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Substantivity of azoic coupling components ''azotols''

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Abstract

A correlation between the chemical structure of azoic coupling components (hereafter referred to as azotols) and their affinity for cotton has been attempted. The theoretically computed correlation equations of the practical affinity with the van der Waals surface, the molecular volume and the hydrophobicity are reported. The hypothesis of microcrystalline multilayered micelles' implication in the sorption of azotols to a cellulose support is sustained.

1. Introduction

One of the characteristics of a fibrous solid is its large specific surface and the intensive sorption of different chemical species. The nature of the support—sorbed interactions are various and not completely known. Strong ionic interactions are characteristic for the dyeing of wool, leather and natural silk with acidic/basic dyes and for the mineral or organic tanning of leather. On the other hand, there are the weak hydrophobic–hydrophobic, van der Waals, interactions with dispersive dyes in artificial and synthetic fibers. Between these two extreme limits, there exist many weak to medium interactions, such as dipole–dipole, hydrogen links and van der Waals interactions, characteristic for the adsorption in cellulose fibers.

$\text{Support}^{\pm}\ {}^{\pm}\text{A}$ $\text{Support}^{\delta\pm}\ \text{A}^{\delta\pm}$ $\text{Support}\ldots\text{A}$

The case of cellulose is peculiar, because it represents a typical adsorption at the support (substrate) surface. The ionic and covalent bonds formed at the binding of ionic and reactive dyes respectively represent chemisorption, whilst the dyeing of hydrophobic fibers leads to a solid solution.

The chemical species adsorbed on cellulose fibers in the dyeing processes are ionic or ionisable under working conditions; direct or reactive dyes are ionic because of the sulfonic acid groups they contain. The reduced forms of vat and sulfur dyes, and solubilised azotols are ionisable, greatly dissociated as alkaline phenolates. Ionic interaction with the negative surface of cellulose fibers, having an electrokinetic potential $\xi = -30\ mV$ at pH = 8–10, has to be counterbalanced by adsorption's nonspecific attraction forces. The large specific surface of wet cellulose, in the range of 260–325 $m^2\,g^{-1}$ [1], makes the nonspecific interface effects, that result from thermodynamic considerations, rather important.

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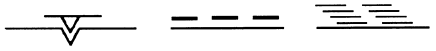
A number of hypotheses regarding the nature of the affinity of substances to cellulose fibers have been elaborated and argued. In practical dyeing processes, this is referred to as "substantivity" and is characterized by constants of adsorbtion isotherms, which express the partition of solute between the dye bath and the fiber.

The specific "sites"—hypothesis for the dyes is taken from the field of biologically active compounds and implies the existence of molecular parts (portions) specialized in sorption. The high crystallinity of cellulose fibers and the regularity of cellobiosic structure alternation does not justify this hypothesis. Similar affinities of some chemical species having different structures, from the linear azoics to the compactly condensed vat and sulfur dyes, excludes the existence of the sites that should be, by definition, specific.

The hypothesis of a monomolecular layer is based on the existence of some weak dipole–dipole and hydrogen links between cellulose and the sorptd compound, which is uniformly distributed at the surface of the fiber pores, and each molecule interacts with the fiber. For some direct dyes, the use of Job's method of continuous variations could provide evidence of a 1:1 dye–cellobiose unit adduct formation [2].

In the last two decades more arguments that support the hypothesis of crystallites superficially included have appeared; the adsorbed species are in the form of microcrystals mechanically included near the external surface of the fiber; the dye forms lamellar micelles. Since the elementary cell accommodates only a single molecule, plane–shaped, a package of 10–20 layered molecules resembling playing cards can be envisaged. These multilayered aggregates have been recorded by electron microscopy in the case of direct and vat dyes on regenerated cellulose; their dimension is about 1 μm [3–6].



