

Synthesis, Spectroscopic, Thermodynamic And Dyeing Properties Of Disperse Dyes Derived From 2-Amino-4-Trifluoromethylbenzothiazole

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ABSTRACT

Monoazo disperse dyes were synthesized using heterocyclic amine by the process of diazotization and coupling. The dyes were synthesized by coupling different components to 2-amino-4-trifluoromethylbenzothiazole. The coupling components used are N,N-dimethylaniline, N,N-diethylaniline, bis(2-cyanoethyl)aniline, 3-acetylamino- N, N-diethylaniline, 5-acetylamino-2-methoxy-N,N-diethylaniline, 2-Naphthol and 1-Naphthol respectively. The different properties of the dyes such as yield, melting point, molecular weight, molecular structure, molar extinction coefficient, degree of exhaustion and wash fastness properties on nylon were analysed. The thermodynamic parameters of the seven dyes on polyester were also investigated. The results showed that the dyes have very good extinction coefficient and excellent wash fastness, thus can be of commercial significance. The standard affinities of the dyes on polyester varied between 10.29 kJmol⁻¹ to 20.60 kJmol⁻¹. The implication of the standard affinities is that dye with $\Delta \mu^0$ 20.6kJmol⁻¹ has highest % exhaustion. [Report and Opinion. 2009; 1(5):58-66]. (ISSN: 1553-9873).

Key Words: Monoazo disperse dye, Diazotization, Exhaustion, Extinction coefficient, Thermodynamic parameters and Standard affinities

1. Introduction

In the early days of dyestuffs, the majority of dyes were prepared from benzene and naphthalene derived intermediates, including heterocyclic dyestuffs such as Mauveine and indigo. However, a recent trend has seen the introduction of an increasing number of heterocycles as dye precursors and nowhere has the impact been felt more than in azo dyes (Griffiths 1976 and Grieder 1976)¹⁻². Numerous heterocyclic dyes are now marketed to the extent that no manufacturer can profess to produce a full range of disperse dyestuffs without handling colorants based on heteroaromatic diazo or coupling components. These dyes are characterized also by having generally excellent brightness and high extinction coefficients, relative to azo dyes derived from substituted anilines. The bathochromic shifts observed with these compounds have been attributed to the sulphur atom imparting enhanced polarizability to the π -electron system. Molecular orbital calculations indicate that the sulphur atom d-orbital are not relevant, and it is the increased diene character of the heterocyclic ring that is responsible for the shifts³

Most heterarylazo dyes of technical interest for application to textiles are derived from diazo components consisting of five-membered rings containing one sulphur heteroatom and to which a diazotisable amino group is directly attached; the ring may also possess one or more nitrogen heteroatom and be fused to another aromatic ring. These diazo

components are capable of providing red to blue disperse dyes that meet the rigorous technical and economic requirements demanded of them by both manufacturer and user. Hence, it was thought to synthesize a series of dyes, prepared from benzothiazole as diazo component, and to examine the dyeing performance of these dyes on nylon fabrics. The relationship between % exhaustion (%E) and the thermodynamic parameter values such as partition coefficient (K), heat of dyeing and standard affinities can be established.

2. Experimental

Materials

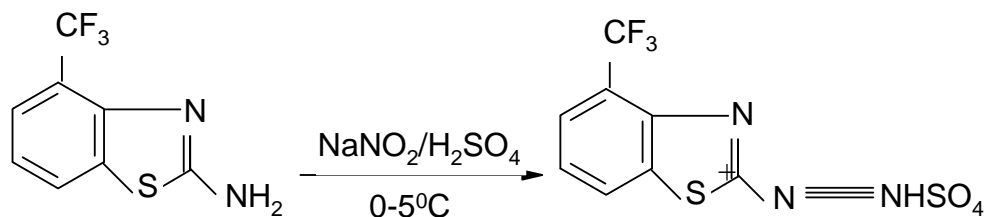
All the chemicals used for the synthesis of dyes (1)-(7) were of commercial grade. All solvents used were either of analytical grade or redistilled commercial grade.

Diazotization of 2-amino-4-trifluoromethylbenzothiazole (Giles1974).

