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Structure Optimization in a Series of Acid Dyes for Wool and Nylon

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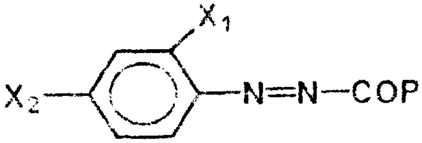
ABSTRACT

A series of acid azo dyes, previously designed by a chemometric approach for silk, has been applied to wool and to nylon, in order to compare the fastness performance of the series on different fibres of analogous structure. Wash fastness and light fastness data have been modelled as a function of the structure, described by the principal properties of the substituents and pK *values of the dyes, experimentally determined. PLS models allowed the identification of the best dyes for each of the fibres. © 1997 Elsevier Science Ltd*

Keywords: QSAR, wool dyes, nylon dyes, acid azo dyes

INTRODUCTION

In previous papers [1,2] a chemometric approach to find out the best structures in a series of azo dyes for silk, of general formula I, has been reported.



In a first step [1] the structure of the amine component was optimized. Using the technique of Experimental Design in Principal Properties, eight amines were selected and coupled with 7-amino-4-hydroxy-2-naphthalensulphonic acid (J acid). The fastness properties of the eight dyes obtained were modelled as a function of structure by the PLS method, and the model established allowed the identification of the optimum dyes of the series.

In a second step [2] the structure of the coupling agent was optimized. Four of the amines were explored and five new coupling agents were taken into consideration. A D-optimal design allowed the selection of ten dyes, which were synthesized and tested. Fastness data of this small training set were modelled as a function of the structure by PLS. The models established allowed the identification of Gamma acid as the best coupling component. Three dyes obtained from the above coupling agent, one in the training set and two in the prediction set, showed excellent fastness both to washing and to light.

In the present paper the same training set of ten dyes has been applied to wool and nylon, in order to compare the fastness performance of the series of dyes on different fibres of analogous structure. Fastness data were modelled as a function of the structure by PLS and the models used to identify the best dyes for each fibre.

PROCEDURES

Training set

The selection of the dyes of the training set, of general formula I, has been described previously [2]. The selected dyes are listed in Table 1.

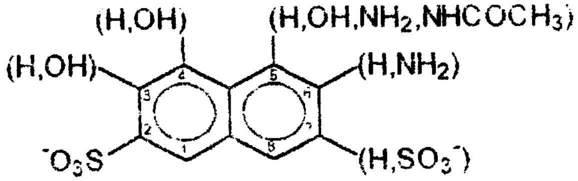
TABLE 1
Structure of the Selected Dyes

Dye	*Amine*		*Coupling agent (COP)*
	X_1	X_2	
1	C_6H_5	NO_2	H acid
2	H	COC_6H_5	Acetyl-H acid
3	H	COC_6H_5	Chromotropic acid
4	H	H	R acid
5	NO_2	COC_6H_5	Gamma acid
6	C_6H_5	NO_2	R acid
7	C_6H_5	NO_2	Chromotropic acid
8	H	COC_6H_5	Gamma acid
9	H	H	Acetyl-H acid
10	NO_2	COC_6H_5	H acid

PLS analysis

PLS analysis was used to model the fastness data of the training set as a function of the structure. PLS is a regression method based on PCA, aimed at detecting cause-and-effect relationships between a *y* variable or a *Y* block (fastness data) and an *X* block (structure descriptors). The PLS method has already been described [1,3].

The structure was described using the Principal Properties from the literature [4] for X_1 and X_2 substituents of the amine component and for substituents at 3, 4, 5, 6-positions of the coupling component (COP, general formula II), and σ_m and MR [5] for the substituent at 7-position. The corresponding values are reported in a previous study [2]. To these descriptors, experimentally determined p*K* values for each dye were added.



II

EXPERIMENTAL

Dye synthesis

Synthesis of dyes has been previously reported [2].