The microcrystalline micelle appears as the result of crystal growth inside the fiber, in the less–ordered regions of the amorphous zones. This infers a stronger hydrophobic–hydrophobic interaction of the dye molecule within the hydrophilic fiber compared to hydrophobic/hydrophilic or ionic/hydrophilic interactions.

This present paper studies the behavior of azotols in their sorption on cellulose; azotols may be regarded as model molecules for sorption studies of direct, vat and sulfur dyes that exhibit a large variety of dimensions and structures. They are a species which have reduced molecular dimensions compared to direct and vat dyes, having a planar shape and enhanced hydrophobicity, so that dipole–dipole interactions and hydrogen bond formation are not significant. Commercial products show different sorption properties, specified by the manufacturer as sorption or exhaustion curves [7].

2. Experimental

The van der Waals surfaces and molecular volumes have been computed via the Monte Carlo method for a series of 20 azotols, as average values of a series of 12 determinations of 20,000 points for each molecule. Computations have been performed for the optimized molecular structure as resulted from conformational analysis by means of molecular mechanics using the MM + program from HyperChem 2 package.

All the molecules proved to be highly planar, except for acetylacetic and terephtaloylacetic anilides, which have been excluded from the correlation.

The theoretical hydrophobicity (lipophilicity) of azotols, expressed as the logarithms of partition coefficient in the system *n*-octylalcohol/water ($\log P$), have been computed by means of Hansch substituted fragmental constants and with the CHEMICALC 2 program. The results are similar; those obtained by the former method being somehow greater. The results are given in Table 1.

The exponents in the Freundlich adsorption isotherm of azotols on cotton at 30 °C and 1/20 bath ratio have been determined from literature data [7] and are presented in Table 3. The correlation coefficients are very good.

Affinities have been computed from laboratory data by means of Henry isotherm constants (K_H)

Table 1
The structure and computed properties of the azotols

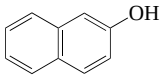
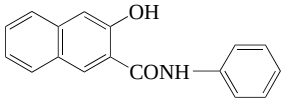
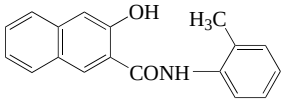
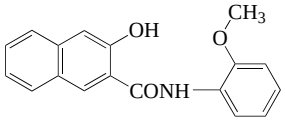
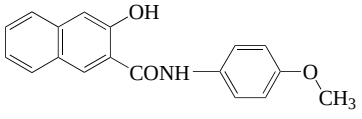
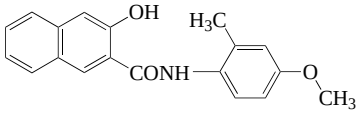
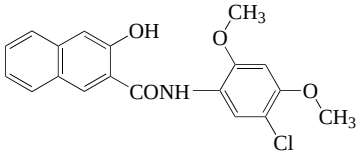
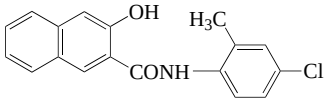
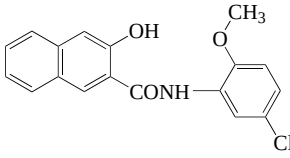
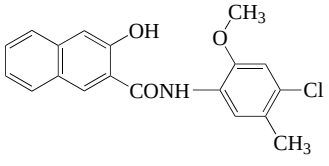
No.	Trade mark	Structure	Colour Index	log *P*	*S*(A^2)	V_M (A^3)	*n*
1	*β*-naphtol		—	2.585	168.6	135.4	—
2	Naphtol AS		—	4.357	273.9	234.9	0.547
3	Naphtol AS-D		37520	4.776	292.6	250.2	0.546
4	Naphtol OL		37530	4.658	303.4	259.6	0.603
5	Naphtol RL		37535	4.165	306.4	259.2	—
6	Naphtol LT		37450	4.584	324.4	275.3	—
7	Naphtol ITR		37550	5.529	357.1	298.7	0.518
8	Naphtol TR		37525	5.423	308.6	265.0	—
9	Naphtol CA		—	5.305	320.8	276.1	0.516
10	Naphtol RS		—	5.724	341.5	289.4	0.498

