

# QUANTITATIVE RELATIONSHIPS FOR DESIGN OF DISPERSE DYES OF HIGH TECHNICAL PROPERTIES

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## Introduction

Study of quantitative relationships between structure and properties of dyes is essential in textile chemistry research [1-7]. In modern literature this kind of research is recognised as *quantitative structure-activity relationships* or *quantitative structure-property relationships* (QSAR/QSPR).

The results of QSPR studies are important for future development of dyes of high technical properties. Selection and design of dyes need the analysis of relationships of several quantities, such as structure of chromophores, their spectral properties, behaviour of dyes in solution, affinity of dyes to textiles, colour characteristics of dyeings, fastness of dyeings and bioelimination in textile waters.

The results of systematic QSPR studies of dyes and generalisation of experimental results supported understanding of dyeing mechanism and behaviour of textile dyes in various dyeing systems [8-13]. Published papers discuss the mechanism of disperse and anionic dyes interaction with cellulose [8-11], vat dyes with cellulose [12], some interesting results deal with design of acid dyes for silk [13]. Chemometric approach was used for analysis of bioelimination of acid, direct and reactive dyes in waste waters [14]. Some recent results of QSPR studies were reported for wool dyeing mechanism and levelness of dyeing from the point of view of amphiphilic properties of acid dyes [15]. At the same time dye affinity and rub fastness of anionic dyes on wool and cotton exhibit correlation with electronic properties of dyes [11, 16].

The analysis of the literature reveals the lack of research devoted to QSPR studies of disperse dyes. On the other hand, a numerous experimental systematic research, reported during the last 50 years, could serve as a basis for analysis structure – property relationships. The aim of the research was to study quantitative structure-property relationships for series of disperse dyes and development of an approach for predicting disperse dye behaviour in dyeing systems and environmental conditions, as well as for predicting wash and light fastness properties of dyes on polyester and polyamide.

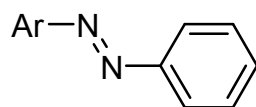
## Results and Discussion

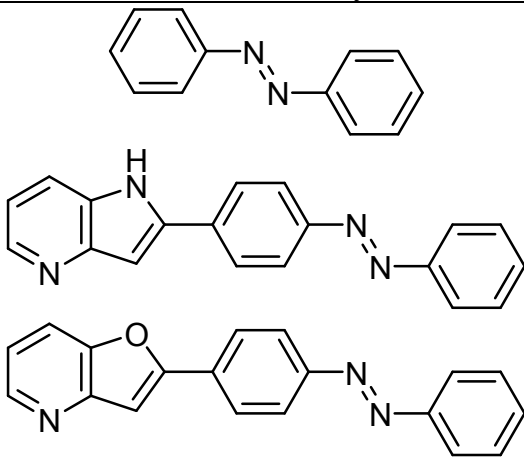
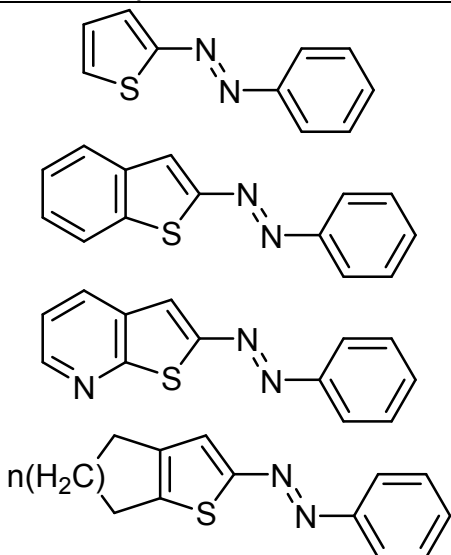
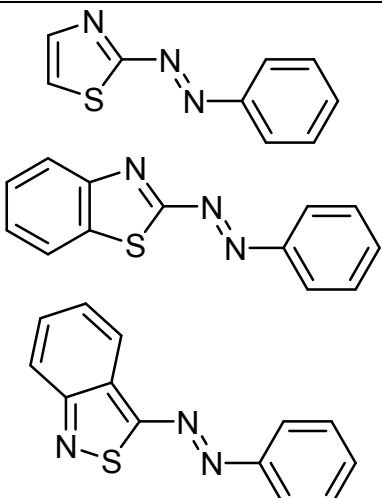
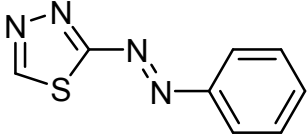
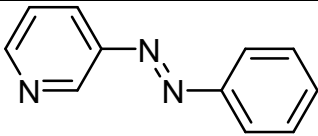
### Development of data base, describing the properties of disperse dyes

