

## KINETIC AND THERMODYNAMIC PROPERTIES OF DYEING ACID DYES DERIVED FROM P-AMINOTOLUENESULPHONE-N-ETHYLANILIDE ON WOOL AND NYLON 6.6

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### Abstracts

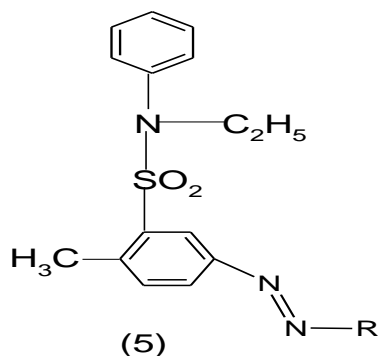
*Kinetics and thermodynamics of dyes derived from p-amino toluene sulphone-N-ethylanilide as diazocomponent on wool and nylon 66 substrates are hereby reported. The activation energy of diffusion decreased as the number of sulphonic acid groups increased. It was also observed that dyes that exhibited azo-hydrazone tautomerism gave lower activation energies than identical dyes that did not show the same effect. Monosulphonated dyes recorded higher values of heat and entropy of dyeing than the disulphonated ones.*

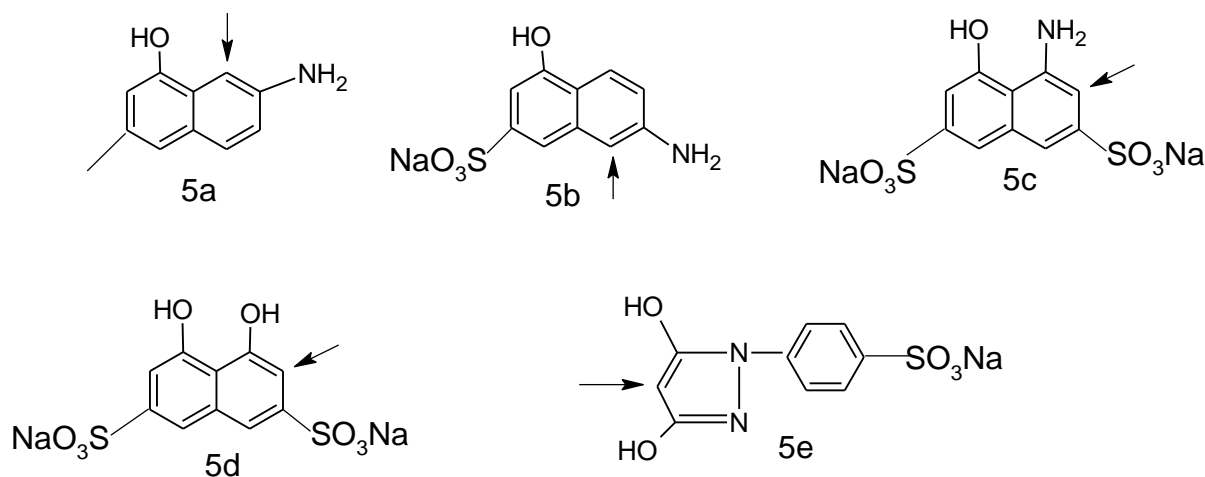
### Introduction

In the first part of this work we reported some physical characteristics of the dyes under study [1]. The influence of intramolecular associations was highlighted both in relation to colour and performance on the substrates. In this part we investigated the thermodynamics and kinetics of dyeing on wool and nylon 66 fabrics.

Kinetics of dyeing deal with the speed at which dyes enter and diffuse through the whole matrix of the fibre, influencing properties such as migration, levelness and fastness. The study is also used to determine dyeing economics as well as for dye-matching. Results of diffusion coefficient at different temperatures also enable the computation of activation energy which gives an idea of the magnitude of resistance posed by the matrix to the penetration of the dye molecules. The thermodynamics of dyeing on the other hand measures the quantitative estimate of the degree of driving force leading to the attraction between the dye and the fabric. From the evaluation of the heat of dyeing, the nature of the bond type i.e hydrogen bonding, Vander waals forces of attraction etc can be determined. Estimation of entropy of dyeing gives the balance of orderliness or otherwise of the process; thereafter the nature of interactive forces and consequently the anticipated fastness properties can be made

