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Synthesis and characterization of new cationic dyes for synthetic fibres

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Abstract

The paper presents a class of new cationic dye derivatives from compact condensed system 2-aminothiazolo[5,4-*c*]pyridine. These dyes were purified and analysed by physical–chemical methods (TLC, HPLC, vis, IR, NMR, melting point, elemental analysis) for the identification of their chemical structures. Also, the conditions of dyeing process and tinctorial tests for the cationic dyes were studied.

Keywords: Cationic dye; Spectral analysis; Tinctorial property; Polyacrylic fibre

1. Introduction

Cationic dyes contain an auxochrome group besides chromophore, a quaternization nitrogen heteroatom or a quaternary group type $-N(CH_3)_3$ tied with an alkilic chain, always existed as a guide anion. This anion does not influence the colour, but has an important role because it has effect on the solubility of the product and its isolation possibility in pure state. The positive charge of colour cation conferred a sufficient solubility in water for having the capacity to dyeing of synthetic fibres (example polyacrylic fibres) from acid aqueous fleets. The attractive electron cationic group has a bathocromic effect and amelioration of resistances at light and industrial gases action, due the increase of electron mobility from chromophore system [1–3].

At the same time with the large utilization of polyacrylic fibres it has beginner a profound study of dyeing process. In this scope the classic cationic dyes are utilised, but their tinctorial performances are very modest. The deficiencies of tinctorial properties of classic dyes refer to dyeing uniformity and the exhaustion of application fleet. In the last years the non-uniform dyeing in "dégradé" was considered a "mode", but it rested only on a technologic failure. In this context the studies which refer to the synthesis and application of some new products for dyeing of synthetic fibres, rested an important problem as of theoretical and practical interest.

In this paper a new class of cationic dye derivatives from compact condensed system 2-aminothiazolo[5,4-*c*]pyridine [4–7] are synthesized. These dyes are obtained by original synthesis and they are unknown in specialty literature. The synthesized cationic dyes with shades of brown-red dark are analysed structurally and also, their tinctorial properties are tested in the dyeing process of polyacrylic fibres.

2. Experimental

2.1. Reagents

Experiments were performed using the following.

- Green disperse dyes obtained by synthesis [8];
- Dimethyl sulfate, $(CH_3O)_2SO_2$, 99% bp = 188 °C (Merck);
- Acetic acid glacial, CH_3COOH, 99.9% (Merck);
- Sodium chloride solid;
- Activated carbon Darco® G-60 power, high purity carbon, especially useful for minimizing contamination in products (Fluka).

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2.2. The general procedures for the preparation of cationic dyes

These dyes were obtained in research lab using an installation formed from: water bath, agitator and refrigerant with reflux, thermometer and ballon flask; at the beginning, in the ballon flask was introduced acetic acid glacial 99.9% and 0.056 mol dimethyl sulfate; 0.0112 mol disperse dye, finely divided, has been added in 10 min, at 20 °C. In approximately 60 min, temperature will increase from 20 °C to 50 °C, and then from 50 °C to 60–70 °C in 30 min. This temperature must be maintained attentively 12–14 h when the chromatogram will indicate 100% conversion. After that, the reaction mass is added above 500 mL water; then, activated carbon Darco® G-60 power is introduced, under stirring, in 15 min, at 80 °C. The reaction mass is filtered. The filtrate, which contains the alkylated dye, is treated with NaCl at 70 °C; it is obtained as a saturated solution from which was precipitated the salt of dye. After, 15 min under stirring, the conditioned dye is cooled at 30 °C very slowly, and again is filtered. After the conditioned dye is washed with NaCl concentrated solution over filter, the final compound is dried at 60 °C. The presented method is applied for all green disperse dyes obtained by synthesis, with small exception, in function of coupler compounds.

Finally, the cationic dyes with colours brown-red dark (Fig. 1 and Table 1), were purified by recrystallization from water and separated by TLC and HPLC methods.

The high performance liquid chromatography results were obtained by using an apparatus, namely *Jasco* 800 with gel permeation columns Nucleogen® 4000-7 DEAE. They were considered to be the most appropriate because they allow retention times long enough for an efficient separation and do not present the colmation phenomenon for the cationic dyes.