The initial step of the research was to develop a data base describing the properties of disperse dyes and dyeings of synthetic fibres. Collected data include the results of experimental studies, published in research papers provided the properties of several hundred of dyes with their spectral and sorption characteristics, fastness of dyeings to washing, light and sublimation. A big family of dyes, which is analysed below, covers different hetaryl derivatives, such as derivatives of azobenzene (as an

especial case), azobenzene with hetaryl residues, thiophene, thiazole, thiadiazole, pyridine, mentioned in the Table I.

Table I. Precursors for homological series of disperse dyes, azobenzene and hetaryl derivatives



Azobenzene with hetaryl residues	Thiophene derivatives
	
Thiazole derivative	Thiadiazole derivatives
	 
	Pyridine derivatives

### Relationship between amphiphilic properties of dyes and their affinity to fibres

Studies of the nature of dye-fibre interactions deals with the evaluation of dye affinity  $\Delta\mu^0$  to fibre or partition coefficient between the solution and fibre  $K_{f/w}$

$$-\Delta\mu_{f/w}^0 = RT \ln(K_{f/w}) \quad (1)$$

Partition coefficient in tern is characterised by the relation of equilibrium concentrations in the fibre  $C_f$  and solution  $C_w$

$$K_{f/w} = \frac{C_f}{C_w} \quad (2)$$

Similar to above amphiphilic properties of dyes are described by partition of dissolved substance between immiscible solvents. As a standard there used a mixture of n-octanol and water, and amphiphilic properties of dyes are characterised by relation of correspondent equilibrium concentrations  $C_O$  and  $C_W$  of organic substances at 20 °C:

$$P = \frac{C_O}{C_W} \quad (3)$$

In the literature it is common to use parameter LogP, which is evidently proportional to dye affinity for organic solvent:

$$-\Delta\mu_{O/W}^0 = RT \ln(P_{O/W}) \quad (4)$$

According to above definition negative values of LogP characterise hydrophilic substances and positive – hydrophobic.

Evaluation of the parameter logP by means of computer software ChemDraw yields good correlation with experimental values for series of azobenzene derivatives [17]. Other software, available for us, provides worse correspondence between experimental and theoretical values.

Disperse dyes are the most suitable class of dyes for such analysis as far as the above definitions are correct for non-ionic substances. Several examples listed below demonstrate applicability of the parameter LogP in the studies of dye structure-property relationships describing behaviour of disperse dyes in different dyeing systems.

Papers by J. Szadowski et al. reported the results of studies of adsorption of azobenzene dyes, containing amido groups (I, II) [18], and naphthylamine derivatives (III) [19] on polyester fibres and films in water dye bath.

Evaluated parameters of LogP with experimental partition coefficients between polyester and dye bath in logarithmic scale exhibits rather good correlation, demonstrated in Fig.2.

