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Structure–Affinity Relationships in Aminoazo Disperse Dyes. A Multivariate Approach

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ABSTRACT

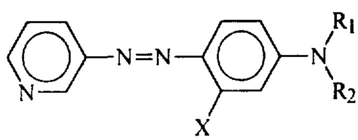
The standard affinity for silk of nine pyridine disperse dyes has been measured. By means of principal component analysis the data have been compared with affinities on nylon and acetate using experimental and theoretical descriptors as explanatory variables, calculated by semiempirical and molecular mechanics methods. The results obtained show that silk can be coloured with disperse dyes to give dyeings of fair quality and its dyeing behaviour resembles that of nylon more than acetate. The presence in the dye molecule of basic centres that can form hydrogen bonds with the polymeric chains is advantageous for the affinity, but hydrophobic interactions also play an important role in the dye–fibre binding. © 1998 Elsevier Science Ltd

Keywords: aminoazo disperse dyes, affinity, structure, silk.

INTRODUCTION

In previous papers [1, 4] we observed that disperse dyes usually employed for colouring cellulose acetate and nylon could also be used to dye natural fibres. Applied on silk [3] these dyes generally reached wet and light fastness scores better than those of acid dyes of the molecular weight. These results suggested that the dyeing of silk with selected disperse dyes could be promising for practical uses, chiefly on account of the facility and cheapness of the dye synthesis and the ease of application.

To better assess the applicability of these dyes to silk, and to highlight structure–affinity relationships, we now have extended the study to the dyes of Scheme 1. The dyeing properties on silk have also been compared to those obtained on nylon and acetate using the methodologies of the multivariate statistic in order to analyse the global correlation between physico-chemical dye parameters and dyeing behaviour.



$R_1 = CH_3, CH_2CH_3, CH_2CH_2OH, CH_2CH_2CN$

$R_2 = CH_3, CH_2CH_3, CH_2CH_2OH, CH_2CH_2CN$

$X = H, CH_3$

Scheme 1.

EXPERIMENTAL

The preparation of the dyes has been described in previous papers [5]. Commercial silk fabric of weight of 90 g m^{-2} was employed. Silk dyeings and affinity determinations were carried out as previously described [3].

Molecular parameters, formation energy and optimised geometries of the dyes were calculated using PC Model [7] Version 4 and MacroModel [8] Version 3.1 packages. Quantum chemical parameters were calculated by using the AM1 method [9] with standard parametrization. Statistical analysis was carried out using the Statgraphics [10] package.

RESULTS AND DISCUSSION

Table 1 reports the affinity and fastness data for all fibres. From the values, it appears that in general the affinity for nylon is lower than that for cellulose acetate and that the affinity for silk matches more or less to that for nylon. The same trend holds for fastness values. Washing fastness for acetate is in general half a point higher than that for nylon or silk. Nylon and acetate have substantially equivalent light fastness values while the values for silk are generally a half point lower. As we can see, notwithstanding that the affinity for silk is lower than that for acetate or nylon, it reaches fair values, certainly better than those generally achievable by acid dyes of equivalent molecular weights.

The objective of the majority of dyeing studies is to find mathematical relationships between the properties under investigation and one or more

TABLE 1
Affinity at 70°C and Fastness Values of the Dyes on Acetate, Nylon and Silk

Dye	R_1	R_2	*X*	$-\Delta\mu^\circ$ kJ mol^{-1}			*Washing 40°C*			*Light*		
1	Me	Me	H	15.69	14.31	12.31	5	4–5	4–5	6	6	5–6
2	ETH	ETH	H	16.06	14.77	15.82	5	4–5	4–5	6	6	5
3	ETH	ETOH	H	12.71	11.86	10.2	5	4–5	4	5–6	5	4–5
4	ETOH	ETOH	H	10.01	8.84	7.7	5	4	3	4–5	5	4
5	ETOH	H	H	11.29	11.02	7.59	5	5	3–4	5–6	5	4
6	ETCN	ETCN	H	14.63	8.9	9.79	5	4	3–4	6	5–6	5–6
7	ETH	H	Me	17.13	14.49	13.6	5	4–5	4–5	6	6	5–6
8	ETOH	ETOH	Me	11.49	10.53	8.16	5	4	4	5	5–6	5–6
9	ETCN	ETCN	Me	15.39	10.01	10.91	5	4–5	4	6	6	4–5