Dyeing of wool

The wool samples were dyed in a refluxing thermostatted bath with a 100:1 liquor ratio (3% dye, 10% Na_2SO_4 concentration) at pH 4. The samples were placed into the dyebath at 60°C; the temperature was allowed to rise to 95°C and maintained for 60 min. The patterns were then removed, rinsed in cold water and dried.

Dyeing of nylon

The dyeings were carried out in round-bottomed flasks immersed in a thermostatted bath and connected to a reflux condenser. For each determination about 1 g of nylon was dyed using a dyebath (liquor ratio 50:1) with 0.02 g of dissolved dye and 0.3% acetic acid at 60°C. The temperature was allowed to rise to 95°C during 20 min and maintained for 60 min.

Fastness assessment

Fastness to light, to washing, to dry cleaning and to perspiration were measured according to standard procedures [6]. The fastness data on wool and nylon are listed in Tables 2 and 3, respectively.

pK determination

Absorption spectra were recorded on a Hewlett–Packard 8452 diode array spectrophotometer; a flow cell was used joined to a titration vessel by a peristaltic pump; all the apparatus was thermostatted at 25°C.

In order to make a reliable spectrophotometric determination of the ionization constant, 15–20 spectra (as presented in Fig. 1) were collected at pH

TABLE 2
Fastness Values of the Training Set of Dyes on Wool

Dye	*Fastness*					
	Washing		*Dry cleaning*	*Perspiration*		*Light*
	Mild	*Medium*		*Acid*	*Alkaline*	
1	4–5	3	5	4	4–5	3–4
2	4	2	5	4	4	3–4
3	5	2–3	5	5	5	5
4	4–5	2	5	5	5	5
5	5	4–5	5	4	5	6
6	5	2–3	5	5	5	4
7	5	3	5	5	5	4
8	5	4	5	5	5	5–6
9	4	2	5	5	5	3
10	4	2–3	5	4–5	4	4

TABLE 3
Fastness Values of the Training Set of Dyes on Nylon

Dye	*Fastness*						
	Washing			*Dry cleaning*	*Perspiration*		*Light*
	Mild	*Medium*	*Strong*		*Acid*	*Alkaline*	
1	5	4	2–3	5	4	4–5	5
2	5	5	3	5	5	5	4
3	5	4–5	3	5	4–5	4–5	4–5
4	5	4–5	1–2	5	5	5	4–5
5	5	5	4	5	5	5	6
6	4–5	4–5	2–3	5	4–5	4–5	4
7	5	4–5	2–3	5	5	5	4–5
8	5	4–5	3–4	5	4–5	5	6–7
9	5	4–5	1–2	5	5	5	3
10	4–5	4	3	5	5	5	4

values equally spaced in a range of ± 2 pH units around the p*K* value to be determined. This was achieved by titrating with a weak non-absorbing -10^{-3} M acid, with a p*K* similar to that to be determined, using a 10^{-1} M