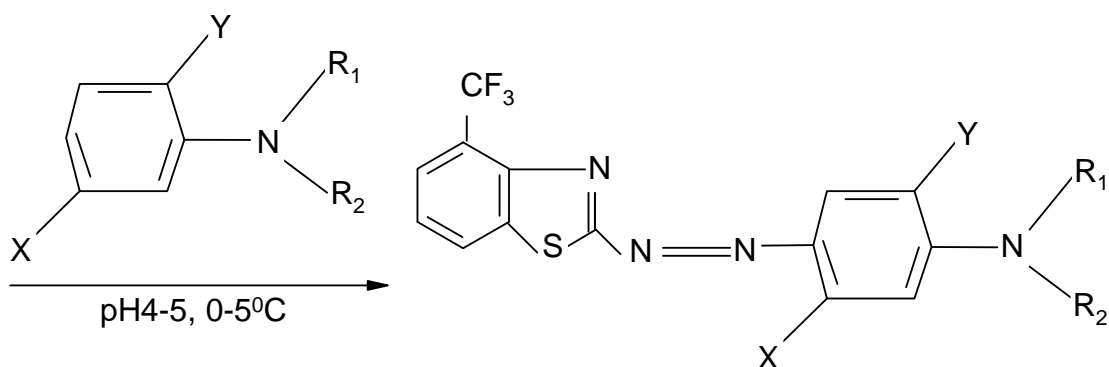
Diazotization was carried out with nitrosylsulphuric acid. A typical example is as follows. Dry sodium nitrite (1.38g, 0.02 mol) was slowly added over a period of 30 minutes with stirring to concentrated sulphuric acid (1.2ml) which was heated on a water bath to keep the temperature at 65°C. The solution was then cooled to 5°C and a mixture (20 ml) of acetic acid-propionic acid (17:3) was added dropwise with stirring, allowing the temperature to rise to 15°C. The reaction mixture was then cooled to 0-5°C, and 2-amino-4-

trifluoromethylbenzothiazole (0.02 mol) was added portion wise and stirring was continued at this temperature for 2 hrs. The excess nitrous acid was decomposed with the required amount of urea. The clear

diazonium salt solution thus obtained was used immediately in the coupling reaction (see Scheme 1 and 2).



SCHEME 1: DIAZOTIZATION OF BENZOTHAZOLE



SCHEME 2: COUPLING WITH ARYLAMINE

Coupling

The coupling reaction occurred readily on adding the resulting diazonium salt continuously to a solution of the coupling component in acetic acid. Frequent addition of ice flakes helped to keep the coupling temperature below 5°C and facilitated the precipitation of the resulting dye. The coupling was usually accompanied by some decomposition; however, by careful addition of the diazonium salt solution at 0-3°C to a solution of the coupling component in acetic acid, good yields of dye were usually obtained. To complete the coupling, particularly when nitrosylsulphuric acid was used in the previous diazotization, the pH of the reaction mixture was adjusted to approximately 4-5. Thus, an appropriate amount of 10% sodium acetate solution was slowly added below 5°C.

Dyeing method

Dyeing of nylon fabric was carried out using a procedure reported in the literature. (Bird, 1975)

Exhaustion study

The percentage dye bath exhaustion of the dyed fabric was calculated by the usual method (SDC, 1978).

Wash fastness test

The wash fastness test was assessed in accordance with IS: 765-1979 (SDC).

General

Melting points were determined by the open capillary method. The visible absorption spectra were measured using (Vogel, 1978) a Spectro UV-Vis Dual Beam 8 auto cell UVS-2700.

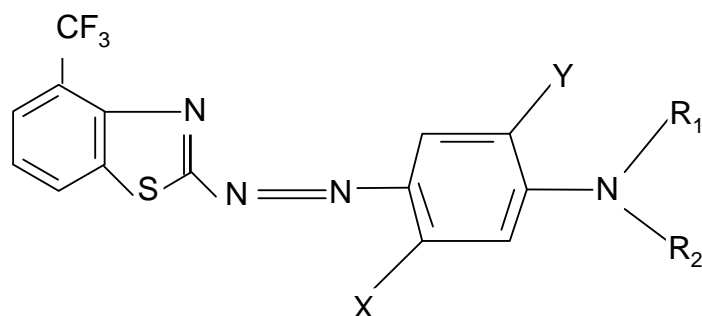
3. Results and Discussion

Synthesis of Dyes

Fig. 1 shows the structures of the seven dyes synthesized. All the dyes were synthesized by diazotizing 2-amino-4-trifluoromethylbenzothiazole using the general method of diazotization of weakly basic amines, and coupled to seven different coupling components namely; N,N-dimethylaniline, N,N-diethylaniline, N,N-bis(2-cyanoethyl)aniline, 3-acetylamino-N,N-diethylaniline, N,N-diethylaniline, 5-acetylamino-2-methoxy-N,N-diethylaniline, 2-naphthol,

