

Relationships Between Sensitizing Dye Structure, Hydrophobicity, And Post-Process Dye Stain

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Abstract

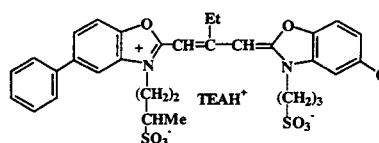
Working on the premise that most retained sensitizing dye stain in color systems is related to partitioning of the dye into a color coupler dispersion, it was possible to derive a relationship between dye substituent hydrophobicity parameters (π values) and dye stain. The π values were obtained from log P values that were calculated, where P is the octanol/water partition coefficient of a dye fragment. These calculations can be used to predict the stain properties of new dye substituents before their synthesis. This paper will discuss these calculations and their use to design new dyes that afford reduced post-process dye stain.

Introduction

The usual function of sensitizing dyes (most often cyanine dyes) is to adsorb to silver halide and to absorb light and transfer an electron to the silver halide grain; thus, rendering the silver halide sensitive to radiation of a wavelength other than the intrinsic sensitivity. Generally, a sensitizing dye should wash out of the film, or paper, during processing. Any retained dye contributes to D-min and this is often referred to as sensitizing dye stain. Dye stain, which adversely affects the image recorded in the photographic material, has been a source of concern for many years. The problem of sensitizing dye stain is further aggravated by the advent of new emulsions, such as tabular grains, which have more surface area and use higher dye levels which accordingly tends to give higher levels of dye stain. Photographic emulsions, especially high chloride emulsions, are also often subjected to rapid processing, which can further enhance dye stain problems by limiting the amount of time available for the dye to wash out of the coating.

Color paper is particularly sensitive to sensitizing dye stain since a low D-min is very important in this application. When a green sensitizer, such as Dye 1, is used in color paper, any retained dye can cause an appreciable increase in D-min. Historically, stain-reducing agents, such as triazinyl stilbene compounds, also known as optical brighteners, have been used in color paper developer formulations to reduce stain due to retained dye. It is believed that the triazinyl stilbene compound complexes to the sensitizing dye and that the complex washes out of the paper faster than

the dye alone. The focus of the work described here was to eliminate, or reduce, the need for expensive triazinyl stilbene compounds in color paper processing solutions by replacing the green sensitizing dye with a dye that gives significantly less dye stain while maintaining all other performance features of the dye.



Dye 1

Results and Discussion

The Dye Stain Model

This paper describes a simple model for the most common mechanism of dye retention in color systems, which is interaction of the sensitizer with coupler dispersions. Other reasons for retained dye such as aggregation or precipitation of the dye in gelatin during processing are not part of this model.

The coupler dispersion in a color coating could be viewed as an "organic" solvent. In this stain model, as the dye is washing out of the coating, it partitions between the coupler dispersion and the aqueous processing solution. It seemed likely that this partitioning process would depend on the dye's hydrophobicity and might be modeled by an octanol/water two-phase system.

Octanol/water partition coefficients (P) are derived by mixing a compound with water and 1-octanol and determining the ratio of the concentration of the compound in octanol to that in water at equilibrium. Log (P) values are well-known measurements of hydrophobicity, that is, the tendency of a compound to be partitioned in a nonpolar phase versus an aqueous phase of an organic/aqueous mixture.¹

If coupler dispersion interactions are the principle cause of dye stain, this model would predict that in a series of

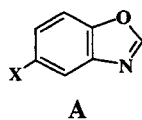
dyes, dye stain would decrease as the dyes become less hydrophobic. If we could predict the impact a structure change has on the dye's log P value we should be able to predict its impact on dye stain.

Calculation of Partition Coefficients

Whereas log P is a measure of the hydrophobicity of an entire molecule, the parameter π is the relative hydrophobicity of a substituent and is defined, for a substituent X, as: $\pi_x = \log P_x - \log P_H$, where P_x is the partition coefficient of a derivative and P_H that of the parent compound.¹ The π parameter is very useful when working with a set of derivatives of a parent compound in which a large portion of the structure remains constant.

