Sulphoquinoxaline Azoic Dyes and Derivated Reactive Triazinic Dyes

MARIN BULEARCĂ*, ION SEBE
Politechnica University of Bucharest, Faculty of Applied Chemistry and Materials Science, Dyes Laboratory, 149 Victoriei Str., 010072, Bucharest, Romania

The main objective of the present paper is the synthesis of some azo sulphoquinoxaline dyes and azoic derived reactive dyes obtained by their condensation reactions with cyanuril chlorides. The obtained dyes were characterized by IR and UV-VIS spectra and were applied on cotton, wool and polyamide, with good tinctorial fastnesses.

Keywords: azoic dyes, reactive dyes, sulphoquinoxaline, cyanuril chloride

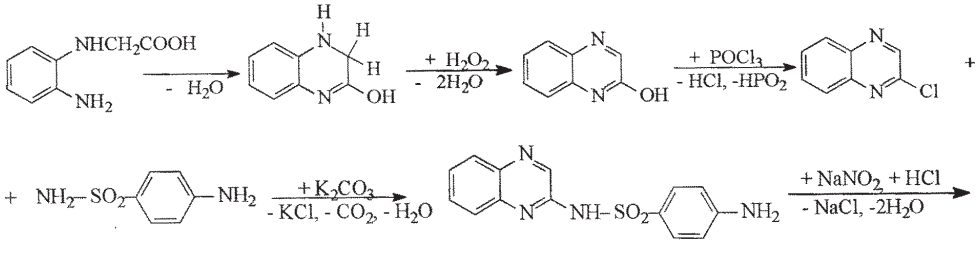
Due to some remarkable tinctorial properties: shades brightness and good resistances to wet treatments, the appearance of reactive dyes was one of the most important novelties from the dyes chemistry and technology.

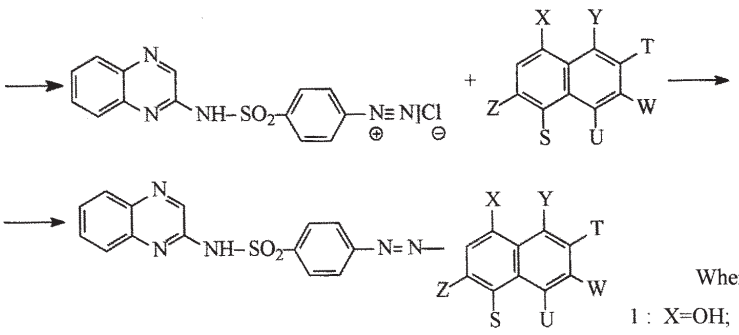
Reactive dyes are products that posses in the molecule groups capable to react with cellulose, proteic and polyamidic fibers. The dyeing process of some cellulose supports (seldom polyamidic ones) with reactive dyes represents an irreversible process between the chemical reaction from the dye and the fiber, giving eteric bonds (covalent bonds). In this way, between the dye and the macromolecule a unique coloured molecule is realized, fact that explains the good fastness to wet treatments of the dyeing processes realized in the presence of these dyes.

The reactive dyes capable to react by nucleophilic substitutions are the dyes that have as reactive system a heterocycle with nitrogen atoms and displaceable chlorine atoms. The presence of the nitrogen atom, with a high affinity for electrons, in the heterocycle determines a labilization effect of the chlorine atom (or atoms), rising the reactivity. Sulphoquinoxaline is a product that can be used for the obtaining of some dichlorotriazinic reactive dyes [1-4].

Previously the syntheses of some reactive dyes with α, β - chlorohydrinic structure in the molecule were studied [5].

In the present work, were obtained a series of dyes derived from sulphoquinoxaline with different acids: H acid, 2-naphtol-6-sulfonic acid, I acid, γ acid, R salt, Clevé acid and Laurent acid, according to the following scheme of reactions:





Scheme 1

Where:

1 : X=OH; Y=NH_2; T=U=S=H; W=SO_3Na; Z= SO_3Na

2 : X'=OH; Y'=T'=W'=S'= Z'=H; U'=SO_3Na

3 : X=OH; Y=T=U=S=H; W=NH_2; Z=SO_3Na

4 : X=OH; Y=V=U=S=H; T=NH_2; Z=SO_3Na

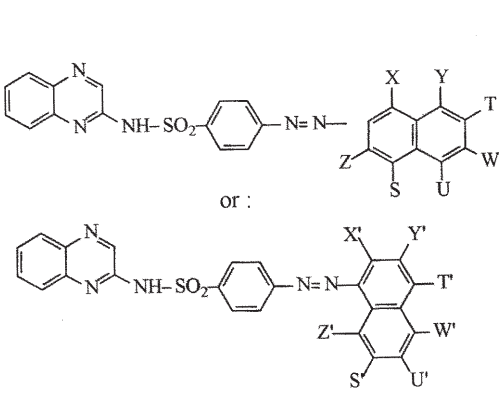
5 : X'=OH; Y'=U'=SO_3Na; T'=W'=S'=Z'=H

6 : X'=Y'=W'=U'=Z'=H; T'=NH_2; S'=SO_3Na

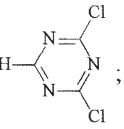
7 : X'=Y'=W'=U'=S'=H; T'=NH_2; Z'=SO_3Na

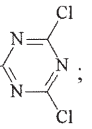
**marinbulearca@yahoo.com, Tel. 021.402.27.20 / 0754.042.710*

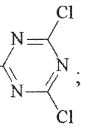
The obtained 1, 3, 4 and 6 dyes were coupled with cyanuril chloride and so A1-A4 reactive dyes were synthesized:

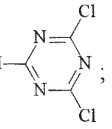


or :

A1: X=OH; Y=  ; T=U=S=H; W=Z=SO_3Na

A2: X=OH; Y=T=U=S=H; W=  ; Z=SO_3Na

A3: X=OH; Y=V=U=S=H; T=  ; Z=SO_3Na;

A4: X'=Y'=W'=U'=Z'=H; T' =  ; S'=SO_3Na

Experimental part

This work presents experimental data regarding the synthesis and characterization of dyes from the physico-chemical characteristics point of view and also from their behaviour point of view to mass dyeing process of polyamide, wool and cotton.

The sulphoquinoxaline synthesis starts by o-phenylen-diamine condensation with ammonium monochloro-acetate, obtaining 2-hydroxi-3,4-dihydroquinoxaline. The condensation reaction is realized in the presence of sodium bicarbonate – morfoline or sodium bicarbonate – acetic acid, using o-phenylendiamine and ammonium monochloroacetate in a 1:1.03 molar ratio, at a temperature of 90 ^{0}C.

Then 2-hydroxi-3,4-dihydroquinoxaline is subjected to oxidation with H_2O_2, 15% concentration solution, at a temperature of 50 ^{0}C, for 1 hour, when 2-hydroquinoxaline is obtained. Product is isolated by acidulation with HCl at a pH value of 5-6, then it is cooled, filtered and dried.

2-hydroxiquinoxaline is treated with phosphorus chloride oxide in order to obtain 2-chloroquinoxaline which reacts with sulphamide in the presence of potassium carbonate and Keisselgur, by heating at 110-120 ^{0}C, during 2 h. The reaction mass is cooled at 50-60 ^{0}C, then it is filtered in order to remove the Keisselgur reactive. The filtrate is collected in a separatory funnel, the inferior layer being formed from the potassium salt solution of sulphoquinoxaline. The aqueous potassium salt solution of sulphoquinoxaline has a value of *p*H equal to 10. The excess of unreacted sulphamide is precipitated by addition of 5% acetic acid solution, until the *p*H is equal to 9. The reaction mass is maintained at a temperature of 15 - 20 ^{0}C for 6 h , in order to complete sulphamide precipitation. It is filtered, on the filter remaining the sulphamide precipitate. The filtrate is acidulated with 5% HCl solution until *p*H reaches 5.5 - 6. It is filtered and sulphoquinoxaline remains on the filter. Then, it is washed with hot water and distilled water. The obtained yield is 85% with respect to 2-chloroquinoxaline.

Dye 1 is obtained according to the following working procedure

In a Berzelius beaker 7 g (0.0233 moles) sulpho-quinoxaline and 30 mL 30% HCl solution are introduced and stirred until they are dissolved. Then, the solution is cooled at 0 ^{0}C. During 10 min time, small portions of 1.75 g (0.0254 moles) sodium nitrite in 5.5 mL H_2O are added under stirring, maintaining the temperature at 3 ^{0}C and the medium acidic (acidic reaction with Congo red paper).