and 1-naphthol respectively. The weakly basic amines contain some electron withdrawing groups which make them insoluble in HCl but are soluble in nitrosyl sulphuric acid, (formed by the dissolution of sodium nitrite in sulphuric acid). The different dyes synthesized

possess distinct characteristics as shown in Fig.1. The structures of the dyes synthesized are planar, thus, can lie flat against the polymer molecules. Their planarity accounts for their good substantivity for hydrophobic fibres. (Fierz-David, 1985).



- (1), $R_1 = R_2 = \text{CH}_3$, $X = Y = \text{H}$
 (2), $R_1 = R_2 = \text{C}_2\text{H}_5$, $X = Y = \text{H}$
 (3), $R_1 = R_2 = \text{C}_2\text{H}_4\text{CH}$, $X = Y = \text{H}$
 (4), $R_1 = R_2 = \text{C}_2\text{H}_5$, $X = \text{NHCOCH}_3$, $Y = \text{H}$
 (5), $R_1 = R_2 = \text{C}_2\text{H}_5$, $X = \text{NHCOCH}_3$, $Y = \text{OCH}_3$

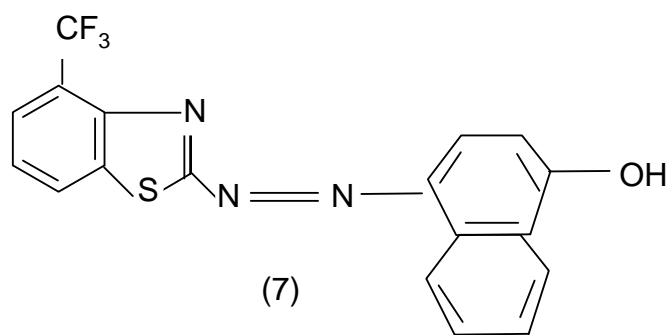
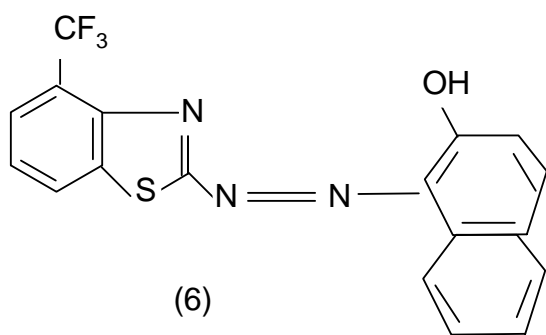


Fig. 1: STRUCTURES OF DYES SYNTHESISED

Spectroscopic properties of the Dyes

The physical characteristics of the dyes are shown in Table 1. The visible absorption spectra of the synthesized dyes in different solvents are summarized in Table 2. Dye (1) which was obtained by coupling the diazo component with N,N-dimethylaniline absorbed at 450nm in acetone and when the N,N-dimethylaniline was replaced with N,N-diethylaniline to give dye (2), the maximum absorption wavelength obtained was 455nm in the same solvent. This results in a red shift of 5nm. When two of the hydrogen atoms of the ethyl group in dye (2) were replaced by cyano group to give dye (3), the resulting dye showed maximum absorption wavelength of 466nm which is more bathochromic than dyes (1) and (2). This was however unexpected since the cyano group is an electron withdrawing group incorporated in the donor ring of the coupler.

