ELSEVIER

Dyes and Pigments 47 (2000) 5–16

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

A review of QSAR for dye affinity for cellulose fibres

Simona Timofei[a,*], Walter Schmidt[a], Ludovic Kurunczi[a], Zeno Simon[b]

[a]*Institute of Chemistry, Romanian Academy, B-dul Mihai Viteazul, Nr. 24, 1900 Timisoara, Romania*
[b]*Western University of Timisoara, Faculty of Chemistry–Biology–Geography, Str. Pestalozzi Nr. 16, 1900 Timisoara, Romania*

Received 25 February 2000; received in revised form 18 March 2000

Dedicated to Dr. A.T. Peters, for his distinguished service as editor, who wisely encouraged the publication of theoretical works

---

Abstract

The structure of cellulose fibre is discussed in relation to the relevance of the ligand–receptor concept for dye–fibre binding. An outline of qualitative SAR (structure–activity relationship) for dye–cellulose fibre binding is given, as well as of QSAR/QSPR (quantitative structure–activity/property relationship) for such binding and calculations of pertinent (electronic, geometric and partition) properties of dye molecules. Modern QSAR methods for dye–fibre adsorption include MTD (minimal steric difference) analysis, CoMFA (comparative molecular field analysis), PCRA (principal component regression analysis) and neural network. Series of anthraquinone vat dyes, mono, bisazo and disperse dyes were studied by these methods. Conclusions from these QSAR studies concerning the effect of structural features of dye molecules upon adsorption on cellulose fibres are discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Structure–activity relationships (SAR); Quantitative structure–activity relationship (QSAR); Quantitative structure–property relationships (QSPR); Dye adsorption; Cellulose fibre; Dyeing

---

1. Introduction

Textile dyeing has been practiced empirically over thousands of years, but theoretical studies on the mechanism of dye adsorption have been carried out only since the end of the nineteenth century.

There is no single interpretation of dyeing theory. The models known especially describe the limit cases (e.g. thermodynamic equilibria), which only partially reflect the practical dyeing processes. Effective dye adsorption by textile fibres has economic and even ecological implications.

This paper presents some qualitative and quantitative experimental arguments for the application of QSAR/QSPR (quantitative structure–activity/property relationships) techniques to dye adsorption on cellulose fibres. QSAR results are reviewed and an insight into the mechanism of cellulose dyeing at the molecular level is thus obtained.

2. Cellulose fibre structure in relation to dyeing

In cellulose supermolecular construction, the basic step is considered the celulose unit cell [1,2]. The next step are fibrillar micelles of 100–150 molecules with parallel arrangement. Microfibrils are formed by 15–25 associated micelles while fibrils are formed by 100–250 microfibrils. In the crystalline parts (around 70% in cotton fibres) cellulose molecules are firmly tied through hydrogen

---

* Corresponding author. Fax: +40-56-191824.
E-mail address: stimofei@icht.sorostm.ro (S. Timofei).

0143-7208/00/$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.
PII: S0143-7208(00)00058-9

bondings. In others, so called amorphous areas of fibres, there is a progressive disordered orientation of molecules [3].

The chemical composition of fibres determines, to some extent, the type of best dye to be applied [4]. The way in which the orientation and crystallinity affects the dye adsorption cannot be predicted. The difficulties are related to the absence of a molecular model for the dye sorption on fibre and to the exact location of the dye bonded to the fibre (in the crystalline or amorphous fibre region). The dye adsorption capacity is determined either by the chemical structure of fibres or the fine supramolecular structure [5].

Since different types of regenerated cellulosic fibres have differences in the fine structure it is difficult to formulate precise relationships between structure and dyeability [6].

Vieira Ferreira et al. [7] considered that the reaction of cellulose with other molecules starts on the less ordered surfaces of the aggregates and then proceeds under favourable conditions into the interlinking region between elementary crystallites, penetrating into them from both ends. From the study of fluorescence emission data of the auramine O dye when adsorbed on microcrystalline cellulose, it was concluded that this dye, in monomeric form, is strongly entrapped and rigidly attached between cellulose polymer chains in all samples prepared with solvents that efficiently swell cellulose.

Kai et al. [8,9] studied the effects of some direct dyes on microbial cellulose by X-ray diffraction, solid state ^{13}C-NMR and deuteration-IR determinations. They concluded that these dyes formed a product with the microbial cellulose which is a crystalline complex composed of a dye and cellulose. The structure of this product indicated that the dye molecule was included between the cellulose sheets corresponding to the (100) plane of the complex, i.e. $(1\bar{1}0)$ planes of microbial cellulose.

In contrast to these experimental results, Daescu et al. [10] proposed a sorption model of some azotols in the less-ordered amorphous regions of cellulose. They considered the hypothesis of the multilayered microcrystalline micelles at the surface of cellulose fibre as region for the azotols sorption as a result of some correlations of azotol affinity with computed hydrophobicity and steric azotol parameters.

The most obvious macrostructural feature of a fibre to affect the dyeing is its specific surface area [11]. Although dyeing cannot take place within the crystalline regions of the fibre, it is not confined to the external surface. The accesible internal surfaces include the voids between microfibrils and the space between elementary fibrils provided that the dye molecules are not prevented from entering by their size.

It is considered that the application of many dyes to cotton is accompanied by a minimum of chemical change in the cellulose of the fibre [12]. Visualization of the location of such materials in the fibre by electron microscopy cannot be accomplished because of the lack of difference in the electron-scattering properties of the dye and the cellulose. In case of cellulose dyed with Congo Red, concentrations of substantive dyes were located at the microfibrillate level in cellulose.