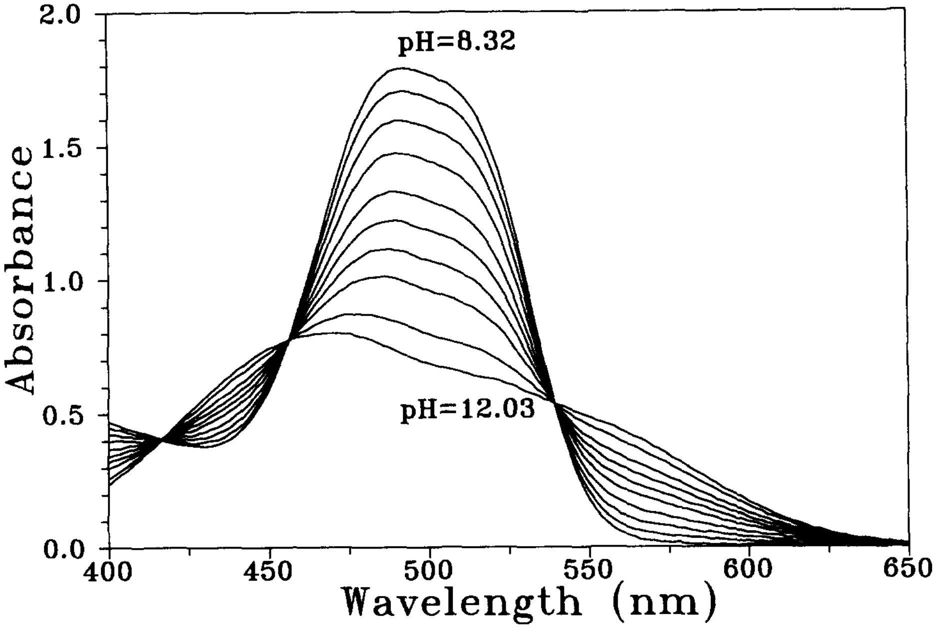


Fig. 1. Spectra of dye **4** in the pH range 8–12. Only ten spectra are presented for the sake of clarity.

TABLE 4
p*K* Values of Dyes

Dye	*pK*
1	6.51 ± 0.01[a]
2	6.27 ± 0.01
3	8.76 ± 0.01
4	10.66 ± 0.01
5	−1.48 ± 0.02
6	10.34 ± 0.01
7	8.86 ± 0.01
8	−2.28 ± 0.02
9	0.80 ± 0.02
10	6.04 ± 0.01
11[b]	1.0 ± 0.1
12[b]	3.8 ± 0.1
13[b]	1.0 ± 0.1

[a] Errors were evaluated as 3σ, where σ is the standard deviation furnished by SPECFIT.
[b] Dye of the prediction set; for structure see Table 8.

base; in this way the concentration of the dye undergoes only a very small dilution.

In order to measure the p*K* of dyes **1–4, 6, 7, 10, 12** (p*K* values 3.8–10.66) in the same medium, a mixture of seven acids with regularly increasing p*K* values was used [7].

It was therefore possible to examine and record the spectra of the dye ($\cong 10^{-5}$ M) at variable [H^+] by titration with KOH at an ionic strength of 0.1 M KNO_3 and moving a portion of the solution to the flow cell after each KOH addition.

In order to evaluate p*K* values ≤1 (dyes **5, 8, 11** and **13**) the measurements were made in hydrochloric acid at variable concentrations using a method previously described [8]. For the p*K* calculation we used the program SPECFIT [9] as in former work [10].

The calculated p*K* values are reported in Table 4.

TABLE 5

Fastness to Medium Washing on Wool: Variable Loadings *b* and Modelling Powers *ψ* for each Component of the PLS Model

	b1	*ψ1*	*b2*	*ψ2*
y variable	1.00	0.69	1.00	0.79
x variables				
p*K*	−0.27	0.28	0.17	0.37
X1-PP1	−0.03	0.00	0.37	0.36
PP2	−0.16	0.05	−0.17	0.07
PP3	0.00	0.00	0.37	0.35
X2-PP1	0.24	0.19	−0.21	0.32
PP2	−0.16	0.04	−0.13	0.03
PP3	0.23	0.18	−0.23	0.35
COP position				
3-PP1	0.16	0.04	−0.24	0.18
PP2	−0.16	0.04	0.24	0.18
PP3	−0.16	0.04	0.24	0.18
4-PP1	0.01	0.00	−0.18	0.00
PP2	0.14	0.02	−0.09	0.00
PP3	−0.06	0.00	0.24	0.06
5-PP1	−0.17	0.06	−0.30	0.32
PP2	0.14	0.02	0.30	0.28
PP3	0.17	0.05	0.31	0.37
6-PP1	0.34	0.61	−0.03	0.59
PP2	0.34	0.61	−0.03	0.59
PP3	−0.34	0.61	0.03	0.59
7-σ_m	−0.34	0.61	0.03	0.59
MR	−0.34	0.61	0.03	0.59
Variance explained (%)	90.6		95.4	

Calculations

PLS analysis was carried out using the SIMCA-3B package developed by Wold and coworkers at the University of Umeå.