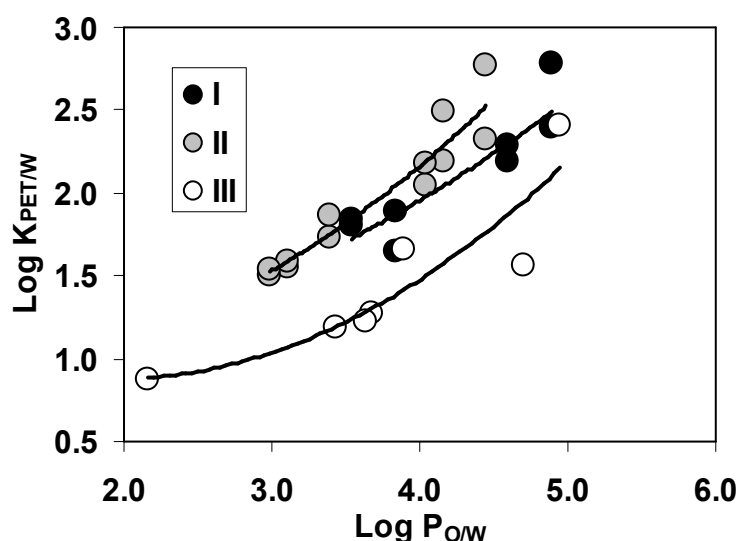


Fig.1. Relationship between experimental value of partition coefficient  $\text{Log } K_{\text{PET/W}}$  for sorption of disperse dyes on polyester film and evaluated parameter  $\text{Log } P_{\text{O/W}}$  for series I, II and III.

Affinity of dyes to textile materials controls several properties of dyeings, which is determined by physico-chemical interactions between dye and fibre, from one hand, and dye and solvent (water) – from another. The most important factor is wash fastness of dyeings. The data, reported by G. Seu [20] for pyridine derivatives and analysed in our study, exhibit good correlations between parameter LogP (Fig.2) and dye affinity as well as with wash fastness on acetate, nylon and silk fibres (Fig.3).

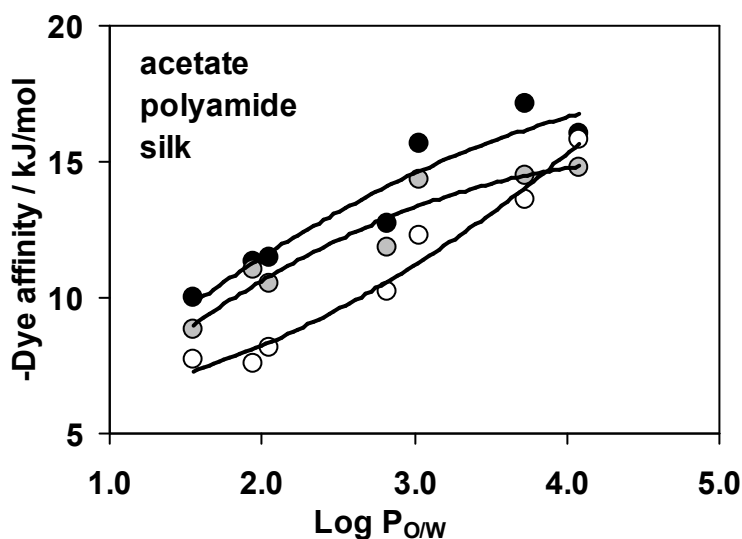


Fig.2. Relationship between parameter Log P<sub>OW</sub> and affinity  $-\Delta\mu$  of disperse dyes to acetate, nylon and silk fibres

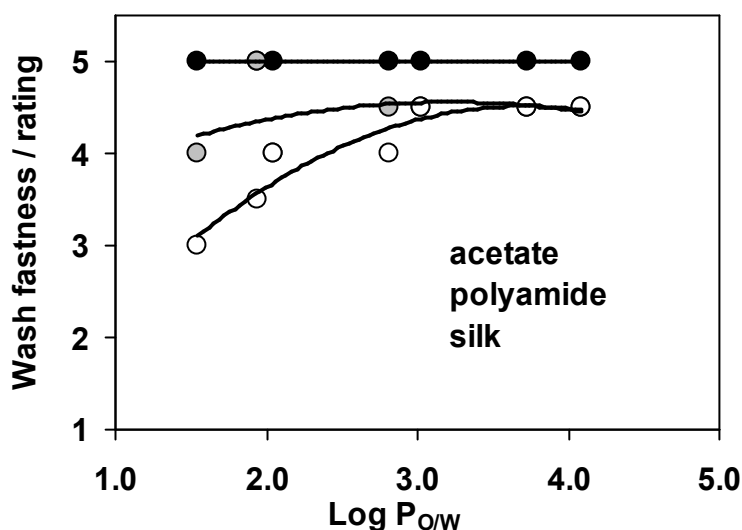


Fig.3. Relationship between parameter Log P<sub>OW</sub> and wash fastness of disperse dyes on acetate, nylon and silk fibres

In addition to above the results by P. Savarino [21] for wash fastness of disperse dyes on polyester also demonstrate good correlation with parameter LogP, depicted in Fig. 4. In this case azobenzene derivatives with hetaryl residues were used.