Dye adsorption at equilibrium represents the maximum sorption from the dyebath under certain conditions [13]. From the final equilibrium concentrations of dyes in fibres adsorption isotherms such as the Freundlich, Langmuir and Nernst isotherms are obtained. Most adsorption isotherms correspond to the Freundlich and Langmuir equations [14]. With reasonable approximation Langmuir isotherms describe the dyeing of cellulose fibres [4]. The applicability of Langmuir type of isotherms in the study of dye–fibre interactions leads to the idea of specific interactions between dye and fibre [13]. The different saturation values obtained for various dye structures, suggest "quantitative correlation between cellulose morphology and dyeing equilibrium" [15].

Lately, the multimodal model of disperse dye adsorption on different types of fibres has been proposed [16,17]. According to this model, competitive Nernst and Langmuir multimodel adsorptions are considered to describe the adsorption isotherms. In this case a partition process between the dye and fibre and processes with '*n*' types of saturable sites on the fibre are considered [18].

The application of QSAR techniques to dye–cellulose binding is based on the hypothesis of specific dye–fibre interactions. Some recent results published by Woodcock et al. [19] point to the specific adsorption of the anionic azo dye Congo Red on crystalline cellulose surfaces.

The binding site for the dye molecule would be on the crystalline region of the cellulose, in the "holes" resulted from the supramolecular structure [20]. The dimensions of these sites between the micro- and macro-fibrils are of the order of few Ångströms or more [21].

3. Structure–activity relationships

Several types of dye–fibre interactions are reported in the literature. Thus, the following intermolecular interactions have been considered: electrostatic [5,14,22,23–31], van der Waals [32–40], hydrogen bonding [22,35,36,41–45] and hydrophobic interactions [46–52]. The same types of binding are also found in ligand–biological receptor interactions.

Electrostatic interactions act between the ionic centres of the dyes and the electrically charged polymers (e.g. the cellulose) [35]. The electrical properties of the exterior fibre surface are responsible for the kinetics and thermodynamics of the surface sorption of ions and molecules of dyes [5]. The diffuse electric layer from the surface neighbourhood and where the charge separation takes place can be treated by the Gouy and Donnan approximations [22]. In case of cotton fibres it has been reported that the values obtained for the electrokinetic potential are very close to those predicted by the Gouy theory [22,53].

van der Waals interactions are efficient in the sorption of dyes in fibres if the distance between the dye and the polymer molecule is very low [34]. For dyes with cellulose affinity this attraction is favoured by a large planar structure of the dye molecule. Artym et al. [37] considered that the formation of van der Waals interactions between vat dyes and cellulose is proportional to the effective π electronic area of the molecule. Valko [54] underlines the importance of the extended area of electronic conjugation in the dye molecules for the dye–cellulose interactions through dispersion forces.

The formation of dye–fibre hydrogen bonds is controlled by the presence of hydrogen bonding functional groups in the fibre and the dye and also by the macromolecular fibre structure [42]. Badilescu et al. [45] consider that the cellulose free hydroxy groups could not participate since they are involved in intra- or inter-molecular hydrogen bonding in the amorphous and crystalline areas of the fibre.

Hydrophobic interactions appear as result of any transfer to a non-polar solute from aqueous solution. In case of cellulose dyeing, as result of a hydration layer around the fibre and of weak alternative binding forces (e.g. dispersion forces) tensioactive dyes would be necessary [35]. These could concentrate at the water–cellulose interface and would strongly aggregate in the concentrated superficial phase. It is considered that the hydrophobic effects depend almost entirely on water structure. As water structure is affected by the presence of ionic centres, the relative position of ionic and hydrophobic centres of the dye molecule can be important in dyeing.

Charge transfer complexes are formed between molecules with strongly different electronegativities and with planar surfaces which allow a large contact surface [55]. Riesz [56] considers that vat dyes would form 'a charge transfer complex' through a donor–acceptor proton complex in cellulose binding.

In many studies reported in the literature, dye molecular parameters have been related qualitatively to the adsorption on fibres. They can be divided according to their different contribution to electronic, steric and intermolecular effects during the dyeing processes.

Concerning electronic parameters it was observed that the presence of conjugated double bonds (as electronic dye parameter in the dye molecules) increased the induction forces and hence their substantivity for fibre [2,37,56]. Alberti et al. [57,58] noted that the mesomeric effect of heteroatoms in some dye molecules also influenced the substantivity for fibre.

Steric dye parameters have been related to dye diffusion in fibres. The molecular dye dimensions have been expressed in various ways. Giles et al. [59] considered the molecular dye dimensions as being expressed by the maximum length×width×thickness, by molecular area and by molecular weight and correlated these structural dye elements with diffusion coefficients. Wilson [60] considered the dye molecular dimension as being defined by bonding lengths, which can be correlated with the width of the biggest channels of a viscose fibre. Shibusawa [61] found a dependence between some molecular dye dimensions (like the molar and the van der Waals volume) and the dye diffusion capacity in aqueous solution. Dye molecular weight, molar and van der Waals volumes have been related to the diffusion coefficients in the case of nylon dyeing by some non-ionic dyes [62]. Dye linearity is considered to bring the dye molecule into close proximity with the cellulose fibre and to be responsible for efficient dye–fibre interactions [14]. The number of azoic groups can influence the dye substantivity [2,63] as well as the presence of conjugated double bonds [36] and the length of planar dye molecules [64]. Coplanarity is also considered an important dye parameter which influences textile dyeing [2,4,57,65–67].

Structural dye parameters have been found to contribute to intermolecular (van der Waals, hydrogen bonding, hydrophobic) effects in textile dyeing.

The cross sectional area of the π electronic system of dye molecules, the length of planar dye molecules and the presence of aromatic nuclei could contribute to van der Waals dye–fibre interactions [64]. An accumulation of aromatic nuclei in the dye molecules and an extended π electronic system lead to the same kind of interactions [37].

The importance of hydrogen bonding in dyeing is indicated by the fact that most dyes contain nitrogen and/or oxygen atoms [2,64]. The availability of the lone pairs of electrons on these atoms in groups such as: amino, azo, carbonyl and amido groups [2,37,58,68,69] influence the dye affinity for cellulose. The number of hydrogen donors and hydrogen acceptor atoms of the dye molecules are considered structural parameters responsible for hydrogen bonding to fibre [70].