### Experimental





Arrow indicates point of coupling

### Determination of Diffusion Coefficient

Fabric Samples (0.025g) each, was dyed using 20% shade, at pH4 and Liquor ratio 400:1, at 60°C and 80°C. Enough time was allowed for temperature to stabilize before dyeing commenced. The time of dyeing was varied from 0-50min at 5min intervals. For each of the dyeings, a sample was allowed to stay for 24hrs. At the end of these periods, 20% pyridine (10cm<sup>3</sup>) was used to strip the dyes from nylon fabric at the boil and 5% NaOH (10cm<sup>3</sup>) was used to dissolve the dyed wool. The solutions were then diluted to the 50cm<sup>3</sup> mark with distil water in each case. Absorbances of these dyes were read up a Corning Colorimeter 253 at the  $\lambda_{max}$  of the dyes [1]. Calibration curves were earlier made with the respective blank solutions; straight lines were obtained for all the dyes in the two solvent systems.

The absorbances given by the stripped dyes at various intervals were represented ( $m_t$ ), whereas the absorbances of the stripped dyes for 24hrs gave ( $m_o$ ). These enabled  $m_t/m_o$  against  $t_{1/2}$  plots [2]. Activation energies were calculated according to the following equation (1). The method was used according to the approximations made by Vickerstaff [3] where a non-steady state condition for an infinite bath was assumed, by such assumptions; Fick's second law reduces to:

$$\frac{m_t}{m_o} = 2\sqrt{Dt/\Pi} \quad (1)$$

When the diffusion coefficients of the two temperatures were computed, the activation energy was calculated using Arrhenius equations, which for two coefficients at two temperatures reduced to equation (2):

$$\ln \frac{D_2}{D_1} = \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (2)$$

Where  $D_1$  and  $D_2$  are the diffusion coefficients at absolute temperatures  $T_1$  and  $T_2$  respectively.  $R$  is the gas constant and  $E$  is the activation energy in joules/mole. The results are summarised in Table1.

Table 1: Diffusion coefficient and activation energy on wool and nylon 66 fabrics

Dye No	Diffusion coefficient x 10 <sup>-5</sup> (sec <sup>-1</sup> )				Activation energy ( J/mole)	
	Wool		nylon		Wool	Nylon
	333K	353K	333K	353K		
5a	1.012	4.596	0.631	1.385	73978	38425
5b	0.962	3.632	1.288	1.964	64932	20596
5c	0.616	1.964	0.0917	2.781	56682	167611
5d	1.476	2.781	0.558	2.507	30969	73466
5e	1.257	4.243	0.874	1.878	59482	37418

### Determination of the thermodynamic Parameters

The direct method of determining affinity was used [3, 4]. Samples (0.05g), Shades 2 & 8%, liquor ratios 10:1 and 200:1, times 48 and 96 hrs, temperatures 80°C and 96°C. The samples were placed into the dyeing test-tubes well covered to discourage evaporation and after the temperatures of treatments were attained.

The absorbances of the dye liquors were determined before and after making necessary dilutions. After dyeing, the dyed samples were cleaned thoroughly with distilled water until no residual dye bled. The dye was then stripped from nylon sample in 20% Pyridine (10cm<sup>3</sup>). Where necessary a second and third strippings were done to ensure that more than 99% of the dye had been stripped from the substrate.

A similar stripping procedure was followed for the dyed wool samples using, 10cm<sup>3</sup>; 5% NaOH solution to dissolve the whole sample. Five different determinations were made for each dye on the two substrates at the two temperatures; using equation (3) the affinity was calculated:

$$-\Delta\mu^o = RT \ln \frac{[D]_f}{v[D]_s} \quad (3)$$

[D]<sub>f</sub> is the quantity of dye in g/kg fabric

[D]<sub>s</sub> is the quantity of dye in g/l solution

v is the assumed internal volume of the substrate; 0.33 l/kg wool and 0.02 l/kg nylon66. The heat of dyeing ( $\Delta H^o$ ) and entropy of dyeing ( $\Delta S^o$ ) were calculated from equations (4) and (5):

$$\Delta H^o = \frac{\left( \frac{\Delta\mu^1}{T_1} - \frac{\Delta\mu^2}{T_2} \right)}{\left( \frac{1}{T_1} - \frac{1}{T_2} \right)} \quad (4)$$

$$\Delta S^o = (\Delta H^o - \Delta\mu^o) / T \quad (5)$$

The results are summarised in Table 2.

