	130	4.75	1247.7	1.56

As shown in Table 3, the partition coefficient increases while the temperature raises. It means the degree of dye (1 and 2) dissolution in high-temperature are more than dye uptake on fiber. Under the condition of high-temperature, the standard affinity increases with the temperature increasing, However, the increase value is small, which means rising temperature will help improve the activity of dyes (1 and 2) on PET.

III.5.4. Enthalpy and entropy change



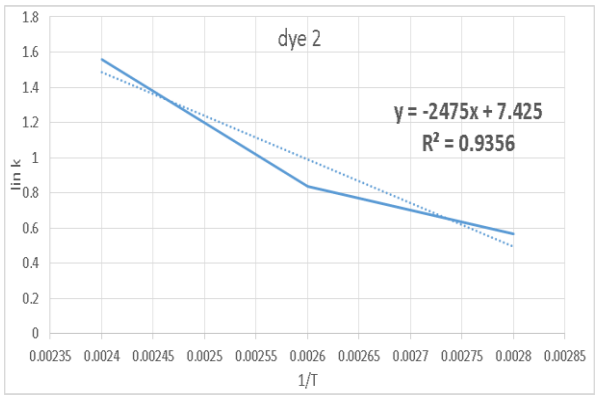
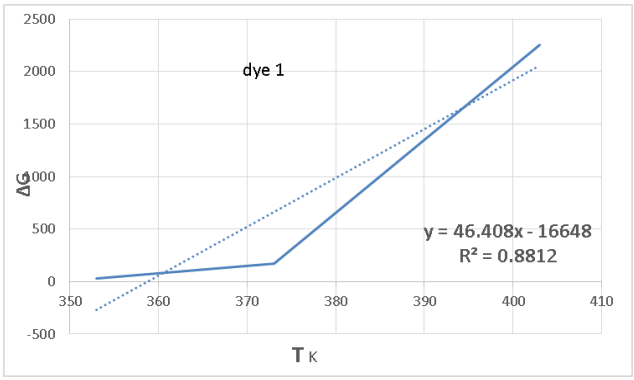


Figure 5. Relationship between ln K and 1/T for dyes .

Table.4 Calculation of ΔG, ΔG/T, and 1/T for the prepared dyes under investigation.

Dye No	(T)^{o}K	1/T	-ΔG$^{\circ}$×10^{3}	ΔG/ T
	353	2.8x10^{-3}	0.029	0.081
Dye(1)	373	2.6x10^{-3}	0.17	0.442
	403	2.4x10^{-3}	2.251	5.4
	353	2.8x10^{-3}	0.398	1.13
Dye(2)	373	2.6x10^{-3}	0.632	1.67
	403	2.4x10^{-3}	1.25	3.1



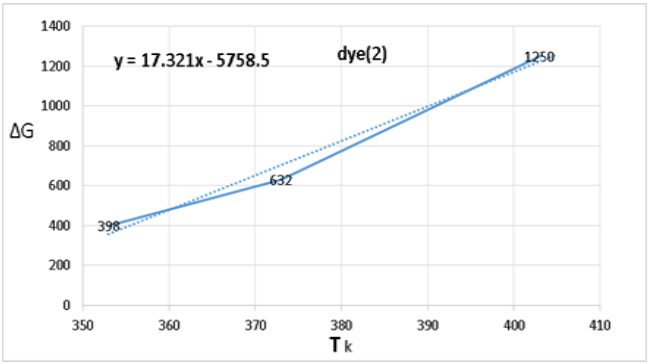
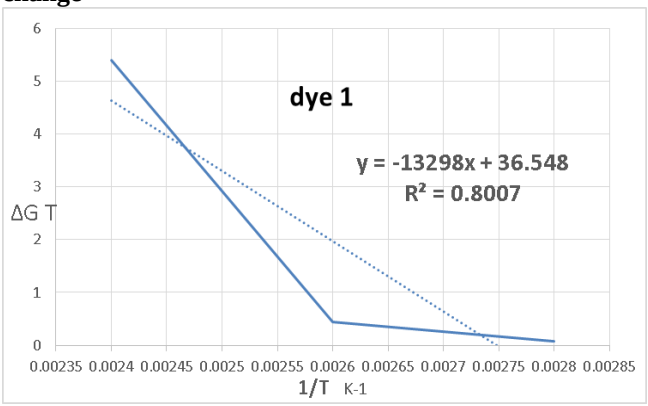