Structural dye parameters which contribute to hydrophobic dye–fibre interactions have been reported. Moryganov et al. [63] considered that the introduction of additional aromatic nuclei in the structure of some direct dyes increased their affinity for fibre by increasing the hydrocarbon–water separation surface. The successive accumulation of benzene nuclei in the azoic dye components increased the dye affinity for cellulose [71]. This phenomenon was attributed to the increase in the hydrophobic surface of the dye molecules. The increase of the conjugated double bond system in the dye molecules increases the hydrophobic surface of these dyes and their polarizability [72]. The effect of the length of the alkyl chain attached to a benzene nucleus in some acid dyes has been studied. [73]. The affinity for fibre increased per methylene group, but not with groups larger than *n*-butyl. The presence of methyl groups attached to a benzene nucleus produces an increase in the non-ionic dye affinity for cellulose [74]. The introduction of methyl groups into some acid dyes was associated with van der Waals dye–silk interactions which increased the dye affinity for fibre [75]. The number of sulfonic groups in the dye molecules influences the solubility and implicitly the affinity of dyes for fibres [72]. Thus an increase in sulfonic groups led to a the decrease of benzidinic dye affinity for cellulose. The same phenomenon was observed by Moryganov et al. [63] in the case of other direct dyes.

4. Quantitative structure–activity/property relationships

Molecular modeling and statistical methods used in the QSAR (quantitative structure–activity relationships) field constitute an important new tool for the study of dye–fibre interactions. The advantages of this new approach to dye adsorption on cellulose fibre are related either to the description of the mechanisms present at molecular level or to the predictability of the proposed models, which can lead to the design of new dyes with higher affinities for the cellulose fibre.

The arguments for the application of QSAR techniques in dye adsorption on cellulose come from both the variety of data of the physical chemistry of dyeing and the complexity of the cellulose fibre structure. In the dyeing process several intermediate equilibria can be considered and the partition coefficient of the dye between the dyebath and fibre could be considered a final thermodynamic equilibrium constant. The Langmuir isotherms proposed for the dye adsorption at equilibrium on specific fibre sites lead to the conclusion of cellulose selectivity for different types of dyes. The structural organization of cellulosic fibres can be compared to the organization of proteins on different levels. A similarity between ligand–biological receptor interactions and dye–fibre intermolecular interactions can be made.

A predominantly parallel orientation of the dye molecules in dyed fibre to the fibre axis was found by electro-optical methods. The above facts suggest the existence of selective specific sites on the fibre for the adsorbed dyes. The binding site for the dye molecule would be situated between the sheets in the microfibrillar microcrystalline region of the cellulose fibre, in the voids resulting from the supramolecular structure.

There are few articles reported in the literature on quantitative relations between the dye structure and their tinctorial properties derived by QSAR/QSPR methods.

Quantitative relationships between chemical structure and technical dye properties were performed by the Free–Wilson and partial least-squares regression (PLS) [76–82].

The effect of substituents of some arylazoindole derivatives on the lightfastness, fastness to washing and affinity for nylon and wool was studied by the Fujita–Ban modified variant of the Free–Wilson method [76]. An important contribution for dye substituents and another small one of the ‘parent structure’ (or common molecular framework) was observed for the nylon lightfastness. The sulfonic group was considered to be an important factor in the nylon fastness to washing. In the study of the effect of dye substituents on fibre affinity, all the dyes studied showed a higher substantivity for nylon than for wool with differences relative to the ‘parent structure’. The influence of substituents was higher for wool than for nylon.

Models for the study of relations between the dye lightfastness and fastness to washing and the structure of some acid 4-aminobenzenesulfonic dyes have been proposed by the Free–Wilson method in the Fujita–Ban variant when applied to nylon or wool [77]. Substituents containing chlorine significantly improved both lightfastness for nylon and wool and fastness to washing for nylon for the ‘parent structure’. Effect of substituents was negligible. The wash fastness on wool is low for the ’parent structure’ but high values were noted for dyes with bulky substituents.

The influence of the substituents in some azo dyes on the nylon lightfastness and fastness to washing and perspiration has been studied by the Free–Wilson approach [78]. It was concluded that electron withdrawing groups were beneficial for lightfastness. The fastness to washing was influenced by bulky dye substituents.

Besides the Free–Wilson approach, the PLS (partial least-squares) method has been applied to the study of lightfastness of some azo dyes applied on polyester fibres [79]. The PLS analysis allowed models to be predicted by relating tinctorial properties to physico-chemical structural dye descriptors and also to ^{13}C-NMR, spectroscopic, chromatographic and calorimetric properties [81].

The relation between polarographic properties and dye lightfastness for polyester fibres was studied by PLS analysis [82] and a non-linear correlation between the lightfastness and polarographic oxidation and reduction properties was obtained.

PLS analysis has been applied to a series of azo dyes [80] in order to study the influence of various substituent physico-chemical descriptors such as the Hammett σ constant, the hydrophobic π-Hansch constant, the molar MR refractivity and the ν steric Charton parameter on lightfastness, fastness to washing and to perspiration. The results indicated an inverse proportional dependence with respect to lightfastness and fastness to perspiration but no relation with washfastness.

There are only a few reported molecular modeling calculations applied to dye molecules. Dörr [83] has underlined the importance of this kind of calculation in the design of molecular dye structures.

Classical QSAR, pattern recognition and 3D-QSAR methods have been employed by us in the study of dye fibre interactions [84–99]. The methodology used is not presented, but the beneficial and unfavourable features of each method are highlighted.