In the same time, a solution from 8.5 g (0.0267 moles) H acid in 15 mL H_2O and with 4 g NaOH is prepared. The solution is cooled with ice at 0^{0}C and the diazonium salt solution of sulphoquinoxaline prepared above is introduced in the azocoupling component solution during 30 min, maintaining the temperature at 5 ^{0}C by cooling and taking the *p*H value at 9.5-10. The dye is formed immediately, observing the crystals formation.

The coupling reaction is finished in approximately 12 h. The dye separation is realized by salifiation with NaCl. The precipitate is filtered and dried at 60 ^{0}C.

The other dyes (2-7) are synthesised by the same way The yields and the working conditions are presented in table 1.

The above mentioned dyes were purified using the recrystallization method.

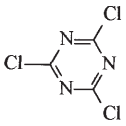
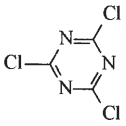
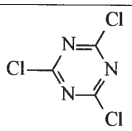
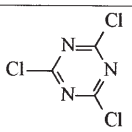
In order to determine the purity of the dyes, the thin layer chromatography was used working with Silicagel 60-G-Merck as stationary phase deposited on aluminium foil and, as mobile phase, a mixture of butylic alcohol : propylic alcohol : ethyl acetate : water (2 : 4 : 1 : 3 vol). The dyes solubilization was realized in the presence of dimethylformamide, having a concentration of 1%, and the samples were spotulated at a level of 10 mL. The identification is realized by direct vizualization of the colored spots. The dyes Rfs are given in table 1.

The obtained 1, 3, 4 and 6 dyes were coupled with cyanuril chloride and transformed into reactive dyes by the following procedure.

Dye A1 is obtained according to the following working procedure

The monoazoic dye wet cake (8 g, 0.0093 moles) is mixed with 200 mL water containing 0.01 g emulsifying surface agent (anionic or ionic) and, under stirring, ice is introduced for cooling at 0-2 ^{0}C, then 2.47 g (0.0133 moles) of cyanuril chloride (in excess because a portion of it hydrolyses) are added under energetic stirring. In order to have a *p*H of 5.5, Na_2CO_3 solution is introduced. The reaction mass is continuously stirred at 3-4^{o}C, maintaining the pH value at 5.5 and then, small amounts of Na_2CO_3 solution are added, in order to obtain a *p*H of 7 at the end of the acilation step. After 0.5 h the solution is filtered to eliminate insoluble products and the filtrate is salified with 50-60 g NaCl, at 3-4^{o}C. The hydrolization of the two chlorine atoms, grafted on the triazinic cycle, is avoided. Then, the cake is compacted, mixed with 1 g of urea (dye stabilizer) and dried at room temperature or at 70^{o}C. The other dyes (A2-

Table 1
WORKING REACTION CONDITIONS FOR 1-7 AND A1-A4 DYES OBTAINING
(REACTION CONDITIONS FOR CONDENSATION AND COUPLING)

Dye	Cyanuril chlorides	Temp. [^{0}C]	pH	Time [h]	Yield [%]	Colour	Rf
1	-	5	9.5-10	12	85	red	0.16
2	-	5	9-9.5	10	80	light orange	0.56
3	-	4	9	8	85	auburn	0.33
4	-	3	9	7	85	reddish light brown	0.64
5	-	4	10	6	80	orange	0.47
6	-	3-4	9	8	85	light brown	0.86
7	-	3-4	9	6	80	dark brown	0.96
A1		3	5.5	0.5	90	cherry red	0.50
A2		3-4	5.5	0.5	85	yellow orange	0.17
A3		3-4	5.5-6	0.5	90	light brown	0.60
A4		3-4	5.5	0.5	85	bright red	0.14

A4) are obtained in the same manner. The reaction conditions are given in table 1.

Results and discussions

Using sulphoquinoxaline as diazo-component and different other coupling agents (H, 2-naphtol-6-sulphonic, I, γ, Clevé and Laurent acids and R salt) were obtained azoic dyes according to the reaction scheme presented above.

The synthesis of 1-7 azoic compounds was realized with no difficulties, according to the usual methods described in the literature [7], with obtained reaction yields between 80-90 %.

The IR spectra were registered for the obtained azoic dyes, in KBr tablets, with a SPECORD M80 [6] apparatus and the obtained signals are presented in table 2.

