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Structure–Affinity Binding Relationships of Some 4-Aminoazobenzene Derivatives for Cellulose Fibre

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ABSTRACT

Dye–fibre interactions were modelled for a series of 20 disperse dyes on cellulose fibre by means of the Free–Wilson and MTD (minimum steric difference) methods. Both methods indicate good correlations with dye affinities $R = 0{\cdot}999$ *and* $s = 0{\cdot}317$ *for the Free–Wilson analysis and* $R = 0{\cdot}895$, $s = 0{\cdot}939$ *for the MTD method. The optimized receptor map resulted from the MTD calculations. Substituent contributions to dye affinity from the Free–Wilson analysis suggest the same attractive regions in the dye molecules (and a few steric constraints). The cross-validated* r^2 *values from the MTD method* ($R^2_{CVi} = 0{\cdot}432$; $R^2_{CVf} = 0{\cdot}613$) *indicate a satisfactory predictability of the proposed model.*

1 INTRODUCTION

Although disperse dye adsorption has been mainly studied for cellulose acetate and triacetate, nylon, polyethylene terephthalate and acrylic fibres, it has been shown that these dyes are also adsorbed to some extent by cellulose.[1] It was suggested that the forces that are operative in binding the dye to molecules in the crystal are of the same magnitude as those which bind the dye to the textile fibre. The contribution of non-

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polar and polar forces to dye-fibre interactions can be seen from the dyed fibre types, i.e. hydrophobic, such as polypropylene, and fibres with polar groups, such as acrylic fibres. It was concluded that a condition for good adsorption of disperse dyes is that the hydrophobic/hydrophilic balance of the dye should match that of the fibre. A steric requirement of dye planarity in the dyeing of secondary cellulose was also found, but linearity and planarity was observed to be a disadvantage in the dyeing of wool.

It has also been reported,[2] that disperse dyes could be taken up by the fibre by a process of a 'solid solution' that must imply solid solvation (an association between the dye molecule and the polymer acting as a solvent), being indistinguishable from adsorption at a fibre site. There is no evidence that disperse dyes penetrate regions of high order in polymers or that they cause any great change in the polymer morphology, except in very unusual circumstances. It could be concluded that there is no distinction between the two models and that disperse dyes are adsorbed by some unusual mechanism.

In the dyeing of cellulose by some 4-aminoazobenzene dyes, Shibusawa[3] concluded that there was no evidence of hydrogen bonding between these dyes and the fibre, and that attraction forces could be explained by dipole interactions on a region of the cellulose where water molecules are absent.

Quantitative relationships between structure and application properties have been established for some arylazo dyes[4–7] by the Free–Wilson method. The MTD method has also been applied to the binding of anthraquinone vat dyes to cellulose fibre,[8] suggesting the importance of steric parameters in the dye–fibre interactions.

We report here a Free–Wilson and MTD analysis applied to the interaction between disperse dyes and cellulose.

2 METHODS

2.1 Experimental dye affinities

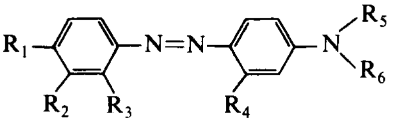
Dye affinity (A) values were calculated as the variation of the Gibbs free energy versus the dye content increase in the fibre phase from the dye partition coefficient between the cellulose and the water phase[3] (see Table 1).

2.2 The Free–Wilson method

In the Fujita–Ban model of this method,[9] the activity (BA) values are

TABLE 1

Experimental (A) and Calculated Dye Affinities (kJ mole^{-1}) for the Free–Wilson ($\hat{A}_1$) and MTD ($\hat{A}_2$) Methods and MTD Calculated Values for 4-Aminoazobenzene Derivatives