Table 1: Physical Characteristics of the Dyes

Dye Number	Melting Point (°C)	Yield (g)	%Yield	Molecular Wt (g/mol)
1	224	1.08	74	378
2	202	0.90	66	350
3	105	0.81	49	428
4	173	0.51	30	430
5	138	0.45	25	465
6	131	0.50	36	373
7	104	1.34	93	373

Table 2: Spectroscopic Properties of the Dyes

Dye Number	Acetone (λ_{\max}) nm	Ethanol (λ_{\max}) nm	Ethanol + HCl (λ_{\max}) nm	$\Delta(\lambda_{\max})$ ethanol-(HCl/ethanol)	Extinction coefficient (ϵ) 1mol ⁻¹ cm ⁻¹
1	450	525	535	+10	40,000
2	455	510	515	+5	28700
3	466	485	540	+55	47100
4	457	485	490	+5	38,200
5	486	560	570	+10	38,000
6	482	486	492	+6	36,600
7	484	489	492	+3	38,400

The introduction of acetamino group into dye (2) gave dye (4) with maximum absorption wavelength of 457nm which is slightly more bathochromic by 2nm when compared with dye (2) and 7nm when compared with dye (1). Increasing the number of electron donating groups by the introduction of methoxy group into dye (4) gave dye (5) with maximum absorption wavelength of 486nm in acetone. This gave a red shift of 31nm when compared with dye (2) and 17nm when compared dye (4). This is the most bathochromic of all the dyes synthesized. This clearly demonstrated that increasing the number of electron donating groups in the coupler ring would produce dyes with enhanced bathochromic shift in the visible absorption region of the spectrum.

Dye (6) was produced by coupling with 2-naphthol, and gave maximum absorption wavelength of 482nm in acetone. This showed that increasing the conjugation of the dye by using naphthalene ring instead of benzene ring led to the production of highly bathochromic dyes. Changing the hydroxyl group from ortho position to the para-position as shown in dye (7) by using 1-naphthol as the coupling component instead of 2-naphthol gave a red shift of 2nm when compared with dye 6. This was however surprising since dye (6) with the hydroxyl group ortho to the azo chromophoric group was expected to be hydrogen bonded and therefore supposed to be more bathochromic than dye (7) in the same solvent.

When the solvent polarity was changed from acetone to more polar ethanol, all the dyes showed red shifts i.e. positive solvatochromism. For example, dye (1) absorbed at 450nm in acetone and 525nm in ethanol, showing a positive solvatochromism of 75nm. Similarly, dye (5) showed a positive solvatochromism of 7nm. This red shift indicates that the excited states of the dyes are more polarized than the ground state and therefore polar solvents stabilized them more in the excited states. It can also be seen from the results summarized in Table 2 that all the dyes exhibited positive halochromism when a few drops of HCl was added to their ethanolic solutions. For example, dye (1) showed a red shift of 10nm on addition of one drop of HCl and dye (3) showed a positive halochromism of 55nm, which is the highest of all the dyes produced.

Effect of Time on Dye Exhaustion

Fig. 2 shows a progression in the percentage exhaustion with increase in dyeing indicating that the longer the dyeing time, the greater the amount of dye molecules absorbed by the fibre, until an equilibrium is attained more dyes penetrate into the polymer at longer dyeing time resulting in high percentage exhaustion and deeper shade. Dye (3) gave a higher exhaustion at the boil for 30min when compared to dyes (5) which has relatively higher molecular weight, 428 and 465g/mol respectively. The naphthol dyes, dyes (6) and (7) have the same molecular weight, 373g/mol each, but their percentage exhaustion at the boil for 30 min varied. Dye (7) gave higher % exhaustion than dye (6) because it is more planar. The ortho position of the hydroxyl group in dye (6) reduces its planarity as compared to the para position in Dye (7).