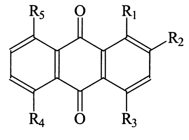
The classical QSAR methods rely principally on the mathematical technique of multiple linear regression (MLR). This means an easy interpretation of the results, especially when the fibre affinities of the dye molecules are related to simple and clearly defined physico-chemical parameters, but implies some risks of chance correlation. These are introduced mainly in the variable selection phase, when one must decide which parameters are relevant for affinity. The number of parameters potentially important for the dye fibre interaction can be large and this leads to the use of multivariate statistical methods, like principal component analysis (PCA), principal component regression analysis (PCRA) or PLS (projection in latent structures). These methods successfully handle large matrices of predictor variables, although sometimes with disadvantage of clarity as well as of physical and chemical interpretation. In these cases, the relation between the dependent variable and the parameters characterizing the dye molecules is much more "hidden" than in the MLR. This later difficulty is the principal disadvantage for the neural network (NN) method too. Although good predictions can be made from a good NN model, one of the principal goals of QSAR applications, the interpretation of the results at molecular level is more tedious.

At the limit between the classical and 3D-QSAR methods, the minimal topological difference (MTD) method supplies interesting information concerning favourable and unfavourable molecular interaction between the target macromolecule and the ligand binding molecule to this target. In the special case of dye–fibre interaction, where the MTD hypermolecule may contain many more vertices than ligand molecules in the series (many "floating" parameters in the MTD optimization process), the main risk is represented by some kind of model overfit. This is equivalent to the risk of chance correlation, i.e. to designate the quality (beneficial, detrimental, irrelevant) of the vertices by chance. This drawback is minimized by the new MTD-PLS variant of the method [84].

The CoMFA 3D-QSAR method is the most evaluated among those applied by our group to dye fibre interaction. Although this interaction seems to be less specific than in the case of ligand–biological receptor interaction, the CoMFA method can supply much useful information about the molecular level processes involved here. This method sometimes also prevents the risk of overfitting the data.

Having in mind the features presented above, an account follows concerning the results obtained by our group in the cases of affinities of four dye classes for cellulose fibre.

4.1. Anthraquinone vat dye adsorption on cellulose fibres



1

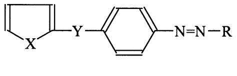
$R_1 = H$, Cl, CH_3, OCH_3, NH_2, $N(CH_3)(COCH_3)$, $NHCOCH_3$, $NHCOC_6H_5$, $NHCOC_6H_4$-4-CH_3, $CONHC_6H_4$-3-Cl, $CONHC_6H_4$-3-CH_3, $NHCOC_{10}H_7$-2′, $CONHC_6H_4$-4-OCH_3, $CONHC_6H_4$-4-Cl, $CONHC_6H_4$-3-OCH_3; $R_2 = NH_2$, $NHCOCH_3$, $NHCOC_6H_5$; $R_3 = OH$, OCH_3, NH_2, $NHCH_3$, $NHCOC_6H_5$, $N(CH_3)(COC_6H_5)$, $CONHC_6H_4$-4-OCH_3, $CONHC_6H_4$-3-CH_3, $CONHC_6H_4$-4-CH_3, $CONHC_6H_4$-3-Cl, $CONHC_6H_4$-4-Cl; $R_4 = OCH_3$, NH_2, $NHCOC_6H_5$, $CONHC_6H_4$-4-CH_3, $CONHC_6H_4$-3-CH_3, $CONHC_6H_4$-3-OCH_3, $CONHC_6H_4$-4-Cl; $R_5 = OH$, NH_2, $NHCOC_6H_5$.

A series of anthraquinone vat dyes (**1**) has been studied by several QSAR methods. The MLR [85,86] and PCRA [87] methods lead to the conclusion that among the most important parameters in this dye series are the length of the conjugated chain of the dye molecule (n) and the number of proton donor groups (σ_D), with equations having squared regression coefficients, r^2, between 0.889 and 0.920 (0.835 for an equation containing only the n parameter). The 'n' parameter can be interpreted as some kind of length of the molecule, along which beneficial interactions can take place between the ligand molecule and the fibre.

Application of the MTD method to the same series of anthraquinone vat dyes [85,86,88–90], gave r^2 values between 0.903 and 0.941, and also "predictive r^2", or cross-validated q^2, values in the range of 0.827–0.878. The great number of the vertices (72 to above 80) in the hypermolecule, question these excellent statistical results. Nevertheless, the vertex attributions for series of 46, 47, 49 compounds (from simple, planar, to multiconformational and multiple vertex hypermolecule construction) show that along the longest dye molecule axis mainly attractive interactions are present; only in lateral pockets were some detrimental vertices found.

The CoMFA study [88] ($r^2 = 0.992$, $q^2 = 0.841$) leads to the conclusion that the electrostatic interaction is the main factor contributing to the dye–fibre interaction. The electrostatic field contributions show that, if vast domains exhibit increasing positive charges, i.e. in the regions of almost all substituents of the anthraquinone moiety, this should yield higher affinities for the cellulose. This fact suggests some kind of electrostatic "attraction" between the dye molecule and the negatively charged cellulose fibre (either in the phase of approach of the dye molecule or in the proper binding phase). This is in accordance with the results of the MTD method, showing attractive regions for many vertices of the substituents belonging to the anthraquinone skeleton. It is interesting however that the analysis of the CoMFA steric field contributions leads to the conclusion that the R_2 substitution (see general formula **1**) will reduce dye affinity, in contradiction to the MTD results, which indicate this region as beneficial for binding. Two compounds from the studied dyes [89], having cyclic aromatic substituents covering the substituent R_2, bind with high affinity to cellulose. It seems that the electrostatic interaction overwhelms the steric one for this substituent position; indeed in all CoMFA models the contribution of the electrostatic term is larger than that of the steric one. Besides the steric and electrostatic contribution, the CoMFA study demonstrates that some importance attaches to the LUMO energy. This parameter can be related to the solubility of the compound [93].