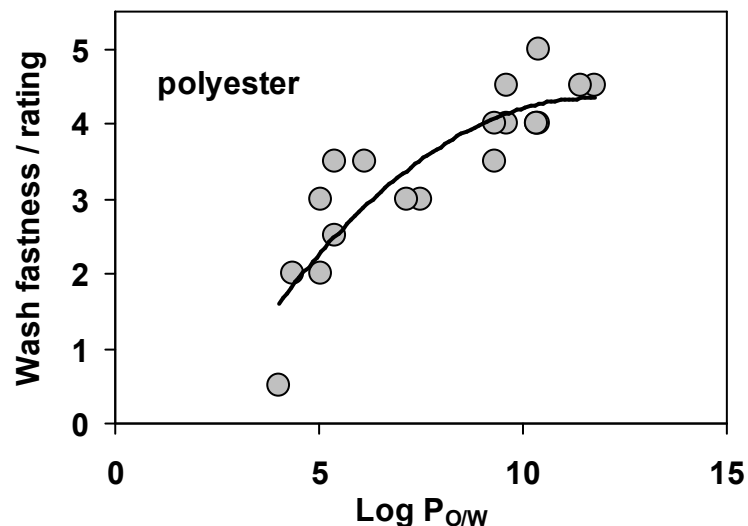


Fig.4. Relationship between Log P<sub>OW</sub> and wash fastness of polyester

### Relationship between electronic properties and light fastness of disperse dyes

The next step of the research was devoted to evaluation the electronic properties of disperse dyes and to analysis of their relationships with wash fastness and light fastness on polyester and nylon fibres.

By the use of molecular modeling technique several electronic parameters were evaluated:

Energy of higher occupied molecular orbital, HOMO, which characterise the ability of dyes for accepting electrons in reactions of oxidation;

Energy of lower unoccupied molecular orbital, LUMO, which characterise the ability of dyes for donation electrons in reactions of reduction.

It is well known that light fastness of dyes is controlled by redox properties of disperse dyes and their photo-destruction follows oxidation or reduction mechanism, therefore correlation of light fastness with oxidation and reduction potentials of dye molecules is quite expected. Several examples below demonstrate this statement.

Analysis of the results by R. Grecu [22] for light fastness of a series of disperse dyes, hydroxypyrazole derivatives, demonstrate typical correlation of this quantity with HOMO energy, characterising photo-oxidation mechanism of azo-group destruction on polyester (Fig.5).

Study of light fastness of azobenzene derivatives on nylon by E. Barni [23] also demonstrates photo-oxidation pathway of dye destruction (Fig.6).

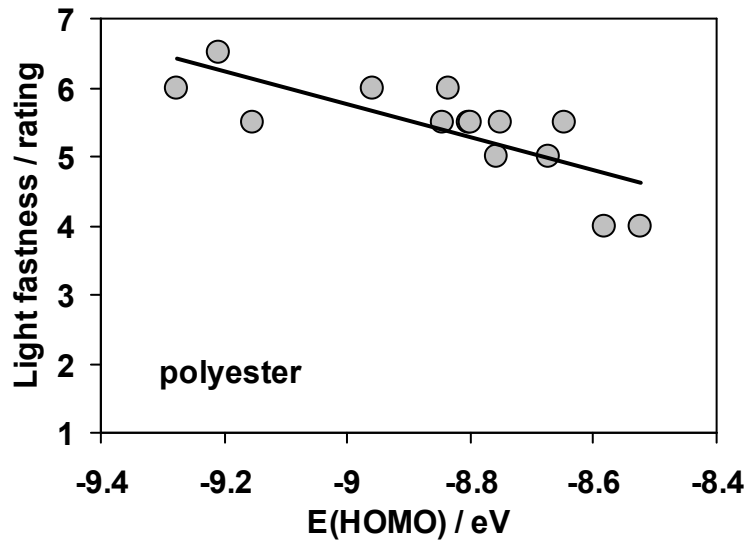


Fig.5. Relationship between HOMO energy and light fastness of disperse dyes on polyester