No.	*R_1*	*R_2*	*R_3*	*R_4*	*R_5*	*R_6*	*A^a (kJ/mole)*	*$\hat{A}_1$*	*$\hat{A}_2$*	*MTD*	*$j(x_{ij} = 1)$*
1	NO_2	—	—	—	C_2H_5	C_2H_4OH	11·06	11·12	10·79	3	1, 2, 4–6, 8–10
2	NO_2	—	—	CH_3	C_2H_4OH	C_2H_4OH	10·89	10·65	10·79	3	1–10
3	NO_2	—	—	—	—	—	9·73	9·73	8·85	4	8–10
4	Br	—	—	—	C_2H_4OH	C_2H_4OH	9·32	9·32	6·91	5	1–6, 8
5	NO_2	—	—	—	C_2H_4OH	C_2H_4OH	8·15	8·34	8·85	4	1–6, 8–10
6	Cl	—	—	—	C_2H_4OH	C_2H_4OH	8·15	8·16	6·91	5	1–6, 8
7	—	Cl	—	—	C_2H_4OH	C_2H_4OH	7·83	7·84	6·91	5	1–6, 11
8	—	—	—	—	C_2H_5	C_2H_4OH	7·27	7·21	6·91	5	1–5
9	—	—	—	CH_3	C_2H_4OH	C_2H_4OH	6·48	6·74	6·91	5	1–7
10	CN	—	—	—	C_2H_4OH	C_2H_4OH	6·46	6·47	6·91	5	1–6, 8, 13
11	—	NO_2	—	—	C_2H_4OH	C_2H_4OH	6·37	6·38	6·91	5	1–6, 11, 14, 15
12	OCH_3	—	—	—	C_2H_4OH	C_2H_4OH	6·14	6·15	6·91	5	1–6, 8, 9
13	—	—	—	—	—	C_2H_4OH	6·03	4·22	6·91	5	1–3
14	—	CH_3	—	—	C_2H_4OH	C_2H_4OH	5·94	5·95	6·91	5	1–6, 11
15	CH_3	—	—	—	C_2H_4OH	C_2H_4OH	5·93	5·95	6·91	5	1–6, 8
16	F	—	—	—	C_2H_4OH	C_2H_4OH	5·69	5·7	4·97	6	1–6, 8
17	—	—	CH_3	—	C_2H_4OH	C_2H_4OH	5·69	5·7	6·91	5	1–6, 12
18	—	—	—	—	—	—	5·29	5·82	4·97	6	0
19	—	—	—	—	C_2H_4OH	C_2H_4OH	4·61	4·43	4·97	6	1–6
20	—	—	NO_2	—	C_2H_4OH	C_2H_4OH	3·14	3·15	3·03	7	1–6, 12, 16, 17

[a] Used in both Free–Wilson (except compound 18) and MTD methods.

expressed as the sum of the contributions a_{jk} of the substituents R_k in each position *j*:

$$\log BA_i = \sum_{j} a_{jk} \cdot x_{jk} + \mu \tag{1}$$

where μ represents the calculated activity value of the unsubstituted compound and x_{jk} has the value of one when the substituent R_k is present in the position *j*, otherwise its value is zero. These substituent contributions include steric, electronic and, also, partition effects.[10]

The Free–Wilson calculations were performed with the SYSTAT program.[11]

2.3 The MTD method

The hypermolecule resulting from the MTD method[8,12] can be considered a topological network representing the fibre receptor, and is obtained by approximate (non-hydrogen) atom per atom superposition of the whole set of molecules $M_i = 1, 2, \ldots, N$. The resulting vertices $j = 1, 2, \ldots, M$ of the hypermolecule correspond to the positions of these atoms. If molecule M_i occupies the vertex j, then $x_{ij} = 1$ and $x_{ij} = 0$ if this vertex is not occupied. The minimal steric difference MTD of the molecule i with respect to the receptor is calculated by the equation:

$$\mathrm{MTD_i} = s + \sum_j \varepsilon_j \cdot x_{ij} \tag{2}$$

with $\varepsilon_j = -1$, 0 or +1 for the vertices attributed to the receptor cavity, exterior vertices or receptor walls, and s = the total number of cavity vertices.

The cross-validation-like procedure[13] was applied in order to validate the proposed model.

The MTD calculations were carried out with a program developed from that of Ref. 12.

3 RESULTS

3.1 Free–Wilson method

The substituent positions on the parent compound are presented in Table 1. The substituent contributions to the dye affinity were estimated by the multiple regression analysis program included in the SYSTAT package.[11] Statistical results are presented in Table 2.

3.2 MTD method

The hypermolecule obtained from the molecule superposition for the 20 disperse dyes is depicted in Fig. 1, and the vertex occupancy ($x_{ij} = 1$) in Table 1. The start standard was chosen by the attribution of beneficial vertices along the longest dye molecule axis:

$$S^0 \begin{cases} j(\varepsilon = -1)\text{: } 11, 14 \\ j(\varepsilon = 0)\text{: } 1-10, 12, 13, 15\text{–}17 \end{cases}$$

The optimization procedure was applied by trial and error, and verified

TABLE 2

Substituent Contributions Calculated for the Free–Wilson Method[a] (*ajk*) and MTD Analysis (X_S)