The thin-layer chromatography method is performed using [9]: the absorbent layer silica gel, the plate material aluminum and the eluents which were chosen different for each dye (if it is the case).

The results obtained from purification methods by TLC and HPLC of synthesized cationic dyes **10–18** are presented in Table 2.

The melting points were calculated with a Boetius apparatus with microscope and heating plate, without correction; the results from the melting points and the yields are centralized in Table 3.

The elemental analysis for the organic products were carried out by using a Carlo–Erba M 1106 analyzer for the determination of carbon, hydrogen, nitrogen content and a Multi EA® 3000 apparatus for the determination of oxygen and sulfur content. The elemental analysis results are centralized in Table 4.

2.3. The spectral analyses

All dyes obtained by synthesis were studied employing chemical, *vis*, *NMR* and *IR* spectroscopies [10,11] confirming the structures proposed.

The *vis* electronic spectrums were performed with *Secoman S* 750 apparatus in quartz cells ($l = 1$ cm) for $c \sim 2 \times 10^{-5}$ M dyes in water. The characteristic absorbance was presented depending on the maximum wavelength (Tables 1 and 3).

The *IR* spectra were obtained including the synthesized compounds in KBr disks; the absorption has been measured with an *FT-IR Jasco* 620 spectrophotometer.

The disperse dyes **10–18** were analysed by *NMR* spectroscopy using *Varian Gemini* 300 *BB* apparatus, with frequency of registration for proton spectrum, *^{1}H NMR*, being 300 MHz and for carbon spectrum, *^{13}C NMR*, being 75 Hz. The purified sample was dissolved in deuterio-dimethylsulphoxide, DMSO-d_6, and the signals were reported at TMS.

3. Results and discussions

The molar extinction coefficients for cationic dyes are calculated and the results are presented in Table 1. The obtained values are a little comparable with theoretical values, because the presence of sodium chloride led to a decrease of ε_{max}.

The IR and NMR spectra are demonstrated the viability of the structures proposed for cationic dyes. The signals obtained in the ^{1}H NMR spectra for each dyes is the same for protons from benzene ring and pyridine ring, the differences appear when R_1 and R_2 can be methyl, ethyl, cyano, ethanol. Then the signals are high and the values are below 3.50 ppm. The protons from methyl group resulted from alkylation reaction presents high signals at values 1.50–1.80 ppm for all dyes. For dyes which are obtained by diazotizing–coupling–alkylated mechanism when the colour couplers are *N*-(β-hydroxyethyl)-aniline, *N*,*N*-di-(β-hydroxyethyl)-aniline, *N*-methyl-*N*-(β-hydroxyethyl)-aniline, *N*-ethyl-*N*-(β-hydroxyethyl)-aniline, for protons from –OH groups, in ^{1}H NMR spectra, there exists a short signal but is visible at 10.18 ppm.

The ^{13}C NMR spectra contain the information about carbon atoms; the values of signals presented very interesting