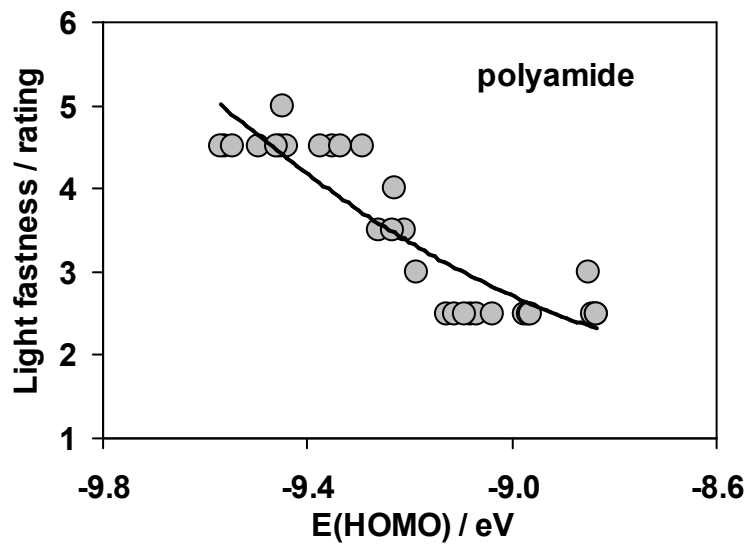


Fig.6. Relationship between HOMO energy and light fastness of disperse dyes on nylon

The results of another research, carried out by G . Hallas [24] for thiophene derivatives, exhibit correlation of light fastness with LUMO energy. In this case destruction of dye molecules follows reduction mechanism due to sulphur atom in thiophene moiety.

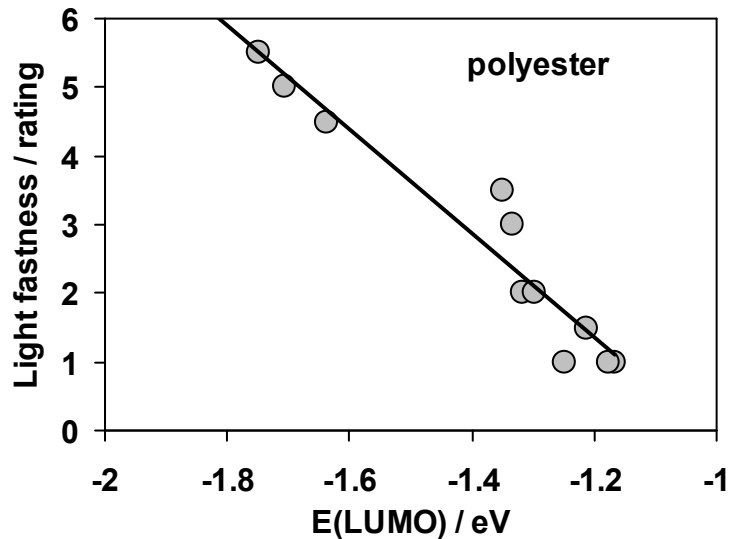


Fig.7. Relationship between LUMO energy and light fastness of disperse dyes on polyester

Similar relationships exhibit two series of disperse dyes, aminoazobenzene derivatives, studied by G. Hallas [25] (Fig.8):