RESULTS AND DISCUSSION

PLS modelling of fastness on wool

Fastness to washing

As fastness to mild washing data showed a low variability along the series, with values near the top of the scale, only medium washing (y) was modelled as a function of the structure descriptors (X block). A two-component PLS

TABLE 6

Fastness to Light on Wool: Variable Loadings b and Modelling Powers ψ for each Component of the PLS Model

	b1	$\psi 1$	*b2*	$\psi 2$
y variable	1.00	0.52	1.00	0.63
x variables				
pK	−0.25	0.18	0.26	0.43
X1-PP1	−0.11	0.00	0.00	0.00
PP2	−0.11	0.00	0.07	0.00
PP3	−0.07	0.00	−0.01	0.00
X2-PP1	0.22	0.13	−0.18	0.19
PP2	−0.08	0.00	0.15	0.00
PP3	0.22	0.13	−0.18	0.19
COP position				
3-PP1	0.05	0.00	−0.40	0.53
PP2	−0.05	0.00	0.40	0.53
PP3	0.02	0.00	0.40	0.53
4-PP1	0.09	0.00	0.10	0.00
PP2	−0.05	0.00	−0.38	0.41
PP3	−0.05	0.00	0.14	0.00
5-PP1	−0.24	0.16	−0.26	0.40
PP2	0.15	0.02	0.16	0.03
PP3	0.22	0.12	0.23	0.27
6-PP1	0.36	0.66	−0.09	0.72
PP2	0.36	0.66	−0.09	0.72
PP3	−0.36	0.66	0.09	0.72
$7\text{-}\sigma_m$	−0.36	0.66	0.09	0.72
MR	−0.36	0.66	0.09	0.72
Variance explained (%)	77.0		86.3	

model was established explaining about 95% of the y variance. The results of the PLS analysis are reported in Table 5.

The most important features appear to be the presence of NH_2 at the 6-position and of SO_3^- at the 7-position of the coupling agent.

Fastness to light

A two-component model was obtained explaining about 86% of the total y variance. The results of the PLS analysis are reported in Table 6.

From the modelling power values, descriptors of the coupling agent and pK appear to be the most important variables.

Validation and prediction

The two QSAR models were used to recalculate the fastness values of the training set and to predict the values of new compounds of the series. The calculated values and the residuals are listed in Table 7.

TABLE 7

Calculated Values of Fastnesses on Wool for the Training Set and Residuals

Dye	*Fastness to washing*		*Fastness to light*	
	Calcd	$\Delta°$	*Calcd*	$\Delta°$
1	3.0	0	3.6	−0.1
2	2.9	0	3.5	0
3	2.5	0	4.3	0.7
4	2.0	0	4.9	0.1
5	4.3	0.2	5.8	0.2
6	2.6	−0.1	4.3	−0.3
7	2.8	0.2	3.8	0.2
8	4.1	−0.1	5.8	−0.3
9	1.9	0.1	3.2	−0.2
10	2.8	−0.3	4.3	−0.3

$\Delta°$, Difference between experimental and calculated values.

TABLE 8

Structures and Fastness Experimental and Predicted Values of the Designed Dyes on Wool

Dye	*Amine*		*COP*	*Fastness*							
	X_1	X_2		*Washing*			*Dry cleaning*	*Perspiration*		*Light*	
				Mild	*Medium*			*Acid*	*Alkaline*		
					Exp	*Calc*				*Exp*	*Calc*
11	Cl	NO_2	Gamma acid	5	4	4.2	5	5	5	5–6	5.5
12	H	C_6H_5	Gamma acid	5	4–5	3.9	5	5	5	5	5.8
13	C_6H_5	NO_2	Gamma acid	5	4–5	4.3	5	5	5	5–6	5.3

The residuals (experimental minus calculated values) show that the model can be used for predictive purposes. As prediction set, the three dyes predicted as the best dyes for silk were used. Predicted and experimental values on wool, listed in Table 8, show a good agreement.