It is observed that the vibrations characteristic to benzene ring take place for frequencies situated between 600-780 cm^{-1}, the ones characteristic to -C=C- groups from aromatic rings (naphthalene) between 1450-1500 cm^{-1}. The –C=N bonds vibrations are between 1530-1620 cm^{-1}. Also, -OH vibrations appear for the 1-5 dyes between 3400-3500 cm^{-1}. Beside the specific vibration bonds that are normally placed in the spectrum (types of bonds from the dyes molecule), there are also vibrations that give information about the presence of impurities in the analyzed solution.

The absorption spectra in UV were realized with a SPECORD UV-VIS apparatus (C.Zeiss-Jena) [8], the absorption maxima and the extinction coefficients are presented in table 3.

The absorption bands appear in the spectrum under the form of maxima, more or less permanent, each absorption band being characterized by the wave length (λ_{max}) and absorption intensity (ε_{max}) in the maximum points of the curve. For 1-7 and A1-A4 dyes, the maxima (λ_{max}) are given in table 3 and they show that a compound has a darker colour than the other when its maximum from the absorption curve (λ_{max}) is shifted to a high wavelength in the spectrum. The colour is more intense when the extinction coefficient from the maximum point is higher. Due to the fact that in the structure of the dye was introduced a triazinic residue, it can be observed that this determines a batochromic effect.

Dyeing with the obtained 1-7 azoic dyes was realized on wool and polyamide fibers and with the A1-A4 reactive dyes on the cotton fibers [9,10].

The technologic parameters of the dyeing process with azoic 1-7 dyes were: dye bath ratio 1-10…1-50, the dye concentration 1.5-4% and the *p*H 3-6 maintained by addition of acetic acid, salt concentration 10-20%, dyeing temperature 60-100°C, duration of the process 45-90 min.

The technological parameters of the dyeing process with A1-A4 reactive dyes were: dye bath ratio 1-20…1-50, dye concentration 0.5-5% and the *p*H 7.5-11, maintained by continuous buffering with Na_2CO_3, salt concentration of 30-60%, dyeing temperature between 20-85 ^{0}C, duration of the process 30-100 min.

Dye	ν =C-H [cm^{-1}]	ν -C=C- [cm^{-1}]	ν -C=N- [cm^{-1}]	ν -SO_2 [cm^{-1}]	ν -C-N [cm^{-1}]	ν -NH_2 [cm^{-1}]	ν -OH [cm^{-1}]	ν -C-O [cm^{-1}]
1	600	1480	1550-1600	1300-1350	1300-1400	1620-1650	3400-3500	1000-1200
2	650	1480	1530-1550	1300-1350	1300-1400	-	3500	1000-1200
3	-	1480	1550-1600	1300-1350	1300-1400	-	3400-3500	1000-1200
4	640	1400-1500	-	-	1300-1400	1630	3400-3500	1000-1200
5	640	1400-1500	1620	1300-1350	1350-1400	-	3400-3500	1000-1200
6	650	1450-1500	1600-1620	1300-1350	1600-1650	1600-1620	-	-
7	780	1400-1500	1580-1600	1380	1600	1600	-	-

Table 2
IR ABSORPTION SPECTRA OF 1-7 DYES

Dye	Solvent	Concentration (%)	λ_1[nm]	λ_2 [nm]	ε_1	ε_2
1	water	0.008	358	383	3.63	9.54
2	water	0.004	370	480	2.45	6.3
3	water	0.002	-	480	-	4.89
4	water	0.02	360	500	15.13	3.98
5	water	0.008	360	480	4.57	9.22
6	water	0.02	-	500	-	12.56
7	water	0.1	-	505	-	2.78
A1	water	0.03	-	530	-	2.29
A2	water	0.03	-	500	-	3.98
A3	water	0.03	-	500	-	1.94
A4	water	0.03	-	520	-	2.75

Table 3
ABSORPTION SPECTRA IN UV-VIS FOR THE 1-7 AND A1-A4 DYES

Conclusions

Starting from the idea of using sulphoquinoxaline as diazo-component for the obtaining of new azoic dyes and condensation with cyanuril chloride for the reactive dyes obtaining, 7 azoic dyes and 4 reactive dyes were synthesised, developing the dyes area of this type. The dyeing process and the obtained dyes showed good values for fastnesses, recommending their use for the dyeing process of the wool, cotton and polyamide fibers.

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