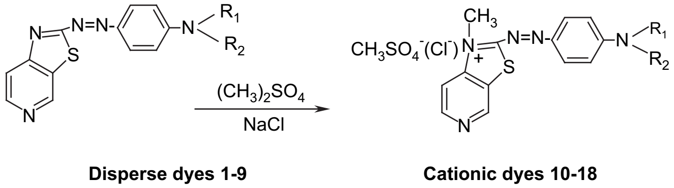
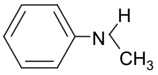
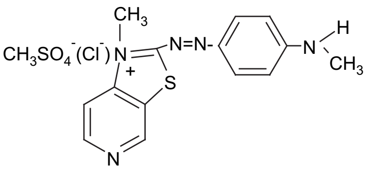
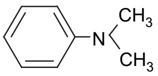
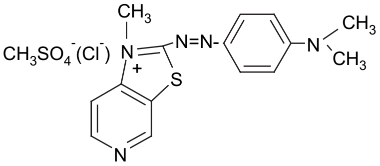
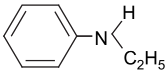
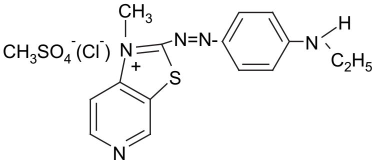
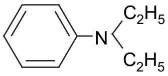
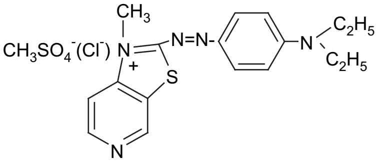
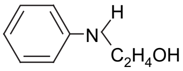
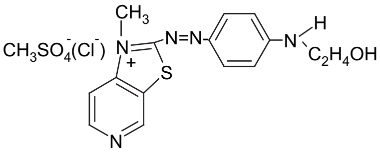
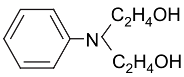
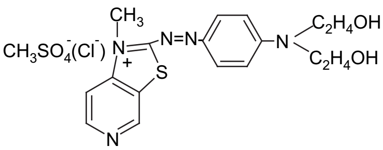
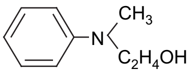
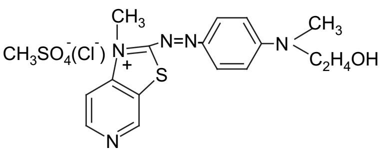
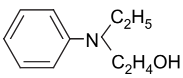
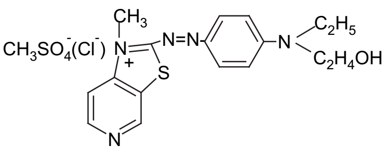
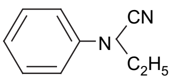
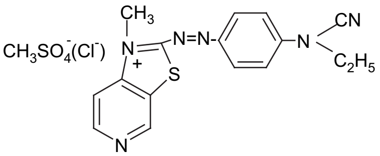


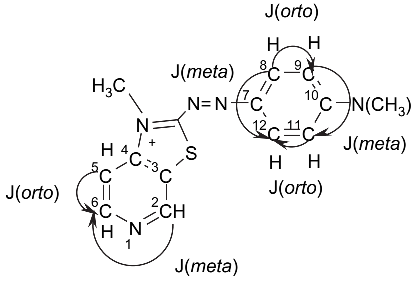
Fig. 1. The synthetic reactions of cationic dyes with $R_1 = H$, CH_3, C_2H_5, C_2H_4OH, CN and $R_2 = CH_3$, C_2H_5, C_2H_4OH in accordance with Table 1.

Table 1
Cationic dyes obtained by synthesis

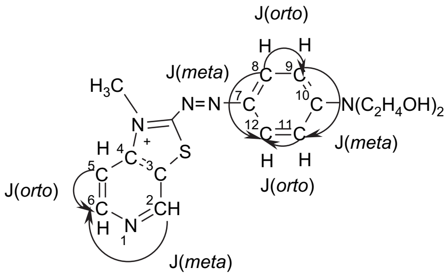
No.	R_1	R_2	Coupling compound	Cationic dye	Colour, λ_{max} (nm), ε_{max}
10	H	CH_3			Brown-red 514.1 nm, 27 200
11	CH_3	CH_3			Brown-red 526.2 nm, 29 400
12	H	C_2H_5			Brown-red light, 539.1 nm, 31 200
13	C_2H_5	C_2H_5			Brown-red, 546.0 nm, 32 800
14	H	C_2H_4OH			Brown-red dark, 551.0 nm, 33 100
15	C_2H_4OH	C_2H_4OH			Brown-red dark, 548.3 nm, 31 700
16	CN	C_2H_5			Brown-red dark, 553.6 nm, 32 100
17	CH_3	C_2H_4OH			Brown-red dark, 558.7 nm, 33 500
18	C_2H_5	C_2H_4OH			Brown-dark, 532.0 nm, 29 300

information about carbon atoms from methyl group resulted after alkylation and from methyl, ethyl and ethanol groups from coupler compounds.

The ^{1}H NMR (DMSO-d_6) and ^{13}C NMR (DMSO-d_6) results for disperse dyes **11** and **15** (illustrative) are presented.