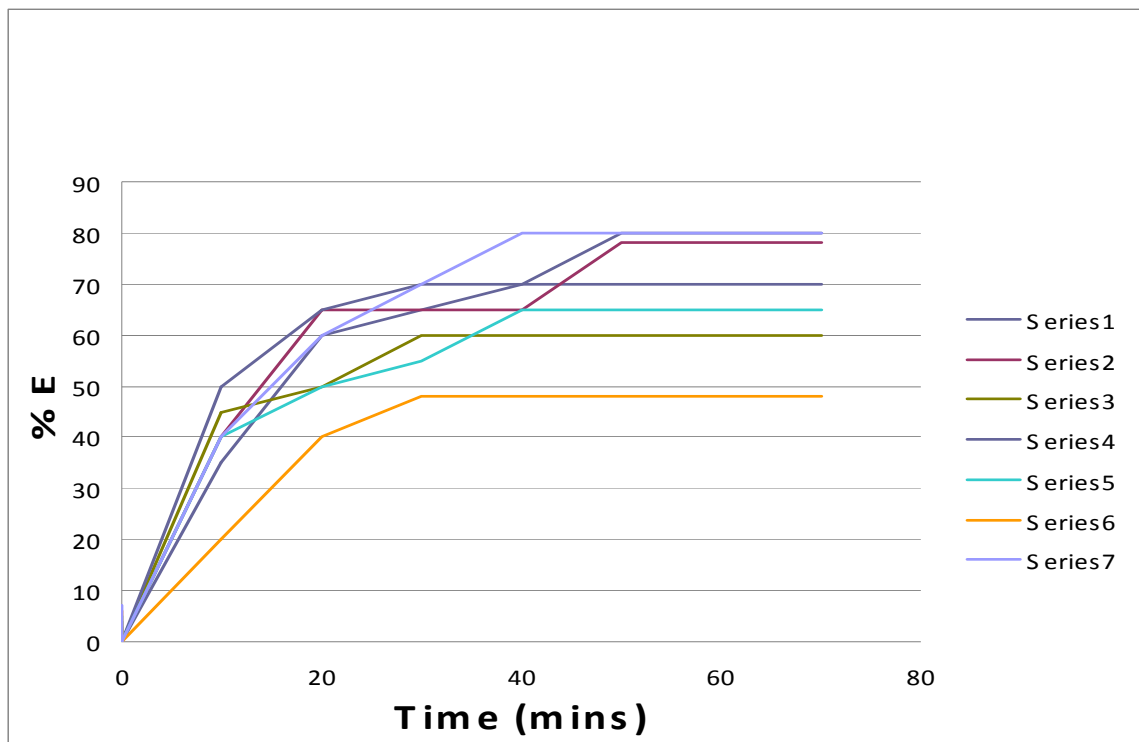


Fig 2: Percentage Exhaustion (% E) at 50°C

It was noted at the course of this research work that all the dyes synthesized showed higher % exhaustion at the longer dyeing time, but it should be however noted, that longer dyeing time will be undesirable in practice as it will increase the cost of fuel and labour cost, and may also lead to damage of the fibre, as a result of prolonged period of contact with the hot dye-liquor¹⁰. Thus it will be profitable to adopt effective means of control of the rate of dyeing using disperse dyes.

Effect of Temperature on Dyeing

It is evidently clear from the results illustrated graphically in Fig. 2-4 that temperature change affects dyeing and the percentage dye exhaustion. All the dyes synthesized and applied to polyamide fibre showed high exhaustion at temperatures near the boil or at the boil. This is so, because, there is greater segmental mobility of the fibre polymer chains at higher temperatures and this cases penetration of dye molecules into the fibre (Moncriff,1975)⁸. At 100°C the % exhaustion of the dyes are 85%, 91%, 74%, 93%, 86%, 57% and 93% respectively for dyes (1) to (7). Dyes (4) and (7) show highest % exhaustion while dye (6) gave the lowest percentage exhaustion of 57% at the boil. In dyeing of polyamides fibres with disperse dyes, temperature control is very essential because, it was noted that while some of the dyed samples showed good levelness at the boil, in some few others there was a little degree of unlevelness.