### Results and Discussions

It can be seen from the results summarised in Table 1 that the diffusion coefficients of dye 5d derived from chromotropic acid are higher than dye5c derived from H-acid. The activation energies of diffusion for dye 5c are much higher than for dye 5d in both substrates. Both dyes have virtually the same molecular weights, same ionic charge etc. The main difference between them is the relative positioning of substituents; 1-position of the coupling component in dye5c is an NH<sub>2</sub> group whereas it is an -OH group in dye 5d. The implication of the difference in the activation energies is that it is easier to manipulate a molecule of dye 5d than 5c. This is

indicative of the smaller molecular volume for dye 5d than 5c. Another factor that can possibly influence this difference is the degree of aggregation of each dye. The dye that aggregated to a larger extent recording higher activation energy and lower diffusion coefficient is this case is dye 5c. The atomic radius of a nitrogen atom has been assigned 71pm whereas that of oxygen atom 60pm. Similarly the van der waals radii of the elements are 150pm and 140pm respectively [5]; these confirm that dye 5c is bigger than dye 5d. These parameters are enough to justify a lower diffusion coefficient and higher activation energy for dye 5c over dye 5d in both substrates. The bigger volume associated with an  $-NH_2$  group also indicates higher polarisability and as such higher aggregating power which again can bring about higher activation energy and lower diffusion coefficients. As explained elsewhere, the ability of dye 5d to exhibit azo-hydrazone tautomerism accorded it higher intra molecular associations at the expense of inter molecular associations [1]. The consequence of this is less aggregation which is synonymous with lower activation energy and higher diffusion coefficients. When dyes 5a and 5b are compared, dye 5a recorded higher activation energy than dye 5b. Dye5a has higher intra molecular association which afforded it lower activation energy. This increased intramolecular association impairs mobility to the chains which as anticipated should slow down the speed of the dye inside the pores of the substrate. Conversely the phenomena will lead to loss of inter molecular associations believed to speed up mobility as explained earlier. The factor that controls the phenomena of diffusion in relative term is therefore a balance of these two effects. It appeared that with respect to the difference between dye 5a and 5b it is the loss of flexibility that is the stronger influence because dye 5a recorded higher activation energy in both substrates. However, with respect to dyes 5c and 5d, in both substrates dye 5c is the slower dye and the one with the higher activation energy. In this case it is the increased intramolecular association in dye 5d that is responsible and as such the loss of flexibility of dye 5d is less important.

A very important point of note from Table 1 is that the dyes that have only one sulphonic acid group recorded higher activation energies in wool fabric than nylon fabric, where as it is the dyes that have two sulphonic acid groups that recorded higher activation energies on nylon fabric than on wool substrates.

**Table2: Thermodynamic Parameters of the dyes on wool and nylon 66 substrates**

Dye No	Affinity of Dyeing ( $-\Delta\mu^\circ$ ) J/mol				Heat of Dyeing( $\Delta H^\circ$ ), J/mol		Entropy of Dyeing ( $\Delta S^\circ$ ), J/mol	
	Wool		Nylon		Wool	Nylon	Wool	Nylon
	369K	353K	369k	353K				
5a	20486	25261	21716	21970	130609	27244	298	15
5b	21477	24323	24590	26253	87113	60785	178	99
5c	17897	18340	19792	20629	28114	38009	28	49
5d	12245	14551	16943	17374	65427	26324	144	25
5e	15301	1605	20820	21029	31537	25369	44	12

Thermodynamics of dyeing give valuable information on the magnitude of the driving force behind the process, the interplay of forces between all the components in the system resulting from molecular interactions in both the fibre and the dye bath and the extent of orientations of adsorbed dye molecules. Studies on entropy changes also throw light on the influence of hydrophobic bonding in some adsorption systems [9].

The heat of dyeing  $\Delta H^\circ$  is the difference in the heat content between that needed on free one mole of dye from the solvent and that required to free the same quantity from the surface or exterior of the substrate by thermal agitation [6]. It is thus the heat of sorption or the heat content of the system when dye is sorbed. A large negative value of  $\Delta H^\circ$  corresponds to

the idea of high potential affinity. If the heat of hydrogen bonding, salt-linkages and all the other polar Van der waals forces of attractions could be added together, their sum is the heat of dyeing [7].