Disperse dye **11**



Disperse dye **15**

Cationic dye **11**: δ_H: 7.22 ppm (1H, C_6H_3N, s, $J(2,6) = 2.20$ Hz); 7.30 ppm (1H, C_6H_3N, d, $J(5,6) = 7.47$ Hz); 7.47 ppm (1H, C_6H_3N, t, $J(6,5) = 7.72$ Hz and $J(6,2) = 2.20$ Hz); 6.83 ppm (2H, C_6H_4, d, $J(8,9) = 8.61$ Hz and $J(8,12) = 1.85$ Hz); 7.78 ppm (2H, C_6H_4, d, J(9,8) = 8.70 Hz and $J(9,11) = 1.85$ Hz); 2.25 ppm (3H, CH_3, s); 2.28 ppm (3H, CH_3, s); 1.67 ppm (3H, CH_3, s) attributed to hydrogen in methyl group bonded to heteroatom N^+ of thiazolic ring; 2.79 ppm (DMSO-d_6, s).

δ_C: 139.0; 137.9; 124.5; 123.4; 112.6 ppm for C^6, C^2, C^5, $C^8(C^{12})$, $C^9(C^{11})$; 145.1; 121.5; 130.0 ppm for carbon atoms C^3, C^4 and $C^7(C^{10})$; 23.9 ppm and 20.6 ppm were attributed of carbon atoms from two methyl group. The value 17.9 ppm was attributed to the carbon atom from $N^+{-}CH_3$ group of thiazolic ring.

The calculated theoretical values for the chemical shifts of the investigated protons, presented illustrative for dye **11**, are as follows: $\delta(H^2)$: 7.16 ppm; $\delta(H^6)$: 7.37 ppm; $\delta(H^5)$: 7.82 ppm; $\delta(H^8, H^{12})$: 6.72 ppm; $\delta(H^9, H^{11})$: 7.69 ppm.

Cationic dye **15**: δ_H: 7.22 ppm (1H, C_6H_3N, s, $J(2,6) = 2.20$ Hz); 7.30 ppm (1H, C_6H_3N, d, $J(5,6) = 7.47$ Hz); 7.47 ppm (1H, C_6H_3N, t, $J(6,5) = 7.72$ Hz and $J(6,2) = 2.20$ Hz); 6.83 ppm (2H, C_6H_4, d, $J(8,9) = 8.61$ Hz and $J(8,12) = 1.85$ Hz); 7.78 ppm (2H, C_6H_4, d, $J(9,8) = 8.70$ Hz and $J(9,11) = 1.85$ Hz); 1.89 ppm (4H, C_2H_4, s); 1.78 ppm (4H, C_2H_4, s); 2.79 ppm (DMSO-d_6, s); the presence of hydrogen atoms from −OH group is visible by the signal which appeared in the spectrum of this dye at 10.18 ppm.

δ_C: 139.0; 137.9; 124.5; 123.4; 112.6 ppm for C^6, C^2, C^5, $C^8(C^{12})$, $C^9(C^{11})$; 145.1; 121.5; 130.0 ppm for carbon atoms C^3, C^4 and $C^7(C^{10})$; 20.1 ppm and 18.2 ppm were attributed to the carbon atoms from two ethylene groups.

Table 2
The purification and separation by TLC and HPLC methods for cationic dyes

Dye	Thin-layer chromatography	HPLC chromatography
10−18	*Substratum*: silica gel F_{254} (Merck) on aluminum layer *Eluent*: dioxane:formic acid:water = 1:3:1	*Column*: Nucleogen® 4000-7 DEAE *Eluent*: 5 M urea, 30 mM potassium phosphate, 2 M potassium chloride *Flow*: 1.0 mL/min
	Solvent: water, solution 0.01%	*Detection*: 514.1−558.7 nm

So, the chemical shifts and coupling constant, *J*, in ^{1}H NMR spectra confirm the structure of cationic dyes, in concordance with the results obtained from *IR* spectra.

In *IR* spectra the absorption bands corresponding to the vibration specific groups for each synthesized compound were identified.

