Synthesis and thermal properties of alkali-clearable azo disperse dyes containing a fluorosulfonyl group

Joon seok Koh, Andrew J. Greaves*, Jae Pil Kim**

Department of Textile Engineering, Konkuk University, Seoul, Korea
*L'Oreal, Ave Eugene Schueller, Aulnay sous Bois, France
**School of Materials Science and Engineering, Seoul National University, Seoul, Korea

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, we reported the synthesis of some diazo components and the subsequent monoazo disperse dyes containing a fluorosulfonyl group, 4-(N,N-diethylamino)-4'--fluorosulfonylazobenzene derivatives as well as the thermal properties of the various dyes prepared.

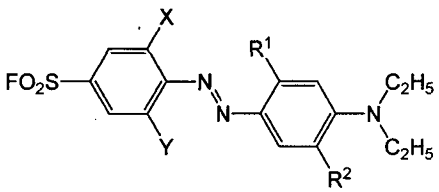

Fig. 1. alkali-clearable azo disperse dyes containing a fluorosulfonyl group

2. Experimental

2.1 Synthesis of dyes

$NaNO_2$/HCl solution was used for the diazotization of 4-fluorosulfonylaniline. The 0.02 mol of 4-fluorosulfonylaniline was diazotized in 6.9 ml of conc. HCl and 70 ml of water, by adding 0.02 mol of $NaNO_2$ at a temperature of 0-5℃. After 4-5 hours, the completion of diazotization was checked using a solution of 4-(N,N-dimethylamino)benzaldehyde and the pH value of the diazo liquor was then adjusted to pH 5-6 by adding sodium acetate. In the case of the substituted fluorosulfonylanilines nitrosylsulfuric acid was used for the diazotization. Nitrosylsulphuric acid (3.8 ml) was added to a mixture of diazo component (0.02 mol) in acetic acid/propionic acid (4:1, 50 ml) at 0-5℃. After 4-5 hours, the completion of diazotization was checked using a solution of 4-(N,N-dimethylamino)benzaldehyde.

The 0.02 mole of diazonium liquor was added to a solution containing 0.02 mol of coupling component, 100 ml of methanol, and 100 g of ice. After 4-5 hours, completion of coupling was checked by 10% H-acid solution, and the pH value of the diazo liquor was then adjusted to pH 5-6 by adding sodium acetate. The precipitated dyes were filtered, washed with water and dried. The dyes were purified by crystallization from methanol.

2.2. Measurement of thermal property

Melting points were determined using a DSC 7, Perkin-Elmer (USA) Differential Scanning Calorimetry (heating rate 5℃/min, N2 gas). The absorption spectra were measured in 1cm quartz cells on UVIKON 860 spectrophotometer (USA, KONTRON, scan speed 250 nm/min).

3. Results and discussion

All the purified dyes exhibited well-defined melting points characteristic of pure compounds. Several dyes, such as dyes 2c, 4a, 4c, 5a and 5c, were decomposed before they reach the melting points(Table 1). The dyes prepared from low melting diazo components tended to have low melting points themselves and the factors determining high melting points were preserved in the dyes from high melting arylamines. The more polar dyes, which contain electron-withdrawing groups, tended to melt at higher temperatures, for example, the nitro-substituted dyes(2-5) generally exhibited higher melting points than non-substituted dyes(1). It was also found that the melting points in a given series of dyes is related roughly to the molecular weight ; the dyes having bigger molecular weight showed higher melting points.

4-(N,N-diethylamino)-4′-fluorosulfonylazobenzene dyes with 6′-cyano groups showed higher thermal stability than analogues with a 6′-chloro or a 6′-bromo group, which may be a result of increased polarity and/or the rod like shape of the cyano group being more conductive to efficient packing in the crystal structure. Of the 4-(N,N-diethylamino)-4′-fluorosulfonylazobenzene derivatives, dye 5c (decomposition at 267.0 C) shows the highest thermal stability and dye 1b the lowest thermal stability (melting at 117.0 C).

Table 1. Yield(%) and thermal properties of synthesized dyes

Dye	X	Y	R1	R2	Yield (%)	m.p. (C)	Appearance
1a	H	H	H	H	97.6	150.1	Scarlet solid
1b	H	H	CH_3	H	86.8	117.0	Shiny purple crystal
1c	H	H	$NHCOCH_3$	OCH_3	54.3	118.5	Greenish brown solid
2a	NO_2	H	H	H	62.7	146.3	Greenish brown solid
2b	NO_2	H	CH_3	H	84.1	142.8	Shiny green solid
2c	NO_2	H	$NHCOCH_3$	OCH_3	38.7	(204.3)[a]	Dark green solid
3a	NO_2	Cl	H	H	44.6	198.5	Shiny purple solid
3b	NO_2	Cl	CH_3	H	50.4	163.0	Shiny violet solid
3c	NO_2	Cl	$NHCOCH_3$	OCH_3	32.6	174.2	Green solid
4a	NO_2	Br	H	H	58.9	(199.8)[a]	Shiny purple solid
4b	NO_2	Br	CH_3	H	63.2	146.3	Violet solid
4c	NO_2	Br	$NHCOCH_3$	OCH_3	33.9	(198.6)[a]	Green solid
5a	NO_2	CN	H	H	28.4	(203.7)[a]	Violet solid
5b	NO_2	CN	CH_3	H	31.1	213.0	Greenish blue solid
5c	NO_2	CN	$NHCOCH_3$	OCH_3	30.2	(267.0)[a]	Dark green crystal

[a]Decomposition temperatures before melting points.

4. Conclusions

Alkali-clearable monoazo disperse dyes containing a fluorosulfonyl group in their diazo component ring have been prepared from the coupling reaction between 4-fluorosulfonylanilinesand corresponding coupling components and their thermal properties were investigated.

References

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