Structure - color Correlation Study in the Class of Pre-formed Acid Azo Chromium (1:1) Complex Dyes Containing the Sulfonic Group in the Diazotation Component

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This paper aims to explain the variation of (UV-Vis) spectral parameters of pre-formed azo chromium (1:1) complex dyes, containing the sulfonic group in the diazotation component, having aryl-azo-pyrazolone and aryl-azo-naphtaline type structures, (aryl=benzene, naphtaline) versus spectral parameters of (1:1) chromium complex of azo dyes (A): 2-aminophenol-4-sulphonic acid → acetoacetanilide and (B): 1-diazo-2-naphtol-4- sulphonic acid ® acetoacetanilide, considered as reference structures, taking into account the electronic effects (σ, π) of substituents.

Keywords: absorption spectroscopy, electronic effects

Pre-formed acid azo chromium (1:1) complex dyes are compounds containing one or two sulfonic groups in the molecule and shows the structure of ortho, ortho'-dihydroxyazo; ortho-hydroxy, ortho'-aminoazo; ortho-hydroxy, ortho'-carboxyazo or ortho, ortho'-diaminoazo, that were previously transformed into chromium (1:1) complex. Commercial products are known for Neolan (CIBA) and Palatine Fast (BASF) and serve to dye wool and some to leather dyeing - Erganil (BASF) type dyes.

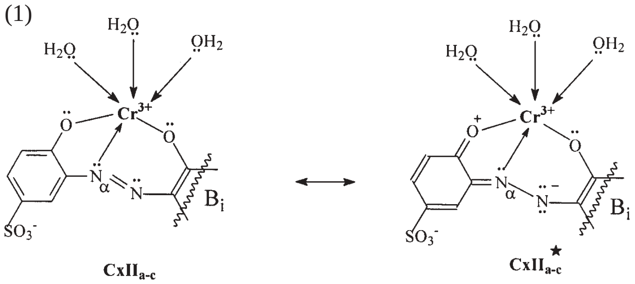
Respective complexes are very stable and do not decompose by heating in strongly acidic or basic solutions. They dye wool in strong acid bath. This paper aims to explain the variation of (UV-Vis) spectral parameters of azo chromium (1:1) complex dyes containing one sulphonic group in the diazotation component, compared to those of (1:1) chromium complex of metallizable azo dye **(A)** and **(B)**, considered as **reference structures**, taking into account the electronic effects (σ, π) of substituents, where:

(A).2-aminophenol-4-sulphonic acid→acetoacetanilide;

(B).1-diazo-2-naphtol-4-sulphonic acid →acetoacetanilide.

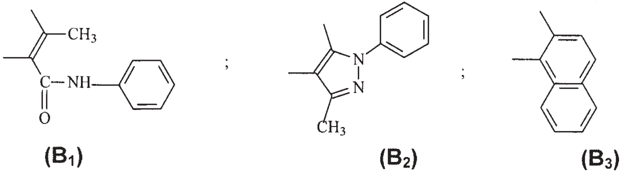
For this we have synthesized a series of known dyes from the PALATINE FAST (BASF, Germany) range, which dye wool in strongly acidic bath. They are part of the class of preformed acid azo chromium (1:1) complex dyes, having aryl-azo-acetanilide, aryl-azo-pyrazolone and aryl-azo-naphtalene type structures (aryl = benzene, naphtalene), which were purified and analyzed. From the dyes category with general structure **CxII**$_{a-c}$ were studied the next compounds: **CxII**$_{a}$ (CxII$_{a-c}$, when B represents an aceto-acetanilide residue), **CxII**$_{b}$ (CxII$_{a-c}$, when B represents a pyrazolone residue), **CxII**$_{c}$ (CxII$_{a-e}$, when B represents a naphtaline residue). Chemical structures of the compounds **CxII**$_{a}$, **CxII**$_{b}$, **CxII**$_{c}$ are presented, both in the ground and excited state.