Methods have been developed that allow calculation of log P and π values.¹ The procedure involves breaking the molecule into fragments and summing the contribution to log P for each of the fragments along with any interaction terms between fragments. These calculations are relatively simple provided the fragment values are known, and have been further simplified by commercially-available software packages such as MEDCHEM, which will calculate log P values upon entering a molecular structure.²

Unfortunately, it is not currently possible to calculate a log P value for a charged molecule like a cyanine dye (such as Dye 1), because the suitable fragment values are not available. Since these calculations would be very useful, a simplified case was examined by considering the substituents on a benzoxazole base, structure A, instead of a benzoxazole dye molecule. Values of π_x were determined by calculating log P values, referred to as CLOGP, for the structure A (substituted with X) and subtracting the CLOGP value (1.435) for the parent benzoxazole nucleus (Structure A, X = H). For example, the π_x value for a phenyl group (X = C₆H₅) is equal to CLOGP (5-phenylbenzoxazole) - CLOGP (benzoxazole) = 3.32 - 1.435 = 1.89.



The $\Sigma\pi$ value for a dye was obtained by adding the π_x values for back-ring substituents. Since the nitrogen substituents on the dyes can differ, a correction term was also needed to compensate for differences in relative hydrophobicity due to these groups. The value for 3-sulfopropyl was arbitrarily set to zero and the remaining nitrogen substituents were estimated relative to the sulfopropyl group. For example, the log P contribution of a 3-sulfobutyl group would equal the 3-sulfopropyl plus a -CH₂- fragment plus a bond factor plus a branching factor and is estimated as 0.00 + 0.66 + (-0.35) + (-0.10) or 0.20 relative to 3-sulfopropyl.¹

As an example, the calculation of $\Sigma\pi$ value for Dye 1

would equal the calculated π value for phenyl group ($\pi = 1.89$) plus the π value for chloro group ($\pi = 0.75$) plus a correction for one 3-sulfobutyl group (0.20) and one 3-sulfopropyl group (0.00): $\Sigma\pi$ (Dye 1) = 1.89 + 0.75 + 0.20 + 0.00 = 2.84.

To test these calculations and the stain/hydrophobicity model, a series of substituents that varied considerably in hydrophobicity and that could be placed on benzoxazole dyes was needed. Calculations indicated that amide groups were very effective at reducing hydrophobicity. It is also fairly easy synthetically to make structure modifications using amides.

Model Dyes





The set of amide substituents having the calculated π values listed in Table I were considered initially. These substituents contain aromatic groups that should promote adsorption of the dye to the silver halide surface and they are also relatively "flat" in shape, thus the dyes should aggregate on silver halide. Some of the dyes that were synthesized initially are shown in Table II.

Table I: Aromatic Amide Substituents.

Substituent	π
	1.89
	0.97
	0.66
	0.14
	-0.17

Table II: Initial Dyes.

Dye	Z ₁	Z ₂	R ₁ , R ₂ ^a	$\Sigma\pi$	RT ^b	Stain ^c
1		Cl	3SB, SP	2.84	30.7	42
2	"	F	SP, SP	2.07	18.3	34

3	"	=Z ₁	SEt,SEt	3.98	68.7	61
4		Cl	SP,SP	1.72	9.7	20
5	"	Cl	3SB,SP	1.92	11.5	21
6	"	F	SP,SP	1.15	6.7	7
7	"	F	3SB,SP	1.35	7.9	^d
8		Cl	3SB,SP	1.61	10.2	17
9		Cl	4SB,SP	1.19	5.5	11
10	"	F	4SB,SP	0.62	3.75	3
11	"	=Z ₁	SEt,SEt	0.48	3.7	8
12		Cl	SP,SP	0.58	6.0	6
13	"	Cl	3SB,SP	0.78	6.5	9
14	"	F	3SB,SP	0.21	4.45	2

^aSP is 3-sulfopropyl, 3SB is 3-sulfobutyl, 4SB is 4-sulfobutyl, SEt is 2-sulfoethyl. ^bIsocratic hplc retention time in min. ^cStain (density x 10³). ^dDye precipitated.