PLS modelling of fastness on nylon

Fastness to washing

As fastness to mild and medium washing showed a low variability along the series, with high values, only strong washing fastness (y) was modelled as a function of the structure descriptors (X block). A two-component model was established explaining about 93% of the y variance. The results of the PLS analysis are reported in Table 9.

The most important variables appear to be substitution at the 6- and 7-positions of the coupling agent, and at X_2 of the amine, together with pK.

TABLE 9

Fastness to Strong Washing on Nylon: Variable Loadings b and Modelling Powers ψ for each Component of the PLS Model

	$b1$	$\psi1$	$b1$	$\psi2$
y variable	1.00	0.60	1.00	0.74
x variable				
pK	−0.27	0.28	0.30	0.60
X1-PP1	−0.06	0.00	0.33	0.14
PP2	−0.15	0.03	−0.24	0.10
PP3	−0.02	0.00	0.35	0.15
X2-PP1	0.29	0.35	0.14	0.37
PP2	−0.18	0.08	−0.41	0.57
PP3	0.28	0.34	0.10	0.33
COP position				
3-PP1	0.21	0.13	−0.10	0.10
PP2	−0.21	0.13	0.10	0.10
PP3	−0.21	0.13	0.10	0.10
4-PP1	0.03	0.00	−0.07	0.00
PP2	0.19	0.09	0.16	0.09
PP3	−0.08	0.00	0.30	0.11
5-PP1	−0.11	0.00	−0.17	0.00
PP2	0.09	0.00	0.26	0.06
PP3	0.11	0.00	0.21	0.02
6-PP1	0.31	0.46	−0.16	0.54
PP2	0.31	0.46	−0.16	0.54
PP3	−0.31	0.46	0.16	0.54
$7\text{-}\sigma_m$	−0.31	0.46	0.16	0.54
MR	−0.31	0.46	0.16	0.54
Variance explained (%)	84.0		93.2	

TABLE 10

Fastness to Light on Nylon: Variable Loadings b and Modelling Powers ψ for each Component of the PLS Model

	$b1$	$\psi 1$	$b2$	$\psi 2$
y variable	1.00	0.56	1.00	0.65
x variables				
pK	−0.26	0.25	0.22	0.42
X1-PP1	−0.05	0.00	0.21	0.01
PP2	−0.14	0.02	−0.02	0.00
PP3	−0.02	0.00	0.20	0.00
X2-PP1	0.23	0.17	−0.20	0.27
PP2	−0.14	0.01	−0.02	0.00
PP3	0.23	0.17	−0.21	0.28
COP position				
3-PP1	0.12	0.00	−0.33	0.32
PP2	−0.12	0.00	0.33	0.32
PP3	−0.12	0.00	0.33	0.32
4-PP1	0.02	0.00	−0.13	0.00
PP2	0.10	0.00	−0.27	0.14
PP3	−0.06	0.00	0.16	0.00
5-PP1	−0.20	0.10	−0.35	0.60
PP2	0.15	0.03	0.31	0.31
PP3	0.19	0.09	0.35	0.57
6-PP1	0.35	0.67	−0.02	0.65
PP2	0.35	0.67	−0.02	0.65
PP3	−0.35	0.67	0.02	0.65
$7\text{-}\sigma_m$	−0.35	0.67	0.02	0.65
MR	−0.35	0.67	0.02	0.65
Variance explained (%)	80.3		87.7	

TABLE 11

Calculated Values of Fastnesses on Nylon for the Training Set and Residuals

Dye	*Fastness to strong washing*		*Fastness to light*	
	Calc.	Δ°	*Calc.*	Δ°
1	2.6	−0.1	4.7	0.3
2	2.6	0.4	3.6	0.4
3	2.9	0.1	4.4	0.1
4	1.4	0.1	4.4	0.1
5	3.9	0.1	6.2	−0.2
6	2.5	0	4.4	−0.4
7	2.7	−0.2	4.3	0.2
8	3.6	−0.1	6.3	0.2
9	1.6	−0.1	3.2	−0.2
10	3.1	−0.1	4.5	−0.5

Δ°, Difference between experimental and calculated values.