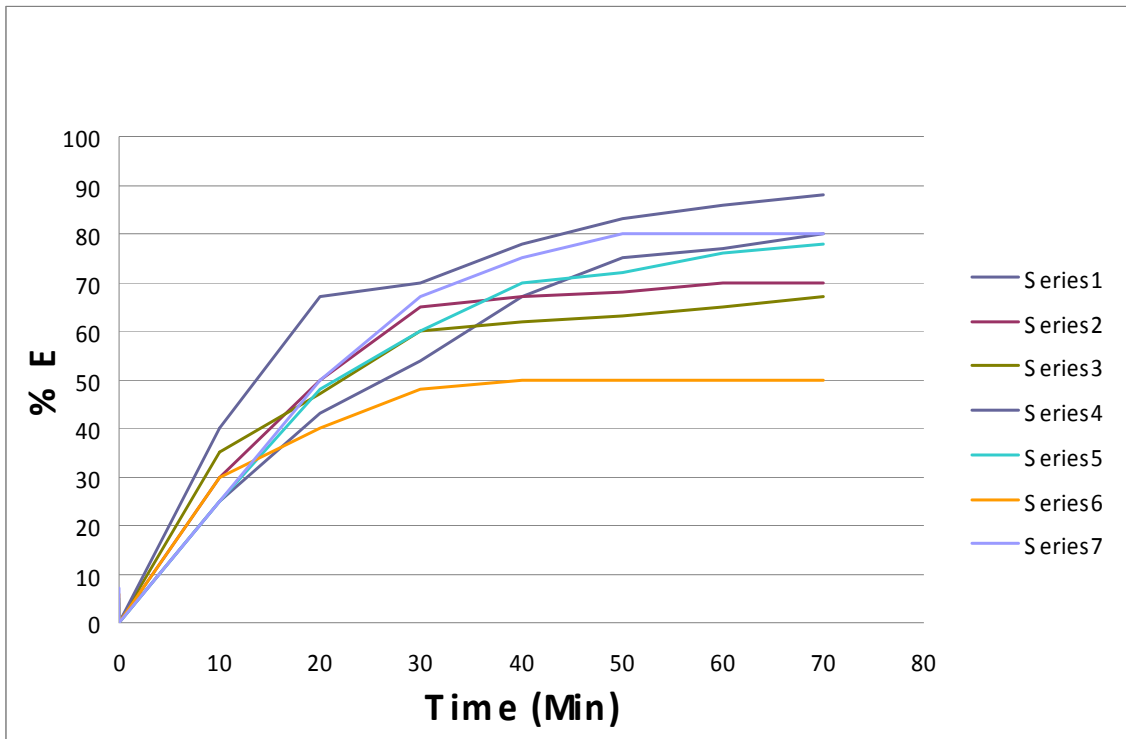


Fig 3: Percentage Exhaustion (% E) at 70°C

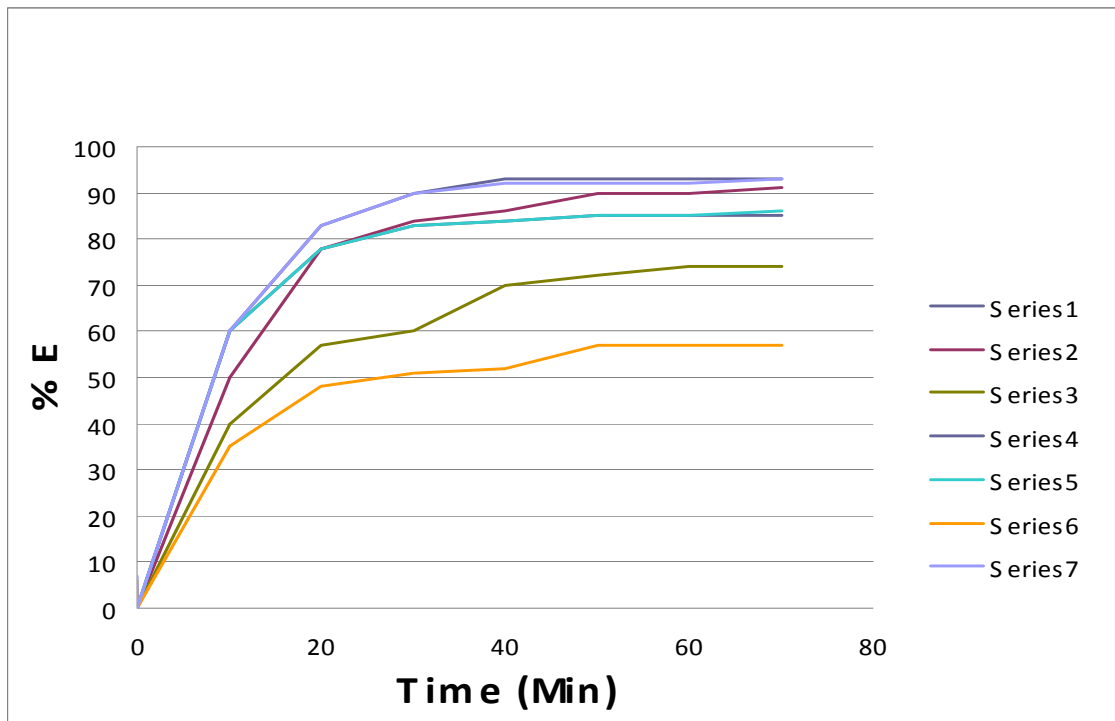


Fig 4: Percentage Exhaustion (% E) at 100°C

Wash Fastness Rating of the Dyes

Table 3 shows the I.S.O 3 wash fastness rating of the dyes synthesized. The results show that all the dyes have very good to excellent wash fastness with corresponding little staining, indicating that all the rating values lies between 4 and 5. The excellent wash fastness of the dyes is due to their hydrophobic character and their polarity, conferred on them by the polar substituent groups. The polar substituent groups on the dye molecules contribute greatly to the strength of the dye-fibre bond. The presence of a donor group on the benzothiazole ring also tends to improve their fastness characteristics. The dyes will also exhibit high light fastness on polyester and nylon and will be useful for transfer printing because the trifluoromethyl group on the diazonium component gives the good thermal transfer characteristics necessary for the sublimation process.

Table 3: Wash Fastness rating of the Dyes

Dyes	Colour Change	Staining of adjacent white
1	4	4
2	4	4
3	4-5	4-5
4	4	3-4
5	4-5	4-5
6	4	4
7	4-5	4

Table 4: Thermodynamic Parameters of the Dyes (1-7) on Polyester

Dye	Equilibrium exhaustion (%E)			Partition Coefficient (K)/l _t kg ⁻¹			Standard Affinity ($\Delta\mu^0$ kJmol ⁻¹)			ΔH^0 of Dyeing kJmol ⁻¹
	50°C	70°C	100°C	50°C	70°C	100°C	50°C	70°C	100°C	
1	70	80	85	116.7	180	283	12.78	14.81	17.51	
2	78	70	91	177.3	300	505	13.91	16.2	19.31	
3	60	67	74	75.0	100	142.0	11.59	13.13	15.38	
4	80	88	93	200.0	380	664	14.23	16.94	20.15	