ET = $-CH_2CH_2-$.
The first column of each group refers to acetate, the second to nylon and the third to silk.

descriptive parameters (descriptors) related to the structure of the dye molecule. This necessarily involves a correlation to many different dye properties (variables) that can be either experimental or calculated. Whatever attempt is made to find correlations between these variables by means of scatterplots would invariably have the effect of reducing an n-dimensional system (where n is the number of variables) to a bidimensional one, and consequently to lose all the information not associated with the investigated variables. In some instances this could be a useful simplification, on considering that sometimes a small number of variables contain the major part of the chemical information whereas the remaining ones add next to nothing to the global information. However, the problem remains to establish which variables are important and which are not in describing the experiment, and hence to make a choice that very often is correlated to subjective criteria dictated by chemical intuition and experience.

In this paper we have analysed the relations between affinity and various dye descriptors, some experimental as solubility and pK, others purely theoretical. Both semiempirical and molecular mechanics methods have been employed.

With regard to the last methods, up to now in studies on structure–activity relationships, a great number of descriptors have been used and the choice among them has generally been a subjective matter. We first took into consideration a large number of quantum-chemical and geometrical variables. Later on, in order to eliminate chemical noise and to retain only the variables useful for the study, we selected those indicated in Table 2. These descriptors were chosen with the intent to characterise bulk and shape, hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) aptitude and polarity of the dyes. However, it should be emphasised that some descriptors can be simultaneously sensitive to different molecular features.

TABLE 2
Descriptors Used Through the Work

Variable	
PK1	pKa value of the pyridine nitrogen[a]
PK2	pKa value of the azo nitrogen[a]
PKA	pKa value of the coupling aniline nitrogen[a]
SDIS	Solubility in 1 $g l^{-1}$ of dispersing agent
SOT	Solubility in *n*-octane
TOR	Torsional energy[b]
VOL	Molecular volume[b]
ELD	Electronic density[c]
DIPM	Molecular dipole moment[c]
SATS	Hydrophobic surface[d]
TOTS	Total surface[d]
UNSS	Unsaturated surface[d]
HBD	Sum of the total net charge values on the hydrogen atoms divided by the number of atoms of the molecule[c,e]
HBA	Sum of the total net charge values on the nitrogen and oxigen atoms divided by the number of atoms of the molecule[c,f]

[a]Ref. 6.
[b]Computed by MacroModel.
[c]Computed by Mopac.
[d]Computed by PC Model.
[e]Taken as measure of the HBD aptitude of the dye.
[f]Taken as measure of the HBA aptitude of the dye.

To find out the relationships among all the dye variables we computed the correlation matrix (Table 3). Since this matrix is very large, we therefore reported only the correlations between affinities and all remaining variables. As expected, affinities are negatively correlated with the aqueous solubilities of the dyes and positively correlated with the solubilities in octane, strongly in the case of nylon and silk and weakly for acetate. The affinities are negatively correlated with the HBD aptitude of the dyes and it therefore seems that the bonds with water are preferred to those with the fibres. In contrast, the affinities are positively correlated with the HBA capability of the dye. The molecular size influences dye affinities for nylon but not for silk and acetate, which evidently are more permeable fibres. From these results it would therefore seem that silk and acetate have very different dyeing characteristics and nylon resembles both of them, perhaps more silk than acetate. To throw more light on the relations between the dye properties and affinity and to attempt to understand which dye variables differentiate mostly the behaviour of the dyes for the fibres, we then carried out a multivariate analysis. By means of the analysis it was possible to make an objective approach to this problem. This statistical methodology in fact allows the simultaneous analysis of all the variables so as to highlight the correlations, and at the

TABLE 3
Correlations Between Dyeing Variables and Descriptors

Variable	*AFAC*	*AFNY*	*AFSI*
AFAC	1.00	0.66	0.88
AFNY	0.66	1.00	0.82
AFSI	0.88	0.82	1.00
WAC	0.00	0.00	0.00
WNY	0.21	0.48	0.22
WS	0.79	0.88	0.83
LAC	0.90	0.53	0.71
LNY	0.88	0.58	0.79
LSI	0.61	0.40	0.46
PK1	0.11	0.76	0.45
PK2	0.11	0.75	0.43
PKA	−0.04	0.68	0.34
SDIS	−0.80	−0.43	−0.85
SOT	0.47	0.70	0.73
TOR	−0.21	−0.32	−0.03
VOL	−0.17	−0.70	−0.28
HBD	−0.61	−0.58	−0.78
ELD	−0.30	−0.77	−0.41
SATS	0.48	0.69	0.77
TOTS	0.00	−0.66	−0.22
UNSS	0.52	−0.10	0.14
HBA	0.93	0.42	0.79

