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Effect Of Position of Substituents on the Exhaustion and Thermodynamic Parameters of 6 Monoazo Acid and Disperse Dyes on Nylon 6

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Abstract

Six monoazo acid and disperse dyes were synthesized using compounds of aromatic amine by diazotizing sulphanilic acid, 4-nitroaniline, sulphanilic acid, and 3-aminophenol. The coupling components used were 1-naphthol and 2-naphthol. The different properties of the dyes such as molecular structure, molar extinction coefficient, and percentage exhaustion were determined. The thermodynamic parameters of the four dyes on nylon fabrics were also determined. The results showed that the dyes have very good extinction coefficient, thus can be of commercial significance. The standard affinities of the dyes on nylon varied between 8.59 $kJmol^{-1}$to 25.51 $kJmol^{-1}$implying very high equilibrium % exhaustion. The implication of the standard affinities is that dye with $-\Delta\mu^0$ 25.51$kJmol^{-1}$ has the highest % exhaustion, which means that there are correlation between standard affinity of a dye on fabric and the equilibrium exhaustion.

Keywords: Monoazo acid, disperse dye, Diazotization, Exhaustion, Extinction coefficient, Thermodynamic parameters, Standard affinities

1.0 INTRODUCTION

There is considerate technical interest in dyes with absorption maxima in certain regions of electromagnetic spectrum. The effect of substituents and indeed the position of substituents will have significant effects on the absorption of the dye. The technical interest in the regions the dyes absorb is borne out of the feelings that they have potential application in areas such as laser and optical data storage technology. There is little record or data as regards those dyes that can absorb and those substituents (electron withdrawing or electron donating groups) that will enhance absorption shift to the red region and even beyond.

So, this work gave an experimental survey of the effect of substituents on the absorption of the dye. The thermodynamic parameter values are also investigated. This will give a data bank on the relationship between the spectroscopic data and thermodynamic values.

2. Materials and Method

2.1 Materials

Nylon fibre
wool fibre

2.2. Method

The principal method of forming azo dyes involves **Diazotization** of primary amines, followed by **coupling** with hydroxyl or amino derivatives of aromatic hydrocarbons or with hydroxyl or with certain aliphatic keto compounds.

2.2.1 Diazotization

Diazotization simply means formation of diazonium salts. Primary aromatic amine on reaction with nitrous acid (HONO) in the presence of hydrochloric acid (or other mineral acid) at 0-5°C yields diazonium salts as discrete intermediate. The diazonium salts similarly derived from aliphatic primary amines decomposes readily even at this temperature to yield the corresponding alcohol (and other products) with the evolution of nitrogen.

$$Ar.NH_2 + NaNO_2 + 2HCI \longrightarrow Ar.N \equiv \overset{+}{N}\}CI. + \overset{-}{N}aCI + H_2O$$

Ar = Aryl

2.2.2 . Coupling

Azo compounds are prepared by the interaction of a diazonium salt with a coupling agents like phenols in the presence of NaOH or with an amine in the presence of sodium acetate (CH_3COONa). The coupling reaction is an electrophilic substitution involving the diazonium ion which reacts at the position of greatest electron availability i.e. the position ortho – or para – to the electron releasing phenoxyl/amino groups.

2.3 Experimental

2.3.1 Diazotization

10.5g(0.05mol) Sulphanilic acid was diazotized by placing it in a 250ml conical flask, followed by addition of 2.65g (0.025mol) of anhydrous sodium carbonate and 100ml of water, the mixture was shaken and a cloudy solution (or milky solution) was obtained, this solution was warmed until a clear brown solution was obtained. The solution was cooled under the tap to about 15°C, and then a solution of 3.7g (0.059mol) of sodium nitrite in 10ml of water was added to give orange solution. The resulting solution was poured slowly and with stirring into 600ml beaker containing 10.5ml of conc hydrochloric acid and cooled in an ice bath to 0° - 5°C before reaction occurred. The reaction mixture was left in an ice-bath for 15minute. Fine crystals of the diazobenzene sulphonate separated out. And it was kept in solution for the next preparation i.e. in suspension (i.e. yellow crystal).