4.2. Anionic monoazo dye adsorption on cellulose fibres

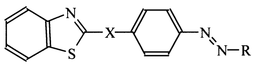


2

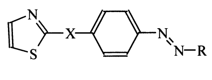
X = –CH = CH–, –S–
Y = –CH = CH–, –CONH–, –CO–
R = naphthionic acid, Nevile–Winther acid, R acid, H acid, chromotropic acid

A series of anionic azo dyes with different coupling components (**2**) was studied by MLR [91]. The correlation of the affinity with the chromatographic lipophilicity index R_M was realized in only two sub-series of dyes having a coupling component with one (12 compounds) or two (18 compounds) sulfonic groups (r^2 of 0.721 and 0.958, with q^2 of 0.565 and 0.952, respectively). In these two sub-series, increasing R_M values lead to higher affinity. An attempt to perform a PCRA study for the last 18 molecules, involving other structural parameters besides R_M, also produced a model, but with smaller correlation coefficient ($r^2 = 0.901$, after elimination of one outlier).

In order to unify the two sub-series of compounds, a MTD study was performed [91]. Using only the MTD parameter for the whole series of 30 dyes, the statistical results are rather weak: $r^2 = 0.667$, with $q^2(\text{LOO}) = 0.560$ (leave-one-out method) and $q^2(\text{LHO}) = 0.527$ (leave-half-out method). Detrimental vertices dominate in the hypermolecule. If besides MTD lipophilicity R_M values are introduced as a supplementary parameter, better statistical results are obtained ($r^2 = 0.850$, $q^2(\text{LOO}) = 0.796$ and $q^2(\text{LHO}) = 0.647$), the dominance of detrimental vertices is conserved (from a total of 31 vertices, only one is beneficial and 14 are "wall" vertices). The detrimental vertices appear mainly in lateral pockets of the common skeleton of the hypermolecule, for example on some of the SO_3H groups. As will be shown in the CoMFA study for the disazo dyes adsorption, this feature appears here also as a detrimental electrostatic interaction between some negatively charged SO_3H groups and the cellulose. Thus, for these compounds the binding affinity seems to depend on the free energy accompanying the transfer of the molecule from the chromatographic mobile phase to the stationary phase (R_M proportional to the lipophilicity) and on some, hypothetically electrostatic, detrimental interactions.



3



4

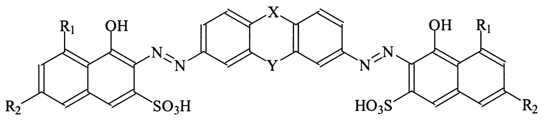
X = NH, O, S
R = chromotropic acid, R acid, Nevile–Winther acid, H acid, γ acid, naphthionic acid, J acid

In [92], R_M was defined as a parameter depending on free energy of transfer from solution in an immobile phase and not necessarily as a hydrophobicity parameter, because we found that for other series of heterocyclic monoazodyes (**3**, **4**), with the same coupling components, the hydrophobicity parameter $C \log P$ was not correlated with the dye affinity (simple linear regression) [93].

A CoMFA study of the affinities of these compounds by different models with electrostatic, steric, LUMO and HOMO energy contributions yields good statistical results: r^2 between 0.886 and 0.977, with q^2 ranging from 0.590 to 0.818. In this case too, as for the anthraquinone dyes, electrostatic effects were found to be predominant. Again, the electrostatic contour maps indicate the predominance of positive over negative charges. Increased positive charges around the negatively charged SO_3H groups, especially on atoms situated near the azo group, but also in other regions around the coupling component, should lead to higher affinities. The steric contour maps suggest that bulky groups should be attached at the naphthyl coupling component moiety with benefic effects on the affinity. Also the steric field indicates that the introduction of a benzothiazole group is detrimental for dye–cellulose binding. Besides the electrostatic and the steric fields, the introduction in the model of the LUMO energy as an independent variable leads to good statistical results. According to [93], this variable may indicate the contribution of dye molecule solvation in the cellulose dyeing.

An important common feature for the two monoazo dye series seems to be that the increase of positive charge in certain molecular regions is beneficial for dye–cellulose affinity (Fig. 1).

4.3. Anionic bisazo dye adsorption on cellulose fibres



5

X = NH, CO, NHCONH, CONH
Y = CO, CONH, NHCONH
$R_1 = NH_2$
$R_2 = NH_2$, SO_3H

For a series of 21 direct bisazo dyes (**5**) [94–96], MLR and NN studies were performed using a set of steric, electronic and hydrophobic parameters. Among them, two sets of molecular shape parameters are mentioned: the "metameters" λ_1, λ_2 and λ_3 (eigenvalues of the correlation matrix corresponding to the (3, N) matrix of the cartesian coordinates, N being the number of atoms from one molecule) and the 'a', 'b' and 'c' semiaxis of an ellipsoid that embeds the molecule [100,101]. After variable selection, two poor MLR models were obtained: the first one, depending on the λ_1, λ_2 and E_{HOMO} (the HOMO energy), and the second on "a" (the longest ellipsoid semiaxis) and E_{HOMO}. The parameters of the first MLR model,

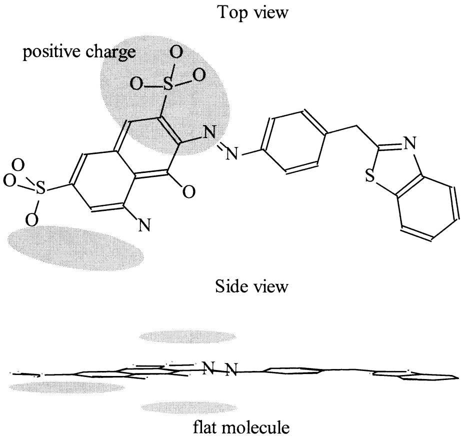


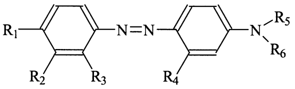
Fig. 1. Summary of useful features for higher cellulose affinity in case of the monoazo dyes.

submitted to a three-layer NN with the back-propagation of errors, lead to a much better model, after elimination of one outlier. The statistical parameters corresponding to this NN model are: $r^2 = 0.884$ and $q^2 = 0.622$. The improvement of the model is explained by the ability of the NN method to take account of non-linear and cross terms in the modeling. Although the predictivity of the NN model is good (see the q^2 value), it is rather difficult to interpret these results at molecular level: we retain that the shape of the molecule is important and maybe these dyes act as donors in the dye-cellulose interactions. It is mentioned that the $C \log P$ hydrophobic parameter is not correlated with the dye affinity.