Figure (6): Relationship between ΔG and T on entropy change



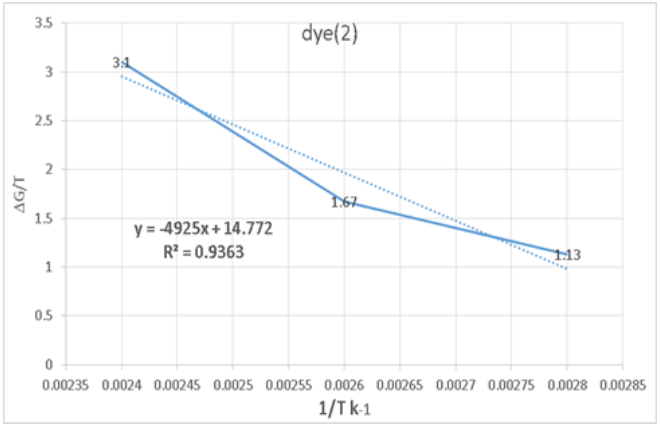


Fig 7. Relationship between ΔG /T and 1/T on enthalpy change.

Table 5. Thermodynamic function of some dyes.

Dye No	- ΔG×10^3 (cal/mol)	-ΔH×10^3 (cal/mol)	- ΔS (cal/mol.K)
Dye(1)	2.251	13.298	46.4
Dye(2)	1.25	4.925	17.3

The obtained results for synthetic dyes on polyester fiber from Tables (5) indicate that:

1). ΔG ranged from 1.25 -2. 251 positive value indicate the real dyeing process on polyester fibre sample.

2). Δ S ranged from 17.3 -46. 4 cal K^{-1} $mole^{-1}$ high negative value this indicate that the dye molecule inside the fibre is regular and arrangement inside the fibre, this module for completing dying process.

3). ΔH ranged from 4.925-13.298 K cal this indicate that the dyeing process completing by diffusion controlled not by chemical bonding reaction, which has the | ΔH| value ranged from 18 -27 K .cal.

4). ΔH has negative value ranged from 4.925-13.298 K.cal this indicate that the dyeing process is exothermic process.

III.6. Color Measurements

Table (6): color measurement of the dyed polyester fabric by dyes (1 and 2)

Dye no	λ_{max}	L*	a*	b*	C*	h	ΔE	K/S
1	385	62.9	18.6	54.5	57.6	71.2	85.3	18.3
2	480	36.5	36.7	33.2	49.5	42.1	62.4	21.7

The dyeing results depend on many factors, for example, temperature and time. Thus, at a temperature of 100 ^oC, the dyes can already diffuse into fiber due to the increased mobility of the polyester at the start of the glass transition.[9] For polyester, as the temperature increased, the diffusion coefficient increased. The results obtained might be attributed to the fact that raising of dyeing temperature above 100 ^oC causes significant increase of the rate of diffusion of disperse dyes into polyester fiber and higher dye uptake. [9]

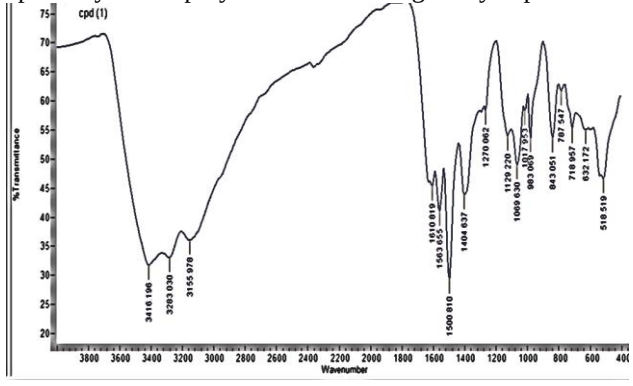


Fig 8. IR Spectrum of compound (1).

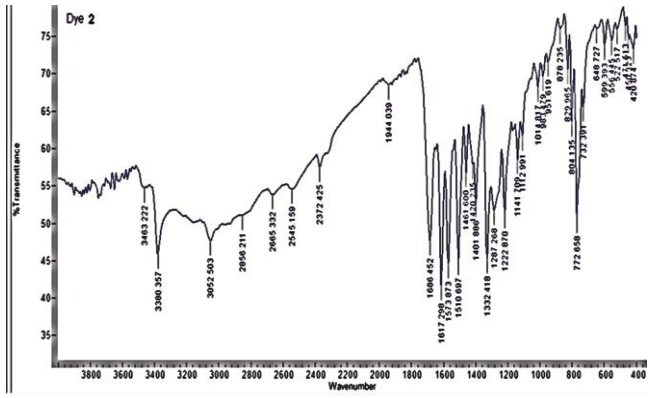


Fig 9. IR Spectrum of dye (2).