The entropy of dyeing on the other hand is described as the degree of disorder of the system which is based on probability. The less negative the entropy the higher the entropy gain, and hence, the higher the contribution of the entropy to the overall affinity. However if the entropy is positive as is the case with some dyeing systems, then the higher it is, the greater is the contribution of the entropy gain to the total affinity. Entropy gain due to dye adsorption is related to the increase in entropy due to release of water of hydration when salt linkage is formed. Otherwise the entropy gain should be negative as the free moving dye molecules get confined in a fibre. Higher contribution of entropy to affinity has been related to higher hydrophobic and other non polar van der waals forces of interactions [8, 9]. The dyeing process which is the adsorption of negatively charged dye anions to a surface with a negative surface potential is believed to be driven by the intrinsic affinity of the dye anion. Initially, when the negatively charged dye anions are adsorbed, the increase in the surface potential due to the adsorbed dye would lead to electrostatic repulsion of further anions. But this will lead to a saturation or thermodynamic equilibrium when the decrease in free energy due to adsorption and the increase in the surface free energy due to the increase in the potential are equal.

A survey of the affinities of the dyes shown in Table 2 indicates that the disulphonated dye 5c and 5d gave lower values than the monosulphonated ones (dyes 5a and 5b) in all the substrates. These results have been anticipated [10, 11]. Polysulphonated dyes have large negative charges than the monosulphonated ones, as such; the increase in surface potential due to adsorption will be higher even at lower levels of exhaustion. This means that equilibrium will be attained by polysulphonated dyes at lower levels of exhaustion than the monosulphonated ones. Dye 5e derived from pyrazolone being monosulphonated, gave higher values than 5d but lower than 5c. It can further be seen that on both substrates, dye 5c gave higher dye affinity than dye 5a. The main similarity between dyes 5d and 5a is the ability to display higher intramolecular association as a consequence; this will reduce aggregation which will lead to decrease in affinity. At higher temperatures the dyes recorded higher affinities on nylon than on wool. One explanation for this is that the wool substrate contains about 30% water which hydrates the charged sites of adsorption; this is quite significant compared to about 3% in nylon. These hydrated sites will reduce the coulombic driving force on union with the negatively charged dye anion [4, 9].

It was observed that with the exception of dye 5c, the dyes recorded higher heat of dyeing on wool. This may be accounted for by the higher polar forces of attraction on wool for the dyes. In other words, hydrogen bonding and polar van der waal forces of attractions are greater on wool substrates than on nylon which is also more crystalline. It is the formation of these polar bonds that further aided adsorption process by eliminating hydrated water molecules around the polar groups on the dye and the substrates. This would enable the dye molecule approach sufficiently close to the fibre so that the dispersion forces can aid the binding of the dye to the surface. In contrast the entropy gain is higher on nylon substrate with the exception of dye 5e. This can be explained from two points of view; firstly, the release of the more highly ordered hydrated water molecules from the polar sites on the wool will rather bring more disorderliness in the system. Secondly, with the more hydrated water molecules on wool, the higher degree of crystallinity in nylon will make for preponderance of hydrophobic and the other non-polar forces of attraction on it, rather than on wool. Both factors made nylon record higher entropy gain. In summary, heat of dyeing contributed more to the observed affinity terms on wool, whereas it is the entropy component that contributed to the higher affinity observed on nylon. It could be seen that to a certain extent the affinity ratings of the dyes especially on wool tallied with those of fastness ratings reported earlier [1].

## Conclusion

From the kinetics and thermodynamics of dyeing of p-aminotoluene sulphone-N-ethylanilide derived dyes, it is observed that as the number of sulphonic acid groups increased, the activation energy of diffusion decreased on wool. On nylon, the activation energy of diffusion decreased with increase in the number of sulphonic acid groups. It was also observed that dyes that exhibited azo-hydrazone tautomerism i.e 5d recorded lower activation energy than those that did not exhibit it i.e dye 5a. Whereas those that exhibited increased intramolecular hydrogen bonding such as dye 5a, recorded higher activation energy compared to those that did not show the effect. In the former case reduced degree of aggregation explained the finding and in the latter, loss of flexibility was cited as the main reason. The monosulphonated dyes recorded higher affinity, higher enthalpies and entropies of dyeing than the disulphonated ones. This is ascribed to the increased negative surface potential on the substrates by the adsorption of the disulphonated dyes leading to less exhaustion due to repulsion with the result that the monosulphonated dyes are exhausted to a higher extent.

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