5	65	78	86	92.9	180	307	12.16	14.81	17.76	
6	48	50	57	46.1	50	66.2	10.29	11.15	13.01	
7	80	88	93	200	375	664.3	14.23	16.89	20.60	

The thermodynamic parameters values are shown in Table 4. A comparison of the standard affinity of Dye 1 and Dye 2 showed an increase in value of ($\Delta\mu$) 1.8kJmol⁻¹. This showed that alkyl groups increase from CH₃ to C₂H₅ (methylene group CH₂) causes increase in $\Delta\mu$ of 1.8kJmol⁻¹. This is in line with the finding of (Meggy *et al*) and Bello *et al* (2006). These results also agreed with the finding of previous workers (Bhattacharyas *et al*). On the other hand, a comparison between Dye 2 and Dye 5 showed a decrease of ($\Delta\mu\theta$) 1.55kJmol⁻¹. This is caused by the OCH₃ and NHCOCH₃ in the ortho and meta position respectively. The substituents in the ortho and meta positions are election withdrawing and therefore reduces, the election cloud on nitrogen, despite the fact that C₂H₅ groups are election releasing.

Comparison of Dyes 4 and 5 is even more interesting, Dye 4 has equilibrium exhaustion %E of 93% while Dye 5 has 84%. The corresponding standard Affinities for Dye 4 and 5 are respectively 20.15 kJmol⁻¹ and 17.76 kJmol⁻¹ respectively. The decrease is $\Delta\mu$ of 2.39 kJmol⁻¹ is caused by the presence of OCH₃ in the ortho position in Dye 5 instead H as in Dye 4. For Dyes 6 and 7, the position of the OH seemed to be a major factor in equilibrium exhaustion of the Dye on fabric (polyester) Dye 7 is more polar than dye 6. There seems to be a similarity between results of spectroscopic studied for these dyes and their thermodynamics parameter values.

