# Spectral properties of alkali-clearable azo disperse dyes containing a fluorosulfonyl group

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## 1. Introduction

Azo disperse dyes containing a fluorosulfonyl group are hydrolysed under alkaline condition by SN2 mechanism, and pseudo first-order kinetics were determined by analysis of the dye hydrolysis under alkaline conditions using HPLC. Also, the use of a fluorosulfonyl containing disperse dye showed a reasonable level of build up, excellent wash fastness and offers the option of alkali clearance to achieve high wash fastness, replacing reductive clearing and particularly sodium hydrosulfite, which places a very high BOD on conventional disperse dyeing effluent and the generates aromatic amines.

In this study, the spectral properties of monoazo disperse dyes containing a fluorosulfonyl group, 4-(N,N-diethylamino)-4'-fluorosulfonylazobenzene derivatives was investigated.
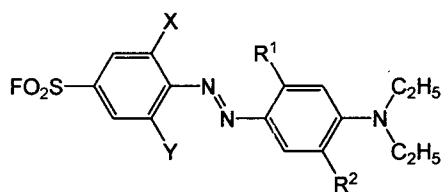


Table 1. Alkali-clearable azo disperse dyes containing a fluorosulfonyl group

| Dye | 1 | | | 2 | | | 3 | | | 4 | | | 5 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | a | b | c | a | b | c | a | b | c | a | b | c | a | b | c |
| X | H | H | H | $NO_2$ | $NO_2$ | $NO_2$ | $NO_2$ | $NO_2$ | $NO_2$ | $NO_2$ | $NO_2$ | $NO_2$ | $NO_2$ | $NO_2$ | $NO_2$ |
| Y | H | H | H | H | H | H | Cl | Cl | Cl | Br | Br | Br | CN | CN | CN |
| $R^1$ | H | $CH_3$ | NHAc | H | $CH_3$ | NHAc | H | $CH_3$ | NHAc | H | $CH_3$ | NHAc | H | $CH_3$ | NHAc |
| $R^2$ | H | H | $OCH_3$ | H | H | $OCH_3$ | H | H | $OCH_3$ | H | H | $OCH_3$ | H | H | $OCH_3$ |

## 2. Experimental

The absorption spectra were measured in 1cm quartz cells on UVIKON 860 spectrophotometer(USA, KONTRON, scan speed 250 nm/min).

The dipole moments of the ground state and first excited states were computed and the differences in dipole moment between two states were calculated in order to predict the solvatochromic effects of synthesized dyes. The 'HyperChem Pro 5.1' software package was used in order to optimise the geometry of the dye structure by using molecular mechanical methods, conducting the iterative energy-minimizing routines with the steepest descent and Polak-Ribiere algorithms. The semi-empirical methods were also examined with respect to geometry optimisation, but were found to be no more satisfactory than the molecularmechanical methods. The optimised geometrical structures of dyes were used in an attempt to quantify the dipole moments by using 'MOPAC' application in 'CS Chem3D Pro' software package. MOPAC is a molecular computation application that features a number of widely-used, semi-empirical methods.

## 3. Results and discussion

The colour gamut of the synthesized dyes spans almost all of the visible spectrum, from orange having max 469 nm, to blue having max620 nm in ethanol. Data concerning the spectra of the dyes in ethanol (max, max and 1/2) are listed in Table 2. This overall colour range of 151 nm demonstrates the facility with which a range of colours may be developed from 4-aminoazobenzene-based dyes containing a fluorosulfonyl group by substitution variations in the diazo components and coupling components.

Applying the Hammett equation to the halochromism of the synthesised dyes, a reasonable linear correlation was drawn between the wavelength shift, (azonium- neutral) and the appropriate Hammett constant in accordance with theoretical expectations. Most synthesized dyes containing two or three electron withdrawing groups and/or powerful electron donating groups in coupling component ring show negative halochromism due to the strong electronic effect.

Table 2. Spectral properties of alkali-clearable azo disperse dyes containing a fluorosulfonyl group

| Dye | 1 | | | 2 | | | 3 | | | 4 | | | 5 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | a | b | c | a | b | c | a | b | c | a | b | c | a | b | c |
| $\lambda_{max}$ | 469 | 478 | 519 | 513 | 524 | 573 | 520 | 539 | 595 | 522 | 542 | 594 | 540 | 580 | 620 |
| $\varepsilon_{max}$ | 36000 | 38000 | 33000 | 38000 | 40000 | 43000 | 32000 | 36000 | 33000 | 34000 | 38000 | 39000 | 39000 | 42000 | - |
| $\lambda_{1/2}$ | 97 | 102 | 107 | 105 | 106 | 100 | 124 | 118 | 98 | 119 | 116 | 100 | 110 | 99 | 78 |

Most dyes exhibited overall positive shifts between cyclohexane and ethanol, however, in a few cases, negative solvatochromism was observed within the general positive trend, for example, the dyes containing a 2-acylamino-5-methoxy substituents, which is due to the intramolecular hydrogen-bonding. A reasonable linear correlation was obtained between the difference in dipole moment and the extent of solvatochromic effects ; difference in dipole moment between the excited state and the first excited state, which was calculated by using HyperChem and CS Chem3D softwares, provided reasonable predictions in the extent and the direction of solvatochromism for the dyes prepared. Therefore, the dipole moments appear to be a reasonable measure for the theoretical prediction of solvatochromism of the 4-(N,N-diethylamino)-4'-fluorosulfonylazobenzene dyes.

## References

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