Table 1—*contd.*

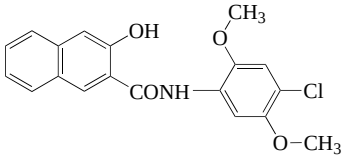
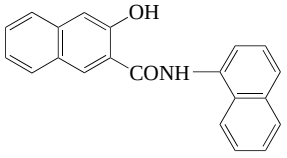
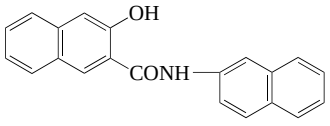
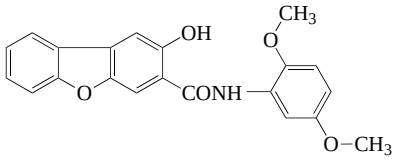
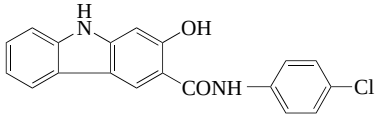
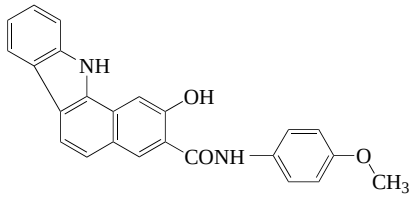
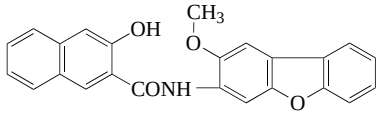
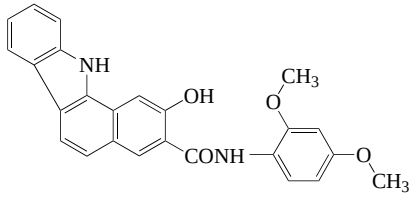
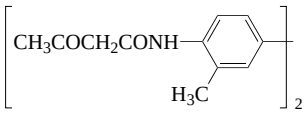
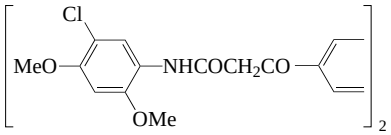
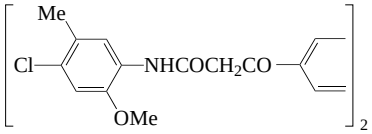
No.	Trade mark	Structure	Colour Index	log *P*	*S*(A^2)	V_M (A^3)	*n*
11	Naphtol LC		—	5.529	353.1	299.3	0.650
12	Naphtol BO		37560	5.551	319.9	278.7	0.467
13	Naphtol SW		37565	5.551	321.2	278.0	0.614
14	Naphtol AS-BT		37605	4.695	366.9	311.0	—
15	Naphtol AS-LB		37600	4.790	323.3	274.4	0.496
16	Naphtol SG		37595	5.145	385.2	337.7	0.936
17	Naphtol S		37580	6.081	380.0	329.3	—
18	Naphtol SR		37590	5.446	416.0	356.4	0.937

Table 1—*contd.*

No.	Trade mark	Structure	Colour Index	log *P*	*S*(A^2)	V_M (A^3)	*n*
19	Naphtol G		37610	2.216	422.0	351.3	—
20	Naphtol LG		37615	5.678	582.7	493.4	—
21	Naphtol L3G		37620	6.068	557.0	473.0	—

from equilibrium exhaustion values at 30 °C and Freundlich isotherm constant (K_F) from the amount of azotol adsorbed on cotton at the same temperature, respectively.