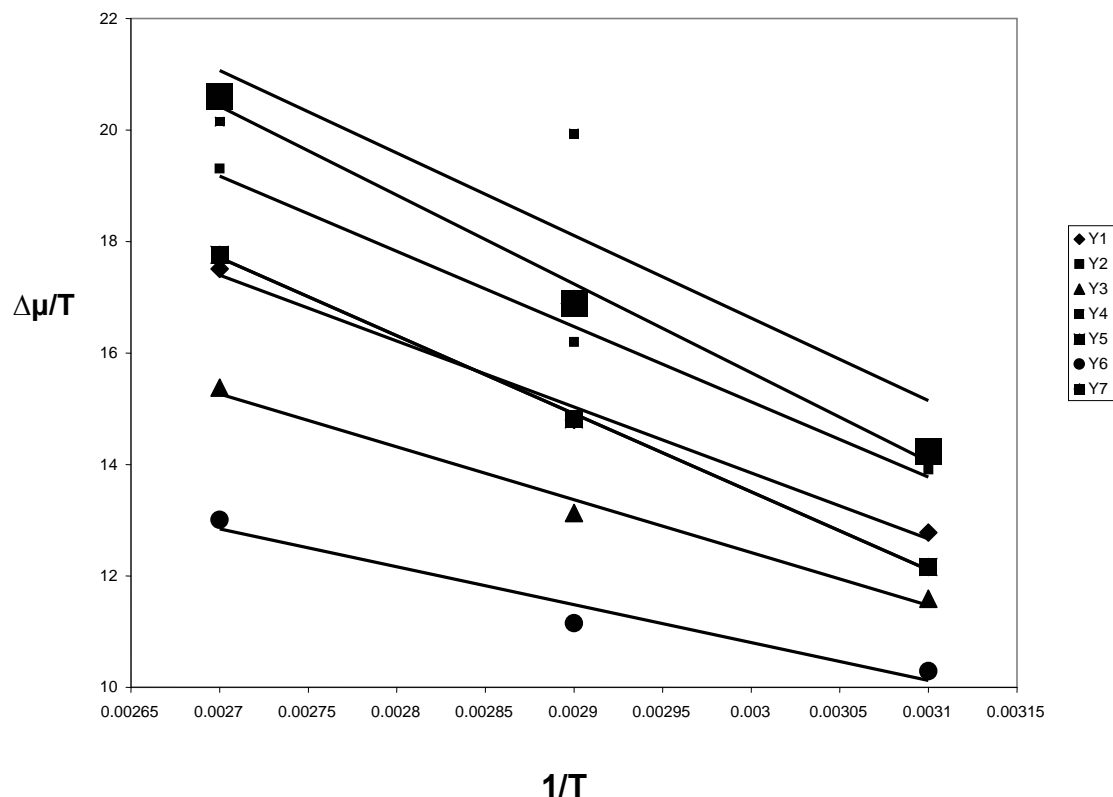


Figure 5. Plot of $\Delta\mu/T$ versus $1/T$ for dyes 1- 7

4. Conclusion

Monoazo disperse dyes containing N, N-dialkylaniline and naphthol coupling moieties have been prepared from 2-amino-4-trifluoromethylbenzothiazole. The dyeing and fastness properties of these dyes have been examined and found to be excellent. A gamut of colour shades ranging from red to blue was obtained by applying the variously substituted dyes on nylon. Bathochromic colours were observed by increasing the numbers of electron donating substitutes and also increasing the conjugation of the coupler ring. The dyes provided a wide range of deep and bright shades on nylon. These dyes gave good exhaustion and level dyeing.

The thermodynamic parameters values of the Dye were determined and the standard affinity ($\Delta\mu^0$) values ranged between 15.38 and 19.31 kJmol^{-1} and the showed that the exhaustion of a particular Dye increases with increase in methyle group (CH_2) of the substituent. The results also showed that decrease in the equilibrium exhaustion and standard affinity decrease with introduction of electron withdrawing groups such as OCH_3 .

For dyes 6, and 7, the standard affinities, at 100°C are 13.0 and 20.6 kJmol^{-1} and the equilibrium exhaustions are 57% and 93% respectively. The pattern

of the results of spectroscopic study and the thermodynamic parameter values for these dyes followed the same explanations. In other words the thermodynamic values of these dyes could serve as models for predicting the spectroscopic values of other similar dyes in the series.

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