2.3.2 Coupling

7.2g (0.05mol) of a good grade p-naphthol was dissolved in 40ml of cold 10% Sodium hydroxide solution in a 600ml beaker, a light brown solution was obtained and cooled to 5°C. To this solution, the well- mixed suspension of diazotized sulphanilic acid was poured with stirring, coupling takes place readily and the dyestuff separates as a crystalline paste. The mixture was stirred well and after 10minutes, the mixture was heated until all the solid has dissolved. 20g of NaCl was added (to decrease the solubility of the product further) and the mixture was warmed until it dissolves. The solution was allowed to cool in air spontaneously for 1 hour, and then cooled in ice until crystallization was complete. (The crystal is orange in colour i.e. Dye). The product was collected on a Buchner funnel by applying gentle suction.. It was then washed with a little saturated salt solution, and dried at 80°C. The product weighed about 22g, and contained about 20% of NaCl. Further purification is unnecessary for dyeing purpose.

3. Results and Discussion

3.1 Light Absorption Properties

The visible absorption spectroscopic properties of the monoazo disperse and acid dyes were recorded in H_2O. The absorption maxima (λ_{max}) of the dyes fall in the range 340- 484nm in H_2O and the values are given in Table 2. The values of the logarithm of molar extinction coefficient (log ε) of all the dyes were in the range of 4.0-4.73, consistent with their high absorption intensity.

It is an established fact that the wavelength values tend to be related to the strength of the electronic power in the aromatic system (1). Consequently the electronic transition in these compounds involves a general migration of electronic density from the electron- donating half or the chromogen toward the electron-acceptor half (azo group), bathochromic shift in usually achieved by placing the substituent in the position ortho or para to the azo group for effective conjugation (2,3)

Moreover, an electron attracting substituent such as – SO_3H and NO_2 in the structure of the dyes increases the polarizability and will result the bath chromic shifts.

This leads to an increase in the energy between the highest occupied molecular orbital and the lower unoccupied molecular orbital and thus the $\pi \rightarrow \pi^*$ electronic transition occurs with a lower frequency photon, resulting in a bathochromic shift of the visible absorption[4].

For instance, Dye (E_1) which contains an electron withdrawing group (-SO_3H) absorbed at 484nm in water and when this electron attractor group at the para position to the azo group was replaced with nitro group (NO_2) to give Dye (E_2), the maximum absorption wavelength obtained was 488nm in the same solvent This results in a bathochromic shift of 4 nm, and this is due to the longer conjugation effect exerted by the nitro group which has a more powerful electron- withdrawing property.

The introduction of another nitro group at the ortho position to the azo group into Dye (E_2) gave dye (E_3) with maximum absorption wavelength of 476nm. This gave a blue shift of 12nm when compared with (E_2). This could be due to the steric hindrance caused by the newly introduced nitro group on the existing chromophores because electron systems conjugate best when the molecule is planar in configuration[5]. Therefore the prevention of planarity in configuration of the dye molecule (E_3) by the auxochromic group (NO_2) altered the visible absorption band and could be responsible for the hypsochromic shift.

Dye (E_4) with maximum absorption wavelength of 478nm in water has the same chemical structure as dye (E_1) except for the position or the hydroxyl group. Changing the hydroxyl group from the ortho position to the para position as in dye (E_4) by using 1- Naphthol as coupling component instead of 2- Naphthol gave a blue shift of 8nm when compared with dye (E_1). This was not surprising since dye (E_1) with the hydroxyl group or the azo chromophric group was expected to be hydrogen bonded and therefore supposed to be more bathochromic than dye (E_4) in the same solvent.[6]

Dye (E_5) was prepared by coupling with phenol, and gave maximum absorption of 340nm in water. This reduced λ_{max} values expected when compared with the remaining of the dyes because using phenol as the coupling component as in dye (E_5) instead of naphthol reduces the length of conjugation of the π electron system in the aromatic ring and this was responsible for the lowest λ_{max} value relative to the remaining of the dyes.

3.1.1 Estimation of % Exhaustion (%E) [1]

The exhaustion is obtained from the equation ; %E = Ao-At/Ao x 100,

Where Ao is absorbance at time zero, At absorbance at time

3.1.2 Estimation of Thermodynamic Parameters (Table3)

3.1.2.1 Standard affinity ($-\Delta\mu^o$)

It is the measure of the driving force in any dyeing process. Dyeing of nylon with these monoazo dyes corresponds to the partition mechanism, and hence the standard affinity ($-\Delta\mu^o$) of the dyes for nylon fabric was calculated using the following equation

$$-\Delta\mu^o = RT\ln\left({[D_f]} \big/ {V \times [D_s]} \right) = RT\ln K_v$$

Where R in the unversed gas constant in (kJ K^{-1} mol^{-1}); T, the temperature of dyeing in K ; $[D]_f$, the concentration of dye in the fibre (g/100g of the fabric); $[D]_s$, the concentration of dye in solution (g/L); and v, the colcine term representing the effective volume of water in the substance (L/kg).