In the first case, affinity may be determined with the simple relationship:

$$\mu^* = -\Delta\mu^0 = RT\ln\frac{[A]_{\text{fiber}}}{[A]_{\text{bath}}} = RT\ln K_H$$

where concentrations are determined from exhausted bath values at equilibrium, in a bath of 5 g/l azotol, on Louisiana cotton, at 30 °C, liquor ratio 20:1, without salt:

$$[A]_{\text{fiber}} = \frac{5}{M}\cdot F\cdot\frac{x}{100}(\text{mol/kg cellulose})$$

$$[A]_{\text{bath}} = \frac{5}{M}\cdot\frac{100-x}{100}(\text{mol/1bath liquor})$$

where: x = bath liquor exhaustion (%); M = molecular weight of the azotol.

The results are given in Table 2.

In the second case, the Freundlich isotherm constant has been used and the relationship is:

$$\mu^* = -\Delta\mu^0 = RT\ln\frac{[A]_{\text{fiber}}}{[A]^n_{\text{bath}}} = RT\ln K_F$$

for the sorption from a bath having 3 g/l azotol at the same temperature and bath ratio; n is the exponent of azotol concentration in the bath liquor and has been determined from the equilibrium concentration of azotol on fiber for 14 different azotol concentrations in the bath liquor, in the range 0.5–7.0 g/l:

$$[A]_{\text{bath}} = \frac{x\cdot F - y}{F\cdot/M}(\text{mol/1bath liquor})$$

$$[A]_{\text{fiber}} = \frac{y}{M}(\text{mol/kg cellulose})$$

where:

x = azotol concentration (g/l);
F = 20 liquor ratio (20:1);
y = concentration of adsorbed azotol (g/kg cotton).

The results are given in Table 3.

3. Results and discussions

An attempt has been made to correlate the practical substantivity (affinity) of azotols with there chemical structure, expressed through theo-

Table 2
The exhaustion and Henry isotherm constant of some azotols at 30 °C

No.	Colour index	Exhaustion, *, %	K_H	$\log K_H$
1	—	1	0.20	−0.695
2	—	12	2.73	0.436
3	37520	12	2.73	0.436
4	37530	14	3.26	0.513
5	37535	16	3.81	0.581
6	37450	16	3.81	0.581
7	37550	19	4.69	0.671
8	37525	19	4.69	0.671
12	37560	21	5.32	0.726
13	37565	31	8.99	0.954
14	37605	44	15.71	1.196
15	37600	44	15.71	1.196
16	37959	90	180.0	2.255
17	37580	95	380.0	2.580
18	37590	95	380.0	2.580

*In bath of 5 g/l azotol, at 30 °C, on Louisiana cotton, liquor ratio 20:1, without salt.

Table 3
The fiber concentration and Freundlich isotherm constant of some azotols at 30°C

No.	Colour index	$[A]^*_{\text{fiber}}$, g/kg[a]	K_F	$\log K_F$
2	—	8.7	0.241	−0.618
3	37520	8.7	0.234	−0.631
4	37530	10.1	0.349	−0.457
7	37550	14.0	0.234	−0.630
9	—	14.0	3.18	0.50
10	—	20.2	0.418	−0.379
11	—	26.4	1.205	0.081
12	37560	15.0	0.272	−0.565
13	37565	26.4	1.06	0.025
15	37600	32.2	0.724	−0.140
16	37595	56.6	18.24	1.261
18	37590	56.6	18.20	1.260

[a]In bath of 3 g/l azotol, at 30 °C, on Louisiana cotton, liquor ratio 20:1, without salt.

retically computed molecular descriptors. The azonaphtol molecules have shapes and dimensions close to those of dyes used for cellulose fibers. For direct, vat and sulfur dyes, determination of adsorbed concentration on fiber surface is more tedious and less precise than for azotols, for which manufacturers give quantitative sorption data. Adsorption of azotols may be regarded as modeling that of dyes and the conclusions can be extrapolated to the dyeing of cellulose materials.

Attempts made to correlate affinity with molecular properties in the case of direct [8] and vat dyes [9] showed that affinity depends on length of conjugated chain. A modern analysis has been made for simple vat dyes [10] without suggesting any interaction.