- The *IR* spectra for heterocyclic system thiazolo-pyridine indicated the presence of piridinic ring at frequencies of 1550 cm^{-1} and 1770 cm^{-1}. The frequency $\nu_{\mathrm{C{=}N(pyridine)}}$ was attributed to the bands at 1475 cm^{-1} and 1490 cm^{-1}.
- The frequencies 1100−1110 cm^{-1}, 1615−1630 cm^{-1}, and 2190−2210 cm^{-1} were attributed to the thiazolic ring, in accordance with the data obtained from *NMR* spectra.
- The methyl or ethylene groups from nitrogen $-NR_1R_2$ were identified in all cationic dyes (depending on structure), because the absorption band for this group is single and appears at 2860 cm^{-1}, or 2870 cm^{-1}, respectively.
- The azo chromophore group, −N═N−, characteristic of all dyes as faint absorptions, appear as small intensity band, at 1550 cm^{-1} and 1565 cm^{-1}.
- The −OH groups characteristic for dyes **14**, **15**, **16** and **17** appear as sharp absorption peak at 3640 cm^{-1}.

3.1. Dyeing process of polyacrylic fibres and tinctorial tests

The affinity of cationic dyes for polyacrylic fibres is the result of their anionic character. The fixation mechanism of cationic dyes on the polyacrylic fibre in the first step is ionic. At the same time, the cationic dyes are dissolved in polyacrylic fibre; the fibre with terminal anionic groups can be considered as an electrolyte. In reality, the dyeing process takes place in four steps [12]: the migration of dye from solution to the external surface of fibre; the adsorption of cation of dye on the

Table 3
The *vis* spectra, the melting points and yields for cationic dyes **10–18**

Cationic dye	Melting point, °C	Wavelength λ_{max}, nm (absorbance)	Yield, %	R_f
10	273–275	514.1 (1.012)	91.9	0.80
11	278–279	526.2 (1.098)	89.74	0.75
12	283–286	539.1 (1.120)	90.2	0.62
13	282–285	546.0 (1.320)	91.8	0.72
14	285–287	551.0 (1.015)	88.6	0.64
15	286–288	548.3 (0.987)	89.3	0.59
16	279–282	553.6 (1.233)	87.9	0.83
17	280–284	558.7 (1.289)	88.3	0.71
18	277–278	532.0 (1.066)	90.6	0.81

external surface of fibre; the diffusion of dye into the inside of fibre; the formation of electrovalent bonds between the cation of dye and the anion of fibre.

The asymmetrical alternation of the crystalline zones with the amorphous zones, from polyacrylic fibre, leads to non-uniform dyeing, because only the amorphous zones are accessible to the dyestuff. The increase of the dye percent through increasing the finishing temperature, in most cases, does not lead to the favourable results because of the following two reasons [13,14].

1. The reaching of the vitrification temperature (or in the proximity) leads at sticking processes of substratum associate of the substantial contribution of the hydrolysis reaction.
2. The extension of the polyacrylic fibres using was based to the fact that they mime the wool.

The solving of these problems have been chosen as the objective of many studies; the resolving being possible only when the dyestuff has manifested a great affinity for substrate: the affinity is doubled by the quick capability of desorption on the primary active centres. Just, in this case the ionisable chain ends can contribute to the first step of the process, to increase the migration rate of the dyestuff from the solution to the external surface of the fibre.

A special importance is the interaction study between two partners, dye and fibre, knowing that each step from dyeing polyacrylic fibre can be a rate-controlling step, like:

- The migration of dye from solution to the external surface of fibre (electrostatic attraction – ends of chain – dyestuff).
- The electrostatic interaction and formation of salts at the external surface of the fibre (the reversible process).
- The migration of the dyestuff to the internal surface of the fibre and the liberation of anionic centres from ends chain of the substratum have permitted the taking again of the dyeing process from the beginning.

So, by admitting these steps we can justify the possibility of achieving some intense dyeing when the number of equivalents of dyes is much more than the anion number which are present at the fibre chain ends. The introduction of a supplementary protonation centre of relatively reduced basic capacity in the structure of cationic dyes can favor the decoupled process, when the dye arrives at the external surface of the fibre. In this case the dye migrated easily to the internal surface of the fibre.