3.1.2.2 Heat of Dyeing

Heat of dyeing (ΔH^o) was calculated using the following equation;

$$\Delta\mu = \Delta H^o - T\Delta s^o$$

The heat of dyeing is considered as a measure of binding force of the dye with the fibre. The enthalpy of heat (ΔH^o) is depicted as energy of broken bonds minus energy of the formed bonds. The greater the value of energy formed between the fibre and the dye the more stable the dyeing will be. If this value is greater than the energy of the broken bonds, the heat of dyeing is negative. Thus more bonds are formed resulting in a negative heat of dyeing.

3.1.2.3 Entropy of dyeing (ΔS^o)

Calculated from $\Delta\mu = \Delta H^o - T\Delta S^o$

The thermodynamic parameter values of dyes (E_1-E_5) on nylon are presented in Table III. Dyes E_1 and E_4 are acid dyes while dyes E_2, E_3 and E_5 are disperse dyes.

From the table, All the dyes showed increase in thermodynamic parameter values at each successive / consecutive temperature. Also there is a marked difference in the magnitude of the thermodynamic parameter values between the acid and disperse dyes. At 100^0C the %E of the dyes are 74.85%, 23.45%, 58.12% 96.14% and 60% for dyes E_1-E_5.Dyes (E_1) and (E_4) showed highest %E while E_2 gave the 1owest % E at the boil. The corresponding values of the partition coefficient and the standard affinities of these of these dyes on nylon followed the same trend as the %E. Dyes E_1 and E_4 are acid dyes

This remarkable difference in the magnitude of the thermodynamic parameters between these two classes of dyes (i.e. Acid and desprese dyes) can be attributed to their molecular structures as well as the degree of dye- fibre interactions.

In view of the structure of dyes E_1 and E_4, it is likely that the dye-fibre attraction depends chiefly on one; ionic attraction arises out of electron rich ($-SO_3H$) groups of the dyes and the electron deficient $-NH_3^+$ groups of the protein fibres (charge transfer force) and also on ; two hydrophobic interactions between the hydrophobic of the dye and that of the nylon fibre attached chemically to the amide groups. Owing to the above facts, the higher magnitude of the thermodynamic values of dyes E_1 and E_4 on nylon fabric should be considered as a resultant effect of (i) idealized electrostatic attraction of the dyes operative predominantly for the protonated nylon fibres under acidic condition and of (ii) the idealized hydrophobic attraction operative between the dyes and the fibres.

Dyes E_2, E_3 and E_5 have lower values of %E and $-\Delta\mu^0$ when compared with the acid dyes E_1 and E_4, meaning that the disperse dyes did not bind easily with the nylon fabric like acid dyes. In view of the structure of these dyes, they contain few number of ionic groups and they are less available and less accessible for the positively charged nylon substrate. However, disperses dyes fix in the fibre largely by physical entrapment of the insoluble dyes within the fibres[1].

By way of comparison, dyes E_1 and E_4 have the same molecular weight 350g/ mol each, but their %E and $-\Delta\mu^0$ values varied near or at the boil. Dyes E_1 has %E of 74.85% while dye E_4 has %E of 96.14%. Their corresponding standard affinities are 18.97 and 25.51 kJ mol^{-1} respectively at 100^0C. Dyes E4 gave higher % E and $-\Delta\mu^0$ because it in more planar. The ortho position of the hydroxyl group in dyes (E_1) reduces its planarity as compared to the para position in dye E_4.

Dye E_2 and E_3 have similar chemical structure except for the addition of nitro group (NO_2) in the ortho position to the azo group in dye E_3. At 100°C the E% of dyes E_2 and E_3 are 23.45 and 58.12% respectively. The corresponding standard affinities are 11.87 and 16.55 kJ mol^{-1}. Considering the structure or these two dyes, there are more number of oxygen atoms in dyes E_3 when compared with E_2, therefore the contribution of hydrogen bonds in the absorption of these dyes into nylon fibre cannot be precluded and the resultant effect of this on dye E_3 in the increased standard affinity. The dyes with higher standard affinity has higher value of %E.