Position	*Substituent*	*ajk*	*b*[b]	X_S[c]
μ		5·82	0·41	
R_1	NO_2	3·91	0·26	3·88
	Br	4·89	0·41	1·94
	Cl	3·73	0·41	1·94
	CN	2·04	0·41	−1·94
	OCH_3	1·72	0·41	1·94
	CH_3	1·51	0·41	1·94
	F	1·27	0·41	1·94
R_2	Cl	3·41	0·41	1·94
	NO_2	1·95	0·41	1·94
	CH_3	1·52	0·41	1·94
R_3	CH_3	1·27	0·41	0·00
	NO_2	−1·28	0·41	−1·94
R_4	CH_3	2·31	0·32	1·94
R_5	C_2H_5	2·99	0·61	1·94
	C_2H_4OH	0·21	0·52	0·00
R_6	C_2H_4OH	−1·61	0·41	−1·94
R		0·999		—
s		0·317		—
EV		0·976		—
F		47·61		—

[a] Statistical parameters resulted from the Free–Wilson method: *R*, multiple correlation coefficient, *s*, standard error of estimate, *EV*, variance in dye affinity explained by the regression, *F*, calculated F ratio.

[b] Standard errors for Free–Wilson substituent contributions.

[c] X_S was estimated by the product between the regression coefficient of the MTD parameter from eqn (3) and the sum $\sum_j \varepsilon_j \cdot x_{ij}$ (see eqn (2)).

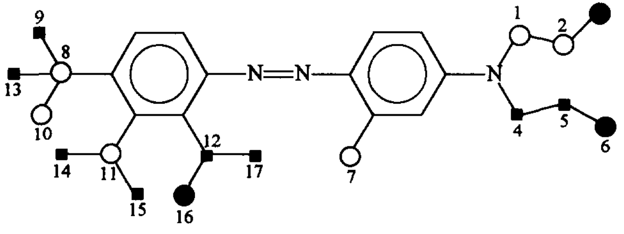


Fig. 1. Hypermolecule with numbering of vertices for disperse azo dyes. Beneficial vertices ($\varepsilon_j = -1$) are marked by white circles, detrimental vertices ($\varepsilon_j = 1$) by black circles, and irrelevant vertices ($\varepsilon_j = 0$) by black squares.

as optimal by the regression coefficient criterion,[12] yielding the following optimized receptor map and correlation equation:

$$S^* \begin{cases} j(\varepsilon = -1)\text{: } 1, 2, 7, 8, 10, 11 \\ j(\varepsilon = +1)\text{: } 3, 6, 16 \\ j(\varepsilon = 0)\text{: } 4, 5, 9, 12\text{–}15, 17 \end{cases}$$

$$\begin{aligned} &\hat{A} = 16{\cdot}617(\pm 1{\cdot}148) - 1{\cdot}941(\pm 0{\cdot}228) \cdot \mathrm{MTD} \\ &N = 20,\ R = 0{\cdot}895,\ s = 0{\cdot}939,\ F = 72{\cdot}45,\ R^2_{\mathrm{CVi}} = 0{\cdot}432,\ R^2_{\mathrm{CVf}} = 0{\cdot}613 \end{aligned} \tag{3}$$

The final MTD values are listed in Table 1.

In the cross-validation-like procedure, the dye molecules were numbered in increasing affinity order and separated into two subseries, ODD for $i = 1, 3, 5, \ldots, 19$ and EVEN, for $i = 2, 4, 6, \ldots, 20$. Two inversions, i.e. $i = 4/5$ and $i = 19/20$, were performed for a balanced vertex distribution in both subseries. The initial hypermolecule S^0 and the optimized receptor map S* (yielding the 'predicted r^2' values: R^2_{CVi}, respectively R^2_{CVf}) were used as start standard.

For the ODD and EVEN subseries in the case of the start standard S^0, the following optimized receptor maps (S_{ODD1}, respectively S_{EVEN1}) and correlational equations were obtained:

$$S_{\mathrm{ODD1}} \begin{cases} j(\varepsilon = -1)\text{: } 1, 8, 9, 10, 11 \\ j(\varepsilon = +1)\text{: } 3, 12, 14, 16, 17 \\ j(\varepsilon = 0)\text{: } 2, 4\text{–}7, 13, 15 \end{cases}$$

$$\begin{aligned} \hat{A}_{\mathrm{ODD1}} &= 11{\cdot}879 - 1{\cdot}124 \cdot \mathrm{MTD} \\ N &= 10,\ R = 0{\cdot}901 \end{aligned} \tag{4}$$

$$S_{\mathrm{EVEN1}} \begin{cases} j(\varepsilon = -1)\text{: } 1, 7, 8, 10, 14 \\ j(\varepsilon = +1)\text{: } 6 \\ j(\varepsilon = 0)\text{: } 2\text{–}5, 9, 11\text{–}13, 15\text{–}17 \end{cases}$$

$$\begin{aligned} \hat{A}_{\mathrm{EVEN1}} &= 13{\cdot}888 - 1{\cdot}714 \cdot \mathrm{MTD} \\ N &= 10,\ R = 0{\cdot}931 \end{aligned} \tag{5}$$