AFAC, AFNY, AFSI = affinity on acetate, nylon and silk.
WAC, WNY, WSI = washing fastness on acetate, nylon and silk.
LAC, LNY, LSI = light fastness on on acetate, nylon and silk.

same time reduce the dimensionality of the problem. In this paper we have used factor analysis and cluster analysis. Fundamentally, factor analysis summarises the information of several variables by extracting linear combinations of them that describe the largest amount of the sample variance. Cluster analysis essentially classifies objects and variables into homogenous groups on the basis of their similarity.

Factor analysis was performed by extracting five factors that describe over 95% of the total variance. Factor loadings are reported in Table 4 and the plot of the scores on the PC1–PC2 plane is shown in Fig. 1. Figure 2 shows the result of the cluster analysis performed on the dyeing variables (affinity, washing and light fastness). Both factor analysis and cluster analysis show that the dyes can be grouped in the same three classes. This similarity of classifications indicates that some correlation exists between the set of descriptors and dye properties.

In Figs 3–5 the results of the multiple regression analysis between the PC's (predictor variables) and the dye affinities (dependent variable) are shown, while the corresponding regression equations are reported in Table 5. One of the

TABLE 4
Factor Loadings

Variable	*PC1*	*PC2*	*PC3*	*PC4*	*PC5*
PK1	0.445	0.018	−0.873	0.017	−0.047
PK2	0.411	−0.008	−0.886	0.071	0.022
PKA	0.554	−0.106	−0.779	−0.080	−0.175
SDIS	0.119	−0.905	0.151	−0.055	0.345
SOT	0.493	0.525	−0.249	−0.579	0.018
TOR	−0.376	0.062	0.060	−0.886	−0.017
VOL	−0.952	0.011	0.163	−0.153	0.028
HBD	0.111	−0.673	0.542	0.344	−0.225
ELD	−0.946	−0.128	0.158	−0.154	0.026
DIPM	0.804	−0.324	−0.309	0.207	0.121
SATS	−0.033	0.518	−0.795	−0.207	0.099
TOTS	−0.906	0.137	0.294	0.158	0.005
UNSS	−0.088	0.468	0.590	0.607	−0.087
HBA	−0.030	0.947	0.180	0.018	0.177

factors present in all correlations is PC1, the loadings (Table 4) of which indicate that it is connected to the dye dimension. Affinities are therefore inversely correlated to dye molecular volume, and this occurs especially for nylon, very little for silk and nearly nothing for acetate, which is a very permeable fibre.

The second principal component (PC2) reflects the hydrophilic/hydrophobic character of the dyes; it is directly correlated to their HBA properties and inversely to their HBD properties.

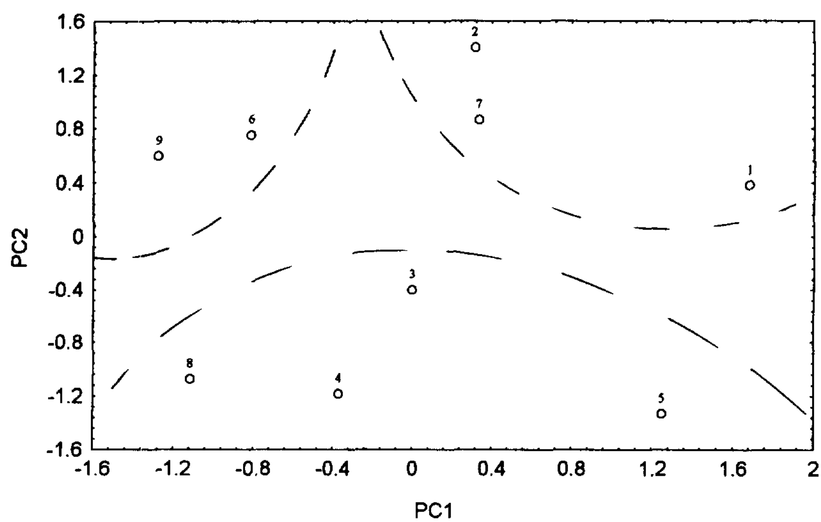


Fig. 1. Plot of the scores on the PC1–PC2 plane.