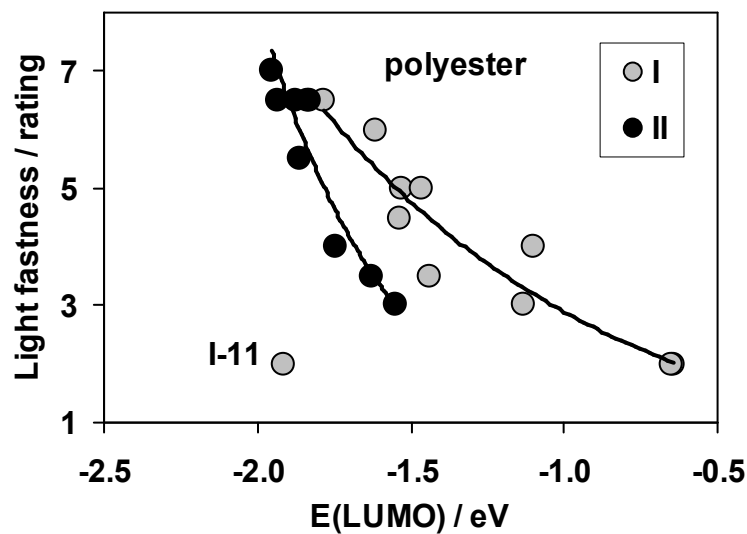


Fig.8. Relationship of LUMO energy on light fastness of disperse dyes on polyester

Reduction mechanism of dye photo-destruction is attributed to polyamide fibres [6, 25] due to the presence of electron-donating amino- and imino-groups. However, study of light fastness of azobenzene derivatives [26] shows the enhancement of light fastness for dye of high reduction ability (Fig.9). The results of the work report by H.S. Freeman et al [27] indicate that increased photostability of dyes could be attributed to a contribution of reversion from light induced trans→cis isomerism of azo bond.

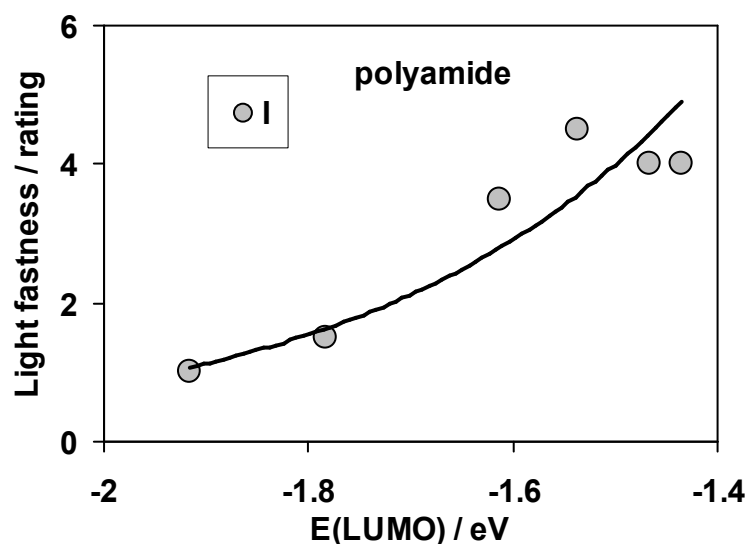


Fig.9. Relationship of LUMO energy on light fastness of disperse dyes on nylon

The above relationships between electronic properties and light fastness of disperse dyes show that the mechanism of dye destruction on polyester and nylon fibres follows oxidation or reduction route depending on dye structure and nature of polymer. Good correlation of HOMO and LUMO energies with light fastness, observed in this study, could be used for optimising dye structure and design of new dyes with high photo-stability.

In addition to above the evaluation of redox properties of disperse dyes could serve some other technical purposes. For example, reduction potential of dye molecules is useful for estimation the sensibility of disperse dyes to reductive cleaning after dyeing of polyester or oxidative domestic washing of textile goods. Finally, redox properties are important for consideration about suitability of dyes for photo-chemical, electrochemical and biological decoloration of textile waste waters.

## Conclusions

QSPR studies of disperse dyes on the basis of the results published in the literature revealed several important results which has both theoretical and practical importance.

Evaluated quantities of water/octanol partition coefficients exhibit correlation with dye partition coefficients between hydrophobic synthetic fibres and dyebath. Hydrophobicity of dyes controls wash fastness of dyeings.

HOMO (higher occupied molecular orbital) and LUMO (lower unoccupied molecular orbital) energies, which characterise the ability of dyes for oxidation or reduction, correlates with light fastness of disperse dyes on polyester and polyamide.

Quantitative relationships between amphiphilic/electronic properties of dyes and their important technical characteristics are useful for physico-chemical analysis of fading mechanism of disperse dyes on fibres of different nature (polyester, polyamide, acetate) and for design of new dyes with high affinity to textile fibres and high wash and light fastness.



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