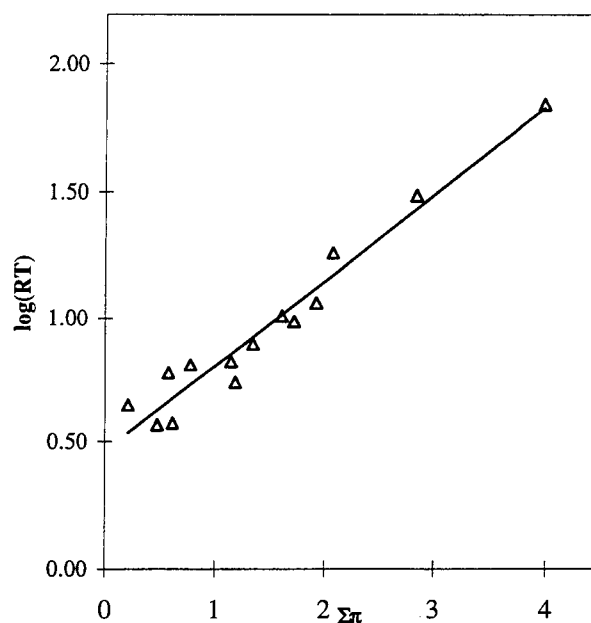


Figure 1. Plot of $\log(RT)$ vs. $\Sigma\pi$.

Photographic Evaluation

The dyes were evaluated in a black and white format on a 0.2 μm cubic silver bromide (2.6 mol % I) emulsion.³ The dyes J-aggregated on the test emulsion and were efficient sensitizers.⁴

HPLC Retention Times

It is relatively difficult to measure partition coefficients for cyanine dyes because they readily associate in water forming dimers or higher aggregates and this leads to erroneous $\log P$ values. An alternative method of measuring relative hydrophobicity is by determining isocratic HPLC retention times (RT). $\log(RT)$ values have been shown to be linearly related to $\log P$ values and thus are a measure of hydrophobicity.⁵ Based on the model, low staining dyes would have low HPLC retention times that correspond to low $\log P$ values.

A plot of isocratic HPLC retention times ($\log RT$) for the model dyes versus $\Sigma\pi$ is shown in Fig. 1.⁶ The good correlation ($F = 226$, $r^2 = 0.949$, $n = 14$) suggests that the method of calculating π values gives a good measure of dye hydrophobicity despite the assumptions that were necessary (i.e., the use of a benzoxazole base rather than a dye molecule in the calculations). Equation 1 can be derived from this relationship.

$$\log(RT) = 0.36(\Sigma\pi) + 0.46 \quad (1)$$

Dye Stain

The dyes were coated in a color format (i.e., in the presence of a color coupler dispersion) and processed without triazinyl stilbene to determine their stain properties. The wavelength and absorbance of any retained dye in the processed strips were measured as an optical density (Table II).

Some dyes were synthesized (e.g., some symmetrical dyes were Z₁ and Z₂ are both aromatic groups) that had unusually high stain. These dyes, in addition to the monomeric dye absorption peak (ca. 510 nm), had absorption peaks at either about 550 or about 485 nm. The latter two peaks correspond to either a J or H dye aggregate. Thus, these dyes appeared to be aggregating in gelatin during processing, which caused much of the dye to be retained in the coating. Dyes that gave stain, due to aggregation, were not included in the coupler dispersion/stain model and are not listed in Table II because they were being retained by a different mechanism.