Dye E_5 has the leastr value of % E and $\Delta\mu^o$ when compared with E_2 and E_3. At 100°C, Dye E_5 has % E of 60% and $\Delta\mu^o$ 17.5 kJ mol^{-1}. The planarity and the reduced molecular weight of this dye seemed to be the major factor responsible for the increased thermodynamic parameter values when compared with E_2 and E_3.

3.2. Effect of Temperature on Dyeing

It is evidently clear from the result presented in table III that temperature affects dyeing and the percentage exhaustion. All the dyes synthesized and applied to the polyamide fibre showed high exhaustion near the boil or at the boil. This is because, there is greater segmental mobility of the fibre polymer chains at higher temperature and this eases penetration of dye molecules into the fibre.

Also, increase in dyeing temperature from 50°C to 100°C resulted in common increase in the value of standard affinity during the application of nylon (polyamide fibre). Increase in kinetic energy of the system, reduction in viscosity [9] and increase of swelling of the substrate [11] with consequent accessibility are the facts responsible for the increased affinity of the dye for the substrate.

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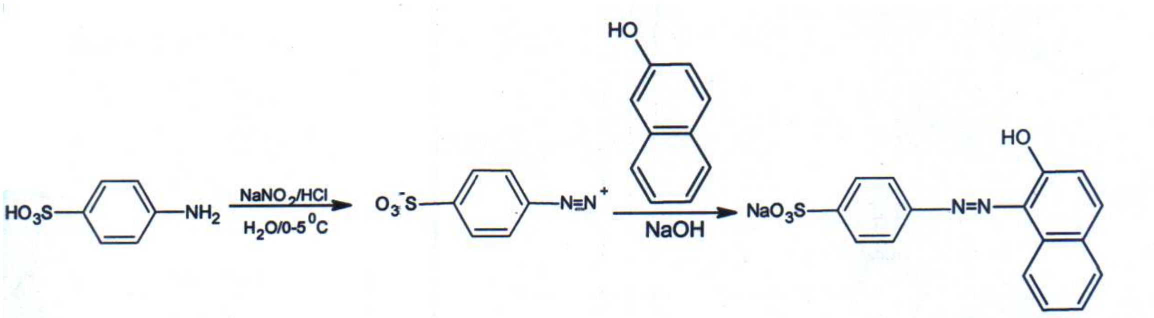

Figure 1 : Reaction scheme for diazotization and coupling for dye production

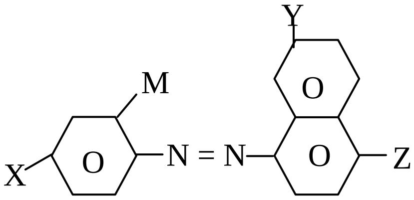

Table 1 Structures of the dyes

	X	Y	Z	M
1	NaO_3	OH	H	H
2	O_2N	OH	H	H
3	O_2N	OH	H	H
4	NO_3S	H	OH	H
5	H	H	OH	H

Table 2:- **Absorption maximung in H_2O(λ_{max}) and the molar extinction coefficients E and log Ɛ for Dyes**

Dyes No	**λ_{max}/nm**	**Ɛ /k $mol^{-1}cm^{-1}$**	**LogƐ**
E_1	484	34,674	4.54
E_2	488	53,703	4.73
E_3	476	29,512	4.47
E_4	478	21,877	4.84
E_5	340	10,000	4.0

Table III: Thermodynamic Parameter of Dyes (E_1-E5) on Nylon

Dye	**Equilibrium Exhaustion %E**			**Partition Coefficient (K) LKg^{-1}**			**Standard Affinity ($\Delta\mu^o$ kJmol^1)**			**ΔH^o heat of dyeing (kJmol^{-1})**	**ΔS^o entropy of dyeing (J mol^{-1}K^{-1})**
	50°C	**70°C**	**100°C**	**50°C**	**70°C**	**100°C**	**50°C**	**70°C**	**100°C**		
E_1	60.44	63.85	74.55	229.17	264.95	446.42	14.59	15.91	18.92	-12-72	51.4
E_2	12.96	16.92	23.45	22.26	30.54	45.95	8.59	9.75	11.87	-18.44	81.0
E_3	22.71	30.96	58.12	44.07	67.27	208.17	10.17	12.00	16.55	-30.63	45.4
E_4	97.12	96.80	96.14	5061.69	4539.42	3740.48	23.61	24.71	25.513	-9.39	43
E_5	30.0	42.0	62.0	46.1	50.0	66.2	13.4	13.4	17.5	-10.5	50.2

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