The CoMFA method applied to these compounds [92] clarifies the important features governing the dye affinities. Again the electrostatic field proved to be more important than the steric one. It is interesting to note that the negative charges on the SO_3H groups lying at the extremities of the symmetrical bisazo dyes decrease the affinity, while the same sulfonic groups situated near the azo groups are beneficial for the dyeing process. From the effects of the steric field it is worthwhile to mention that deviations from the planarity, especially in the central region of the molecules, are predicted to be disadvantageous. This is in accordance with the fact that λ_3 (a shape parameter) has negative slope in the MLR model and it is consistent with the NN model.

The bisazo dyes, similarly with the monoazo dyes, will be better dyeing agents for cellulose if the negative charge, represented for example by SO_3H groups, can be reduced. Certainly such an operation would reduce the solubility of these dyes.

4.4. Disperse dye adsorption on cellulose



6

$R_1 = NO_2$, Br, Cl, CN, OCH_3, CH_3, F; $R_2 = Cl$, NO_2, CH_3; $R_3 = CH_3$, NO_2; $R_4 = CH_3$; $R_5 = C_2H_5$, C_2H_4OH; $R_6 = C_2H_4OH$

The affinity for cellulose fibre of a series of 20 disperse dyes (4-aminoazobenzene derivatives) (**6**) was first studied by means of the Free–Wilson and the MTD methods [97]. A good agreement was obtained between the results of these two QSAR methods, showing beneficial dye–fibre interactions along the longest molecular axis. For the same series, a MLR study implying steric, electronic and hydrophobic parameters showed that an important factor in the above interactions would be of electrostatic (electronic) nature [91].

The series of 20 disperse azo dyes was completed with other 7 similar disperse dyes in addition possessing also condensed heterocyclic moieties, and afterwards the MTD study was repeated [98]. Most of the cavity vertices in this case appeared in the region of the heterocyclic substituent, thus prolonging the molecular surface with beneficial interaction along the longest molecular axis. The PLS variant of the MTD method, applied to the same series of compounds [99], strengthened this image. This later study also differentiated the local steric, hydrophobic, electrostatic and hydrogen bonding effects. The results indicate both cellulose O-atoms and OH groups are involved in hydrogen bonding with the dye molecules. Charge effects are often important but are not always related to hydrogen bonding.

Simple MLR models [98] indicate that hydrophobic transferability does not play an important role in binding, since $C \log P$ does not correlate with the affinity, but a simple geometric parameter (the molecular length descriptor, λ) explains 75% of the variance of the affinity values, generating the simplest predictive model with $r^2 = 0.748$.

The CoMFA study [98] of the compounds ($r^2 = 0.925$, $q^2 = 0.776$) emphasised the importance of steric contributions for enhancing the dye affinity to cellulose over the influence of the electrostatic field. This is in contradiction to the results obtained for anthraquinone vat dyes and for monoazo and bisazo dyes. The beneficial steric interactions are mainly in the region of the condensed heterocyclic moiety. The positive electrostatic contributions are located around the benzene ring bonded to the azo group, rather than the 4-aminophenyl group.

For these disperse dyes, the favourable features for high affinity can be summarized as long linear structures and substituents that maintain linearity. Fig. 2 presents a general view of beneficial dye regions for higher affinity for cellulose fibre in the case of the disperse azo dyes.

5. Conclusions

Our QSAR-type studies for dye–cellulose fibre interaction presented in this review, as well as the qualitative SAR-type relationships, demonstrate at least an appreciable similarity of dye–fibre interactions with receptor–ligand interactions. Series of anthraquinone vat dyes, mono and bisazo and disperse dyes were studied by several variants of classical QSAR and 3D-QSAR and of other modern methods. A comparison of the results demonstrates that these methods usually agree in the prediction of structural features favourable for dyeing. Attractive dye–cellulose interactions are generally favoured along the molecular axis of the dye molecule and by the length of the molecular conjugated system. Electrostatic and steric interactions are more important for dye–cellulose binding than hydrophobic interactions. Perhaps the most interesting result, as indicated mainly by CoMFA studies concerning the contribution of electrostatic fields, is that an increase of positive charges in the dye molecule favours dye adsorption on cellulose. Detrimental interactions were noticed for sulfonic groups in the dye molecules, which seem to contribute only to dye solubilization in the dyeing environment. For anionic mono azo dyes an increase in lipophilicity contributes to dye–cellulose binding. In the case of disperse dyes, steric interactions are also important for this binding. Our QSAR results concerning structural features which contribute to dye–cellulose affinity agree with the conclusions of earlier SAR-type studies. Our results are compatible with cellulose as a receptor for dye molecules with several similar binding sites. Quantitative dye–fibre adsorption studies will be necessary in order to clarify the unique or multiple character of binding sites on cellulose fibre.

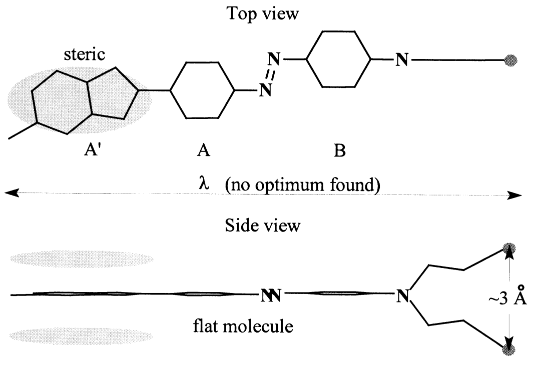


Fig. 2. Summary of useful features for higher cellulose affinity in case of the disperse azo dyes.