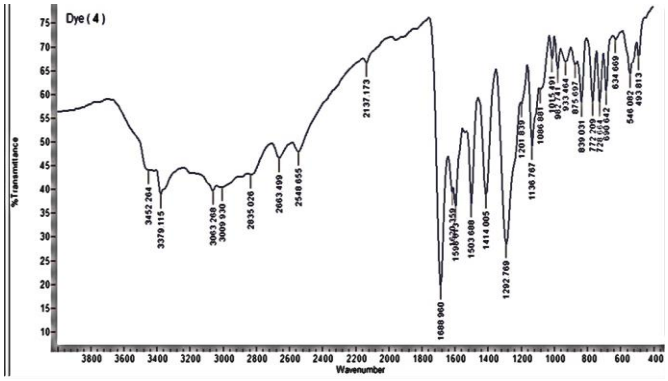


Fig 10. IR Spectrum of dye (4).

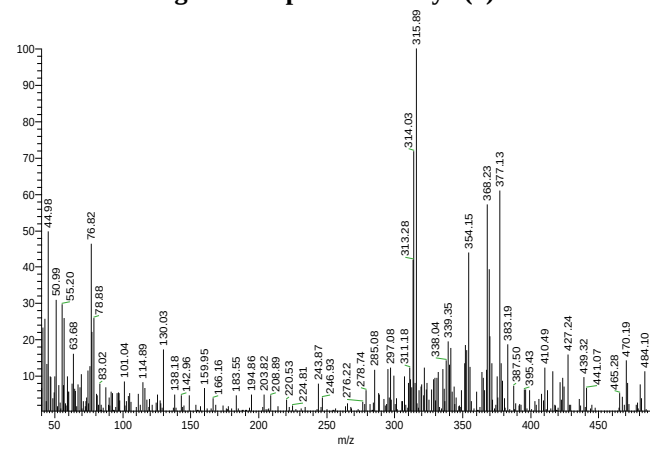


Fig 11. Mass spectrum of dye (4).

IV. Conclusion

The K/S values of dyeing of polyester fabrics carried out by using of HT dyeing method at 130°C were higher than those obtained during carrier, solvent assisted and conventional dyeing methods, which could descend the dyeing temperature to about 100°C.

A novel simple and efficient route to the synthesis of hetero-aromatic compounds as an intermediate for disperse dyes were also discussed.

This observation can be explained that the adsorption of dyes is an exothermic reaction process, resulting the freedom of dyes movement increases after adsorbing to the fibers. The character of dyes in dyeing conform to disperse dyeing, it can prove that dyes can be used as disperse dye. But the dyeing temperature should be 130℃.

References

[1] Al-Etaibi, A., M.A. El-Apasery, and M.M. Kamel," Dyeing of polyester with disperse dyes: Part 1. Antimicrobial activity and dyeing performance of some disperse dyes" Int. J. Curr. Microbiol. Appl. Sci,. 4, 2015: p. 923-928.

[2] Mathur, M.R., M. Sankhe, and M. Bardhan, "Energy conservation in wet processing: Development of low energy dyeing machine". Man Made Textiles in India, 47(6), 2004 pp. 200-207.

[3] Chakraborty, J, "Fundamentals and practices in coloration of textiles", WPI Publishing, 2014.

[4] Shen, J.J. and Y. Yang."Kinetics and thermodynamics studies of prodigiosin dyeing on polyester", in Advanced Materials Research. 2013. Trans Tech Publ.

[5] Derbyshire, A., E. Harvey, and D. Parr, "Solvent-assisted Dyeing of Nylon 6.6 and Polyester Fibres", Coloration Technology, 91(4) 1975, p. 106-111.

[6] Modi, V.P. and H.S. Patel," Synthesis, Characterization of Novel Bis heteroaryl Bis azo Dyes, and Their Dyeing and Solvatochromic Behavior", Heteroatom Chemistry,24(3), 2013, p. 208-220.

[7] Narayana Swamy, V., K.N. Gowda, and R. Sudhakar, "Natural dye from the bark of Casuarina equisetifolia for silk", Int. J. Pharm. Bio. Sci,. 4(3), 2013, p. 94-104.

[8] Maulik, S.R., Studies on kinetic and thermodynamic parameters of natural dye extracted from punica granatum.

[9] El-Apasery, M.A.," Solvent-free one-pot synthesis of some azo disperse dyes under microwave irradiation: Dyeing of polyester fabrics". Journal of applied polymer science, 109 (2), 2008, p. 695-699.