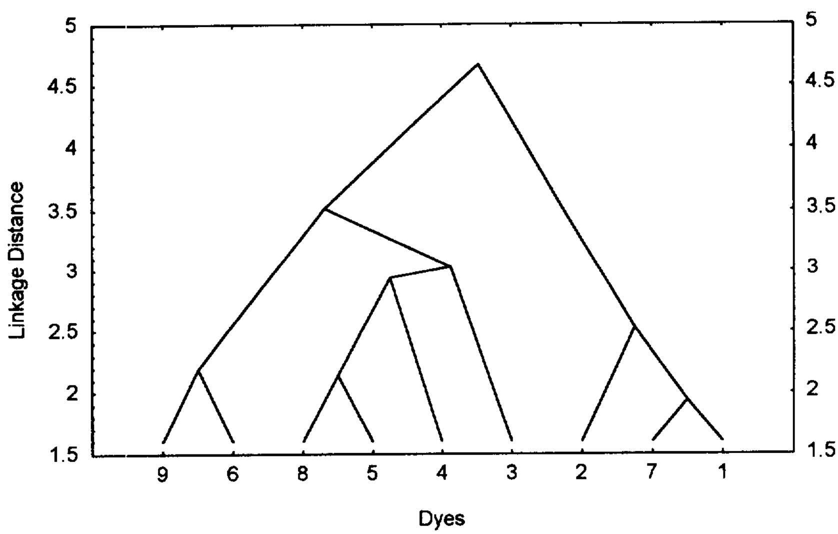


Fig. 2. Tree diagram. Clustering using the dyeing variables.

From the loadings it is evident that the affinity for each fibre decreases, while the aqueous solubility or HBD properties of the dyes increase. On the contrary, it increases if the HBA capacity of the dyes increases. The values of the PC2 coefficients in the regression equations (Table 4) indicate that this is the most important factor in determining the affinity, with the exception of nylon for which PC1 (dye dimension) is similarly important.

The loadings of the third component show that the affinity increases as well as the dye basicity, and that the hydrophobic interactions between fibre and dye

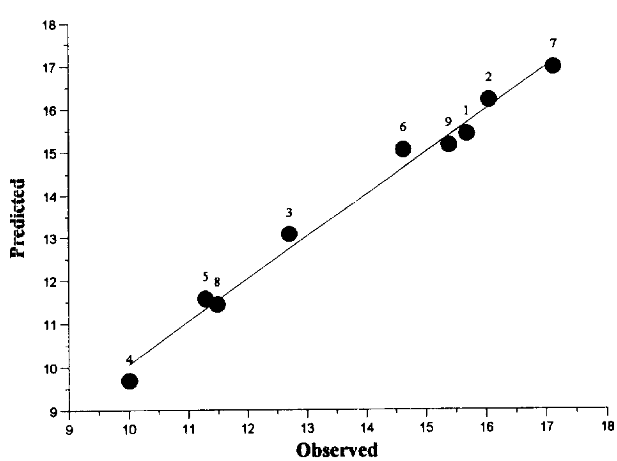


Fig. 3. Plot of the affinity values for acetate. Predicted vs. observed values.

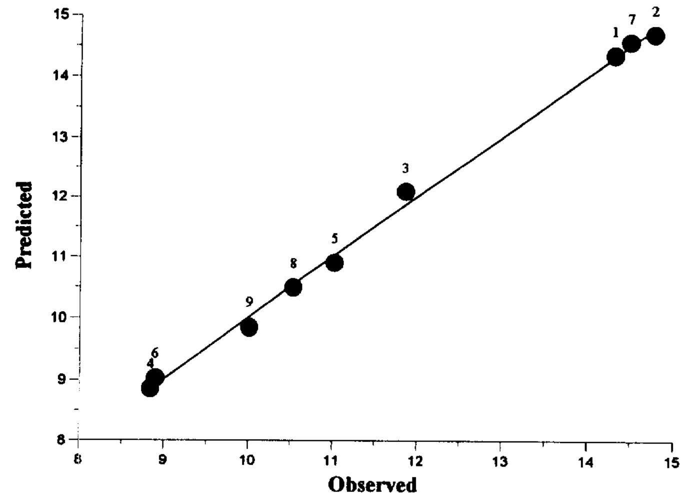


Fig. 4. Plot of the affinity values for nylon. Predicted vs observed values.

are very important for substantivity. All that holds for nylon and silk, but not for acetate. Evidently, to dye this fibre a high hydrophobicity is not required.