If these problems, which appear always in the dyeing process are known, then a new class of non-toxic, cationic dyes, which can be degraded from wastewaters resulting from the dyeing process of polyacrylic fibres can be synthesized.

The polyacrylic fibres are hydrophobic and they can be dyed with cationic dyes obtained by synthesis. But, dyeing with cationic dyes can be performed at temperatures below 100 °C without carriers. Furthermore, due to the good migration properties of disperse dyes, leveling agents are not required. Batch dyeing is commonly applied for cable; the pH = 4–5 in acetic acid.

The polyacrylic fibres submitted the qualitative tests by estimation of fastness shades with grey scale; the results were expressed by note from 1 to 5.

The perspiration/light fastness of cationic dyes increases if the used colorant solution is 3%. This aspect determines the improvement of the dyeing fastness with 1/2–1 ton.

The disperse dye derivatives from 2-aminothiazolo[5,4-*c*]pyridine dyeing polyacrylic and polyester fibres in green-dark and green-blue shades, show good perspiration/light fastness, good ironing fastness, friction fastness and good washing fastness at 40 °C (Table 5).

The relationship between colour and perspiration/light fastness test was influenced by coupler colorant (Table 1). Also, the number of electrons from the donating groups in cationic dyes molecule leads to the displacement of absorption maximum at the greatest wavelengths and implicit diminution of light fastness.

Table 4
Elemental analysis results for cationic dyes obtained by synthesis

Cationic dye	Molecular weight	C (%)		H (%)		N (%)		S (%)		O (%)	
		Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
$C_{14}H_{14}N_5S$	284	59.15	59.03	4.92	4.88	26.02	26.11	11.89	11.78	–	–
$C_{15}H_{16}N_5S$	298	60.40	59.98	5.36	5.22	24.73	24.66	11.30	11.22	–	–
$C_{15}H_{16}N_5S$	298	60.40	59.87	5.36	5.25	24.73	24.62	11.30	11.23	–	–
$C_{17}H_{20}N_5S$	326	62.57	62.41	6.13	6.17	22.50	22.57	10.28	10.33	–	–
$C_{15}H_{16}N_5SO$	314	57.32	57.11	5.09	5.19	23.41	23.31	10.70	10.64	5.35	5.39
$C_{17}H_{20}N_5SO_2$	358	56.98	56.72	5.58	5.47	20.40	20.46	9.32	9.25	9.32	9.42
$C_{16}H_{18}N_5SO$	328	58.53	58.31	5.48	5.31	22.36	22.23	10.22	10.17	5.11	5.03
$C_{17}H_{20}N_5SO$	342	59.64	59.69	5.84	5.81	21.40	21.49	9.78	9.86	4.89	4.81
$C_{16}H_{15}N_6S$	323	59.44	59.07	4.64	4.49	27.27	27.32	10.38	10.46	–	–

Table 5
The fastness test of cationic dyes on polyacrylic fibres

Cationic dye	Fastness to cool water	Fastness to light	Fastness to washing at 40 °C	Fastness to acid perspiration (pH = 5.5)	Fastness to alkali perspiration (pH = 8)	Fastness to ironing	Fastness to friction
10	5	4	4	4–5	4	4	4
11	5	4	4	4–5	4	4–5	4
12	5	4	4	4–5	4	4–5	4
13	5	4	4	4–5	4	4–5	4
14	5	4	4	4	4	4	4
15	5	4	4	4	4	4	4
16	5	4	4	4	4	4	4
17	5	4	4	4	4	4	4
18	4–5	4–5	4	4	4	4–5	4

4. Conclusions

In this work nine new cationic dyes, unknown in specialty literature were synthesized. For these dyes were established the process optimal parameters and also, they were purified and separated by TLC and HPLC methods. The dyes were characterized by elemental analysis, *IR*, *vis* and *NMR* spectroscopies. The cationic dye derivatives from compact condensed system 2-aminothiazolo[5,4-*c*]pyridine can be used with success in dyeing process of polyacrylic fibres because their tinctorial properties are good and toxicity is insignificant. Soon, these cationic dyes are to be tested in dyeing process of polyacrylic fibres in textile fabrics from Romania.

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