In the case of start standard S*, the similar optimized receptor maps (S_{ODD2}, respectively S_{EVEN2}) and correlational equations were obtained:

$$S_{\mathrm{ODD2}} \begin{cases} j(\varepsilon = -1)\text{: } 1, 2, 7\text{–}11 \\ j(\varepsilon = +1)\text{: } 3, 6, 12, 16 \\ j(\varepsilon = 0)\text{: } 4, 5, 13\text{–}15, 17 \end{cases}$$

$$\begin{aligned} \hat{A}_{\mathrm{ODD2}} &= 14{\cdot}919 - 1{\cdot}338 \cdot \mathrm{MTD} \\ N &= 10,\ R = 0{\cdot}887 \end{aligned} \tag{6}$$

$$S_{EVEN2}\begin{cases} j(\varepsilon = -1)\text{: } 1, 2, 7, 8, 10 \\ j(\varepsilon = +1)\text{: } 3, 6, 16 \\ j(\varepsilon = 0)\text{: } 4, 5, 9, 11\text{–}15, 17 \end{cases}$$

$$\hat{A}_{EVEN2} = 13{\cdot}888 - 1{\cdot}714 \cdot \text{MTD} \qquad (7)$$
$$N = 10,\ R = 0{\cdot}931$$

The final 'predicted r^2' values from eqn (3) indicate a predictable MTD model.

4 DISCUSSION

In the Free–Wilson analysis, there are some limitations imposed by the substitution pattern; in the dyes studied the substituents C_2H_4OH and C_2H_5, at position R_5 are always accompanied by the C_2H_4OH substituent at position R_6. Therefore, the net effects of C_2H_4OH and C_2H_5 at R_5 cannot be assessed with accuracy.

From the data in Table 2 for the substituent contributions from both methods (Table 2) it can be concluded that the most important positions are R_1 and R_2. This can also be visualized from the optimized receptor map (Fig. 1), positions R_1 and R_2 having beneficial and irrelevant vertices. The detrimental vertices are not present in these positions.

For position R_1, the Free–Wilson method predicts the order: Br > NO_2 > Cl > CN > OCH_3 > CH_3 > F. In accordance with the MTD method, the largest substituent contribution could be attributed to NO_2, other substituents having the same contribution. All these substituents occupy the beneficial vertex 8, but also, irrelevant vertices: 9 for NO_2 and OCH_3 and 13 for CN. The presence of two beneficial vertices (8 and 10) for the NO_2 group can be seen.

For position R_2, according to the Free–Wilson method Cl > NO_2 > CH_3. Even if the MTD substituent contributions are the same for these substituents, Fig. 1 shows that they also occupy the irrelevant vertices 14 and 15.

Both methods predict the same results for positions R_3–R_6. For position R_3, the NO_2 group has a negative contribution; it occupies irrelevant vertices 12 and 17, but also the detrimental vertex 16. The CH_3 substituent in position R_3 has a small positive contribution in the Free–Wilson method and results as irrelevant in the MTD analysis. This could be probably explained by the steric hindrance of this group, in the ortho position with respect to the azo group, which could decrease the extended conjugation in the dye molecule.

For position R_4, both methods predict a positive contribution of the CH_3 substituent to the dye affinity, by occupation of the beneficial vertex 7.

For R_5, according to Free–Wilson and MTD methods C_2H_5 > C_2H_4OH; this result is confirmed by inspection of the 1–3 vertices.

The same results were observed for the C_2H_4OH substituent from position R_6. The negative substituent contribution and the detrimental vertices 6 and 3 for position R_5 demonstrate the steric hindrance with the fibre site in this region of the dye molecule, but also possible hydrophobic interactions (see the beneficial vertices 1 and 4).

Statistical results of both methods indicate a good correlation with the dye affinity and predictability of the proposed MTD model. Similarly, the inspection of the optimized receptor map from Fig. 1 suggests many dye–fibre attractive interactions and only a few steric hindrances. As the MTD parameters could include electronic, steric and hydrophobic effects and, also, because of the low polarity of the substituents inserted on the parent structure, dipole–dipole and possible hydrophobic interactions could be expected to be important in dye–fibre binding.

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