As regards the basicity effects, it seems that the bonds of the dye nitrogen atom with the NH of the amido groups are more effective than the bonds with the hydroxyls of the cellulose. This, and the previous observation that the affinity increases with the HBA capacity of the dyes clearly indicates that, in general, the bonds between the fibre as HBD and the dye as HBA are

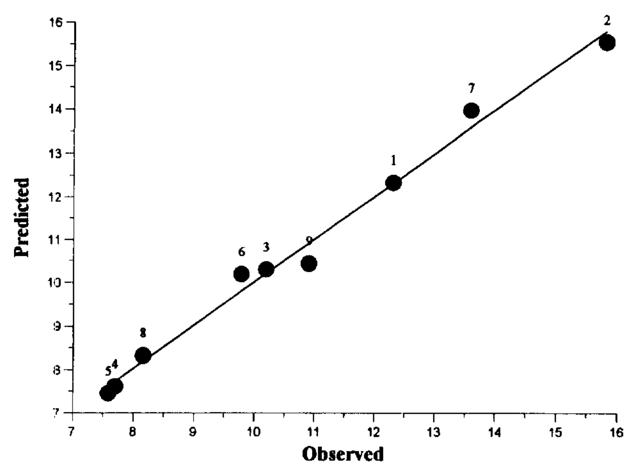


Fig. 5. Plot of the affinity values for silk. Predicted vs observed values.

TABLE 5
Regression Equations

AFAC[a] = 0.156 PC1 + 0.938 **PC2** + 0.218 **PC4** + 0.196 **PC5**
AFNY[b] = 0.631 **PC1** + 0.526 **PC2** – 0.53 **PC3** + 0.183 **PC5**
AFSI[c] = 0.252 **PC1** + 0.889 **PC2** – 0.36 **PC3**

[a] $R = 0.993$; $n = 9$; $p < 0.0005$; $F = 74$.
[b] $R = 0.998$; $n = 9$; $p < 0.0005$; $F = 212$.
[c] $R = 0.995$; $n = 9$; $p < 0.0005$; $F = 158$.
Statistically significant factors are reported in bold.

definitely important in the dye–fibre bonding. In contrast, the HBD aptitude of the dye is more important in determining its solubility.

PC4 correlates with the affinity for acetate but not with that for nylon or silk. The variables TOR that measure the torsional energy of the dye molecule and UNSS that is also a relative measure of the surface of the aromatic portion of the molecule, load on the fourth component. Therefore it would seem that dyes with a flat surface and an adequate π-electron system can bond to cellulose more effectively than to nylon or silk. In contrast, other authors [11] postulated that the π-electron system of an extended conjugate system can interact with the hydrogen atom of the hydroxyl groups in the cellulose to form a linkage that could be described as a weak hydrogen bond.

PC5 correlates with the affinity for acetate and nylon but not for silk. It explains about 2% of the total variance and from the plot of the loadings it appears that it discriminates between the HBA and HBD aptitude of the dyes. This PC also indicates that HBA dyes are substantive for the fibre whereas HBD dyes are not.

From this work it emerges that disperse dyes can be used favourably to colour different fibres. To colour acetate, dyes with a large molecular sizes and fair idrophylicity, but with a wide π-electron system, are also suitable. On the contrary, to colour nylon, dyes are required with small molecular sizes and sufficient hydrophobicity. With regard to silk, we may conclude that it can be coloured with disperse dyes to give dyeings of fair quality. Its dyeing behaviour resembles nylon more than acetate. The presence in the dye molecule of basic centres that can form hydrogen bonds with the polymeric chains is advantageous for the affinity, but hydrophobic interactions also play an important role in the dye–fibre binding. Finally also, the dye molecular size does not have a marginal importance in determining the dye affinity.

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