Plotted in Fig. 2 is dye stain (optical density) versus $\Sigma\pi$ values for the model dyes. A relatively good correlation exists and based on this relationship, it is possible to calculate an equation that relates dye stain and $\Sigma\pi$. This equation will be used as the model to predict dye stain.

$$\text{Stain (optical density)} = (16.0(\Sigma\pi) - 5.1) 10^{-3} \quad (2)$$

$$F = 206, r^2 = 0.949, n = 13$$

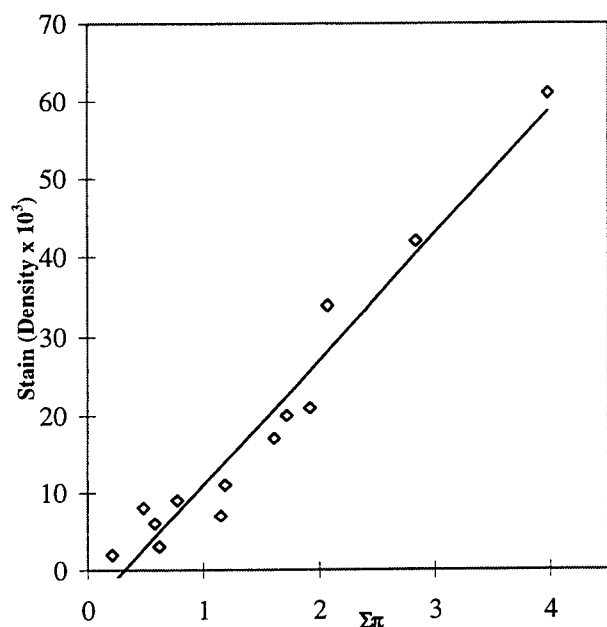
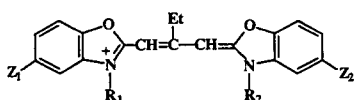
Figure 2. Plot of Stain vs. $\Sigma\pi$.

Table III: Acetamidophenyl Substituted Dyes.



Dye	Z ₁	Z ₂	R ₁ , R ₂ ^a	$\Sigma\pi$	Stain ^b	
					Obs	Cal
15		Cl	SEt, SP	1.56	21	23
16	"	F	SP, SP	1.05	14	12
17	"	F	SEt, SP	0.95	9	14
18		Cl	3SB, SP	2.16	28	25
19	"	F	3SB, SP	1.59	18	16

^a SP is 3-sulfopropyl, 3SB is 3-sulfobutyl, SEt is 2-sulfoethyl.

^bStain (density $\times 10^3$), Obs is the observed value, Cal is the calculated value.

Acetamidophenylbenzoxazole Dyes

To test the model, it was used to predict the properties of a set of dyes before they were made. The *p*-acetamidophenyl and *m*-acetamidophenyl substituents would be alternative ways of connecting an amide group and an aromatic group to a dye molecule and appeared to be interesting new dye substituents. Equation 2 was used to predict the stain properties of the target dyes (Table III) and indicated that these dyes would be relatively low in stain (compared to Dye 1) and it would be worthwhile to make these synthetically more difficult molecules. Several dyes were synthesized and the new dyes were evaluated for photographic performance and stain as described previously; the results are also recorded in Table III. The dyes were excellent sensitizers and had stain values close to that predicted by the model.⁴

Conclusions

The simple dye stain model has proven successful at predicting post-process stain for oxocarboxyanine analogs that are retained because of coupler dispersion interactions. The model has been used in a cost effective manner to design new substituents that give reduced dye stain.⁷

Acknowledgements

The authors would like to thank Dr. Fred Sauter, and Dr. Steve Link of Eastman Kodak Company for valuable discussions and suggestions.

References

1. A. Leo and C. Hansch, *Substituent Constant for Correlation Analysis in Chemistry and Biology*, Wiley, New York (1979).
2. CLOGP values were calculated using the Medchem software package, release 3.54, developed and distributed by Pomona College, Claremont, California.
3. The authors would like to thank Tom Dobles, Teresa Hosmer, and Freddy Price for assisting with this evaluation.
4. See US Patent 5,316,904.
5. See for example, J. M. McCall, *J. Med. Chem.*, **18**, 549, (1975).
6. The authors would like to thank LuAnn Weinstein for assistance with the HPLC measurements.
7. For additional examples of low-stain dyes see US Patent 5,418,126.