A plot of azotol affinity, expressed through the adsorption isotherm constants, with molecular weight, hydrophobicity ($\log P_{\text{Hansch}}$) molecular surface and van der Waals volume reveals the well known elliptic spreading, together with a tendency of proportional increase. Single-parameter correlational equations give weak correlation, with coefficients not greater than 0.8.

The fact that similar results are obtained both in Henry (K_{H}) and Freundlich (K_{F}) adsorption hypothesis suggests that the process does not significantly depend on the support (substrate). More probable is a dependence on the molecular characteristics of adsorbed species.

Better results are obtained when the correlation is made with more structural parameters, using a linear multiparameter regression (MLR). In order to avoid the overlap of information contained in studied parameters, i.e. surface and van der Waals volume, these descriptors were orthogonalized and normalized considering the following priority: $\log P > S > V_M > \log^2 P$. A correlation of the type (1) results, and emphasizes the importance of lipophilcity in sorption, a characteristic of azotol–azotol interaction.

$$\log K_H = 2.7(\pm 0.546)\log P - 1.466(\pm 0.425)(S) + 1.059(\pm 0.646)(V_M) - 0.752(\pm 0.45)\left(\log^2 P\right) \quad (1)$$

$n = 15$; $r = 0.963$; $s = 0.271$; $F = 31.67$

where:

(S) = orthogonalized and normalized surface (the second parameter);
(V_M) = orthogonalized and normalized molecular volume (the third parameter);
$\left(\log^2 P\right)$ = orthogonalized and normalized $\log^2 P$ (the fourth parameter);

n = number of data;
r = correlation coefficient;
F = Fisher test.

Considering the hydrophilic—hydrophilic interaction, as expected between azotol and the substrate, lipophilicity should be less significant. Including in the correlation the surface square, characteristic for the interaction between the two surfaces of the azotol adsorbed in a multilayered structure, as that of microcrystals, poorer results have been obtained.

Analyses run with affinity, expressed as the Freundlich isotherm constant, do not lead to better results. Though the phenomenon is well described by the Freundlich adsorption, for the azotols under discussion, ($r > 0.99$), the new relationships show even a weaker correlation when $\log P$ stands for main parameter (2).

$$\log K_F = 0.659(\pm 0.435)\log P - 1.609(\pm 0.427)(S) + 0.895(\pm 0.475)(V_M) \quad (2)$$

$n = 12$; $r = 0.943$; $s = 0.254$; $F = 21.24$

where:
(S) = orthogonalized and normalized molecular surface (the second parameter);
(V_M) = orthogonalized and normalized molecular volume (the third parameter).

The precision of the model increases if the surface is accepted as main orthogonalization parameter (3), which suggests the importance of a plane shaped molecule in hydrophobic interaction with a similar one.

$$\log K_F = -1.71(\pm 0.505)S + 1.943(\pm 0.617)(\log P) + 0.766(\pm 0.567)(V_M)$$

$n = 12$; $r = 0.949$; $s = 0.254$; $F = 15.73$

where:
S = molecular surface;
$(\log P)$ = orthogonalized and normalized logP (the second parameter);
(V_M) = orthogonalized and normalized molecular volume (the third parameter).

Results thus obtained show an essential contribution of hydrophobic–hydrophobic interactions, i.e. of azotol molecules to each other. The solvated molecule has greater affinity for a similar molecule than to the hydrophilic fiber. This supports the hypothesis of multilayered microcrystalline micelles in the case of azotols studied.

4. Conclusions

Correlation of azotols' affinity with computed hydrophobicity, surface and molecular volume indicates the greater importance of hydrophobic–hydrophobic interaction compared to the hydrophilic–hydrophilic one in the sorption of azotols to cellulose materials. This supports the hypothesis of multilayered, microcrystalline micelles in attachment to the cellulose fiber surface, against the hypothesis of monomolecular layer at pore surface.

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