References

[1] Textile Faserstoffe. Leipzig: VEB Fachbuchverlag, 1963. p. 76.
[2] Venkataraman, K. The chemistry of synthetic dyes. Vol. II. New York: Academic Press, 1952.
[3] Aspland JR. Text Chem Color 1991;23:14–20.
[4] Peters, RH. Textile chemistry. The physical chemistry of dyeing. Vol. III. Amsterdam: Elsevier, 1975.
[5] Krichevskij GE. Zh Vses Khim O-va 1981;26:381–9.
[6] Shore, J. editor. Cellulosics dyeing. The Society of Dyers and Colourists, 1995. p. 70.
[7] Vieira Ferreira LF, Garcia AR, Rosário Freixo M, Costa SMB. J Chem Soc Faraday Trans 1993;89:1937–44.
[8] Mondal IH, Kai A. Polym J 1998;30:78–83.
[9] Kai A, Mondal IH. Int J Biol Macrom 1997;20:221–31.
[10] Daescu C, Hadaruga D. Dyes and Pigments 1999;40:235–41.
[11] Trotman ER. Dyeing and chemical technology of textile fibres. 4th ed. London: Griffin, 1970. p. 410.
[12] Hearle JWS, Peters RH. Fibre structure. London: Butterworths, 1963.
[13] McGregor R. Text, Chem, Colour 1980;12:306–10.
[14] Vickerstaff T. The physical chemistry of dyeing. London: Imperial Chemical Industries Limited, 1954.
[15] Porter JJ, Perkins WS. Text Res J 1970;40:81–8.
[16] Shibusawa T, Nakamura T. J Polym Sci Part B: Polym Phys 1995;33:159–65.
[17] Shibusawa T, Chigira Y. J Polym Sci Part B, Polym Phys 1992;30:563–8.
[18] Silverman BD. J Appl Polym Sci 1993;47:1013–8.
[19] Woodcock S, Henrissat B, Sugiyama J. Biopolymers 1995;36:201–10.
[20] French AD, Battista OA, Cuculo JA, Gray DG. In: Kirk–Othmer encyclopedia of chemical technology. 4th ed., vol. 5. New York: Wiley, 1993, p. 476.
[21] Nugmanov OK, Pertsin AI, Zabelin LV, Marchenko GN. Usp Khim 1987;56:1339–59.
[22] Rattee ID, Breuer MM. The physical chemistry of dye adsorption. London: Academic Press, 1974.