TABLE 12
Structures and Fastness Experimental and Predicted Values of the Designed Dyes on Nylon

Dye	*Amine*		*COP*	*Fastness*								
	X_1	X_2		*Washing*				*Dry cleaning*	*Perspiration*		*Light*	
				Mild	*Medium*	*Strong*			*Acid*	*Alkaline*		
						Exp	*Calc*				*Exp*	*Calc*
11	Cl	NO_2	Gamma acid	5	4–5	3	3.4	5	5	5	6–7	6.1
12	H	C_6H_5	Gamma acid	5	5	4	3.4	5	5	5	6	6.1
13	C_6H_5	NO_2	Gamma acid	5	5	4	3.4	5	5	5	7	6.2

Fastness to light

A two-component model was obtained explaining about 88% of the y variance. The results of the PLS analysis are reported in Table 10.

From the modelling power values, descriptors of the coupling component and pK appear to be the most important variables affecting the fastness.

Validation and prediction

The two PLS models were used to recalculate the fastness values of the training set. The calculated values and the residuals are listed in Table 11.

The residual values indicate that the model can be used to predict the fastness of the prediction set dyes. Predicted and experimental values, listed in Table 12, show a good agreement.

CONCLUSIONS

The series of dyes here examined on wool and nylon has been previously applied to silk [2] and it is interesting to compare the results obtained on the three fibres.

The fastness performance of the series on silk and on nylon appears to be generally similar, with the highest values of light fastness reached on silk (dye **13**). On the contrary, the fastness performance on wool is neatly inferior. The different behaviour towards the two protein fibres has been previously evidenced in an analogous set of azo dyes derived from J acid as coupling agent [11]. The results obtained showed that, keeping the coupling agent constant, the best dye for each fibre was produced from different amine components.

In this series both the coupling and the amine component varied and the QSAR models evidenced the prevailing influence of the coupling component. Gamma acid was shown to be the optimum coupling agent for the three fibres. Four derivatives of Gamma acid, dyes **5**, **8**, **11**, **13**, with interesting values of wet and light fastness for the three fibres, have been identified: two of them belonged to the training set (dyes **5**, **8**) and two (**11**, **13**) were predicted from the model.

This work shows the validity of the application of Experimental Design and QSAR modelling by PLS to find out, with a limited synthesis and testing work, the best dyes in a series for each of the fibres examined.

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REFERENCES

1. De Giorgi, M. R., Cerniani, A., Carpignano, R. and Savarino, P., *Journal of the Society of Dyers and Colourists*, **109** (1993) 405.
2. De Giorgi, M. R. and Carpignano, R., *Dyes and Pigments*, **30** (1996) 79.
3. Carpignano, R., Savarino, P. and Barni, E., *Dyes and Pigments*, **6** (1985) 189.
4. Skagerberg, B., Bonelli, D., Clementi, S., Cruciani, G. and Ebert, C., *Quant. Struct.-Act. Relat.*, **8** (1989) 32.
5. Hansch, C. and Leo, A., *Substituent Constants for Correlation Analysis in Chemistry and Biology*. Wiley, New York, 1979.
6. *Methods for the Determination of the Colour Fastness of Textile and Leather*, 4th edn. The Society of Dyers and Colourists, Bradford, 1978.
7. Casula, R., Crisponi, G., Cristiani, F., Nurchi, V., Casu, M. and Lai, A., *Talanta*, **40** (1993) 1781.
8. Aragoni, M. C., Arca, M., Crisponi, G., Nurchi, V. and Silvagni, R., *Talanta*, **42** (1995) 1157.
9. Maeder, M. and Zuberbuhler, A., *Analytica Chimica Acta*, **181** (1986) 287.
10. De Giorgi, M. R., Colonna, G. M. and Crisponi, G., *Ann. Chim.*, **82** (1992) 475.
11. De Giorgi, M. R., Carpignano, R. and Scano, P., *Dyes and Pigments*, **26** (1994) 175.