[23] Iyer SRS, Jayaram R. J Soc Dyers Colour 1971;10:338–42.
[24] McGregor R, Iijima T. J Appl Polym Sci 1992;45:1011–21.
[25] McGregor R, Iijima T. J Appl Polym Sci 1990;41:2769–82.
[26] Alberghina G, Amato ME, Fisichella S. J Soc Dyers Colour 1989;105:163–6.
[27] Alberghina G, Amato ME, Fisichella S. J Soc Dyers Colour 1988;104:279–83.
[28] Alberghina G, Fisichella S, Occhipinti S. Text Res J 1990;60:501–7.
[29] Alberghina G, Chen S-L, Fisichella S, Iijima T, McGregor R, Rohner RM, et al. Text Res J 1988;58:345–54.
[30] Sumner HH. J Soc Dyers Colour 1986;102:392–7.
[31] Filonenko VI, Androsov VF, Chursina LA, Kotii VS. Izv Vyssh Uchebn Zaved, Tekhnol Tekst Prom-sti 1977;120:64–9.
[32] Cadariu, I. Chimie fizica, vol. 1. Bucuresti: Editura Tehnica, 1967.
[33] Autorenkollektiv. Van der Waals systems. Berlin: Akademie-Verlag, 1981.
[34] Zollinger H. Color chemistry. Synthesis, properties and applications of organoc dyes and pigments. Weinheim: VCH, 1987.
[35] Rattee ID. J Soc Dyers Colour 1974;10:367–72.
[36] Schaeffer A. Melliand Textilber 1958;39:68–74.
[37] Artym MI, Moryganov PV. Izv Vyssh Uchebn Zaved, Tekhnol Tekst Prom-sti 1961;3:110–6.
[38] Bird CL. J Soc Dyers Colour 1965;72:343–51.
[39] Feichtmayr F, Würz A. J Soc Dyers Colour 1961;77:626–37.
[40] Giles CH, MacEwan TH. J Chem Soc 1959;4:1791–8.
[41] Scheiner, S. In: Lipkowitz KB, Boyd DB, editors. Reviews in computational chemistry II. New York: VCH, 1991. p. 165–217.
[42] Bezdadea M, Bourceanu M, Kerekes A, Muresan F, Ivan C, Corduneanu G, et al. Ind Usoara: Text Tricotaje Confectii Text 1987;38:172–80.
[43] Campbell DS, Cathcart D, Giles CH. J Soc Dyers Colour 1957;73:546–53.
[44] Lead WL. J Soc Dyers Colour 1959;75:195–6.
[45] Badilescu II, Badilescu S. Legatura de hidrogen. Bucuresti: Editura Stüntifica si Enciclopedica, 1981. p. 247–62.
[46] Hori T, Zollinger H. Text Chem Color 1986;18:1925.
[47] Hori T, Zollinger H. Trends in dyeing and finishing, International Dyeing Symposium. Research Triangle, NC., AATCC, 1986;38:27–37.
[48] Holfeld WT, Shepard MS. Text Chem Color 1978;10:18–28.
[49] Bach H, Pfeil E, Philippar W, Reich M. Angew Chem 1963;75:407–16.
[50] Gombkete Ja, Krichevskij GE, Bajbeuk-Melikova TV. Izv Vyssh Uchebn Zaved, Tekhnol Tekst Prom-sti 1977;117:76–9.
[51] Lunjaka KV. Izv Vyssh Uchebn Zaved, Technol Tekst Prom- sti 1991;6:63–5.
[52] Asquith RS, Kwok WF, Otternburn MS. Text Res Inst 1980;50:333–6.
[53] Herrington TM, Midmore BR. J Chem Soc Faraday Trans 1984;1:1539–80.
[54] Valko EI. Text Res J 1957;27:883–98.
[55] Simon Z. Biochinie cuantica si interactii specifice. Bucuresti: Stiintifica, 1973.
[56] Riesz E. Textilveredlung 1990;25:20–3.
[57] Alberti G, Cerniani A, De Giorgi MR, Passerini A. Ann Chim (Rome) 1982;72:393–7.
[58] Alberti G, Cerniani A, De Giorgi MR, Seu G. Ann Chim (Rome) 1983;73:265–72.
[59] Giles CH, Montgomery AP, Tolia AH. Text Res J 1962;32:99–107.
[60] Wilson D. J Soc Dyers Colour 1960;76:84–94.
[61] Shibusawa T. Seni Gakkaishi 1987;43:401–15.
[62] Shibusawa T. Seni Gakkaishi 1991;47:657–63.
[63] Moryganov PV, Mel'nikov BN. Colloid J (USSR) 1957;19:100–3.
[64] Giles CH, Hassan ASA. J Soc Dyers Colour 1958;74:846–57.
[65] Zollinger H. Textil-Rund 1959;14:113–25.
[66] Schaeffer A. Melliand Textilber 1958;39:182–6.
[67] Alberti G, Cerniani A, De Giorgi MR, Seu G. Ann Chim (Rome) 1983;73:155–9.
[68] Daruwalla EH, Mehra RH. Text Res J 1959;29:595–611.
[69] Hamada K, Iijima T, McGregor R. Polym J 1987;19:709–17.
[70] Giles CH. Text Res J 1961;31:141–51.
[71] Krasovitzkij BM, Titarenko NI. Ukrain Khim Zh 1958;24:481–6.
[72] Krasovitzkij BM, Moryganov PV, Titarenko NI, Mel'nikov BN. Dokl Akad Nauk SSSR 1957;116:425–8.
[73] Grieder K. J Soc Dyers Colour 1976;92:8–13.
[74] Aspland JR, Bird CL. J Soc Dyers Colour 1961;77:9–12.
[75] Dohmyo M, Shimizu Y, Kimura M. J Seric Sci Jpn 1987;56:116–9.
[76] Grecu R, Pieroni M, Carpignano R. Dyes and Pigments 1981;2:305–18.
[77] Carpignano R, Barni E, Di Modica G, Grecu R, Bottaccio G. Dyes and Pigments 1983;4:195–211.
[78] Carpignano R, Savarino P, Di Modica G, Savia G. Tinctoria 1984;4:97–110.
[79] Carpignano R, Savarino P, Barni E, Di Modica G, Papa SS. J Soc Dyers Colour 1985;101:270–6.
[80] Carpignano R, Savarino P, Barni E, Clementi S, Giulietti G. Dyes and Pigments 1985;6:189–212.
[81] Carpignano R, Savarino P, Barni E, Viscardi G, Clementi S, Giulietti G. Anal Chim Acta 1986;191:445–50.
[82] Carpignano R, Savarino P, Viscardi G, Barni E, Clementi S, Cruciani G. Melliand Textilber 1989;70:276–8.
[83] Dörr M. Textilveredlung 1992;27:284–7.
[84] Oprea TI, Kurunczi L, Olah M, Simon Z. Quant Struct–Act Relat Submitted.
[85] Timofei S, Simon Z, Schmidt W, Kurunczi L. Tendinte si proprietati in sinteza si aplicarea colorantilor, Zilele Academice Iesene. Romania, 5–7 noiembrie, 1992. p. 119–122.
[86] Timofei S, Schmidt W, Kurunczi L, Simon Z, Sallo A. Dyes and Pigments 1994;24:267–79.

[87] Timofei S, Kurunczi L, Schmidt W, Fabian WMF, Simon Z. Quant Struct–Act Relat 1995;14:444–9.
[88] Fabian WMF, Timofei S, Kurunczi L. J Mol Struct, THEOCHEM 1995;340:73–81.
[89] Timofei S, Kurunczi L, Schmidt W, Simon Z. Rev Roumaine Chim 1997;42:687–92.
[90] Timofei S, Kurunczi L, Schmidt W, Simon, Z. 7th International Conference on Organic Dyes and Pigments, Colorchem '98. Pardubice: Rybitivi, 1998. p. L10.
[91] Timofei S, Kurunczi L, Schmidt W, Simon Z. Dyes and Pigments 1996;32:25–42.
[92] Fabian WMF, Timofei S. J Mol Struct THEOCHEM 1996;362:155–62.
[93] Timofei S, Fabian WMF. J Chem Inf Comput Sci 1998;38:1218–22.
[94] Timofei S, Kurunczi L, Suzuki T, Fabian WMF, Muresan S. Dyes and Pigments 1997;34:181–3.
[95] Timofei S, Kurunczi L, Suzuki T, Fabian WMF. 6th symposium on computational chemistry. Tokyo. 1996. p. 102–5
[96] Timofei S, Kurunczi L, Muresan S, Fabian WMF, Suzuki T. 29th Autumn meeting of the society of chemical engineers of Japan. Kyoto, 1996. p. 269.
[97] Timofei S, Kurunczi L, Schmidt W, Simon Z. Dyes and Pigments 1995;29:251–8.
[98] Oprea TI, Kurunczi L, Timofei S. Dyes and Pigments 1997;33:41–64.
[99] Kurunczi L, Olah M, Oprea TI, Simon Z. Quant Struct–Act Relat Submitted
[100] Mager PP. Eur J Med Chem 1994;29:369–80.
[101] Mager PP. QSAR in design of bioactive compounds. Proc. 2nd Telesymp. Med. Chem. Barcelona: J. R. Prous Sci. Publ., 1992. p. 446–69.