(1)



in which: **B**$_i$ **(i = 1, 2, 3)** may be an acetoacetanilide, pyrazolone or naphtaline residue, as follows:

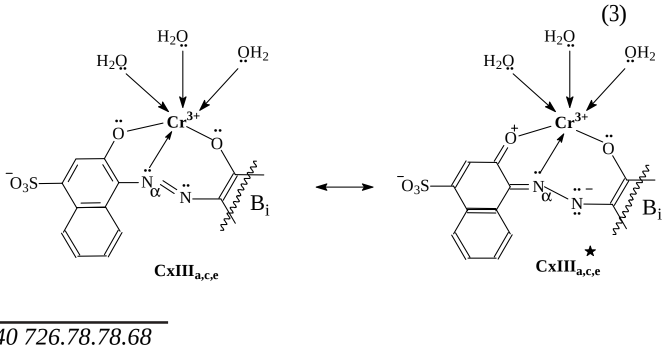
(2)



From the dyes category with general structure **CxIII**$_{a-f}$ were studied the next compounds:

CxIII$_{a}$ and **CxIII**$_{b}$ (CxIII$_{a-f}$, when B_1 represents an acetoacetanilide residue), **CxIII**$_{c}$ and **CxIII**$_{d}$ (CxIII$_{a-f}$, when B_2 represents a pyrazolone residue), **CxIII**$_{e}$ and **CxIII**$_{f}$ (CxIII$_{a-f}$, when B_3 represents a naphtaline residue). Chemical structures of the compounds **CxIII**$_{a}$, **CxIII**$_{b}$, **CxIII**$_{c}$, **CxIII**$_{d}$, **CxIII**$_{e}$, **CxIII**$_{f}$ are presented, both in the ground and excited state:

(3)



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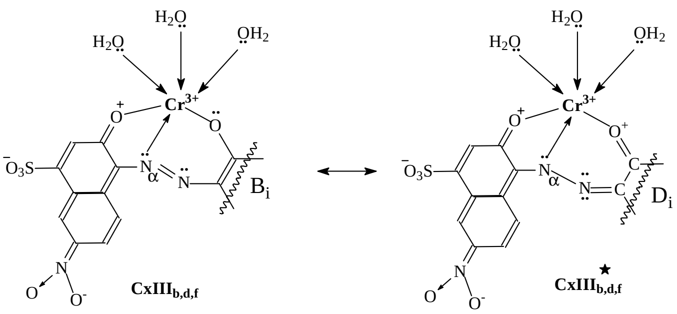
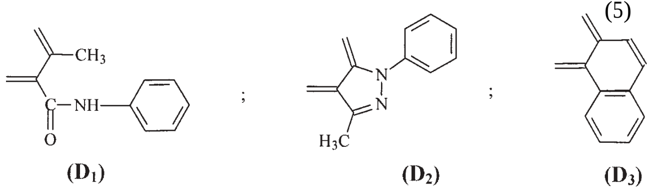
(4)



in which: **D_i (i = 1, 2, 3)** represents quinone-imine form corresponding to **B_i** :

(5)



Experimental part

Materials, methods and equipment

Diazo components: 2-aminophenol-4-sulphonic acid (AFS), 1-diazo-2-naphtol-4-sulphonic acid (diazoxid) (DO), 6-nitro-1-diazo-2-naphtol-4-sulphonic acid (nitrodiazoxid) (NDO).

Coupling components: acetoacetanilide (AAA), 1-phenyl-3-methyl-5-pyrazolone (FMP), 2-naphtol (2N).

The chromium (1:1) complex dyes of the following metallizable azo dyes containing the sulphonic group in the diazotation component were synthesized: AFS→AAA; 2) AFS→FMP; 3) AFS→2N; 4) DO→AAA; 5) DO→FMP; 6) DO→2N; 7) NDO→AAA; 8) NDO→FMP; 9) NDO→2N. The yields for the preparation of acid azo chromium (1:1) complex dyes with one sulfonic group in the diazotation component are between 80-90%.

IR spectra were measured with a FT / IR –JASCO 6300 spectrophotometer, using KBr pellets and UV –Vis spectra were performed in distilled water with a UV/Vis/ NIR JASCO V570 spectrophotometer. Were used cells with 1 cm pathlength, working in the range dye concentrations of 1.75 -3.65*10^{-2} g/L in distilled water.

Chromium (1:1) complexes dyes (**$CxII_{a-c}$** and **$CxIII_{a-f}$**) were synthesized according to the literature **[1]**, from corresponding azo dyes by complexation with chromium, in a mixture of ethylene glycol-water at a volume ratio of solvent: water of between 1:2 ... 1:6, at 90 – 110°C temperature, in 8-20 h, depending on the structure of the metallizable azo dye containing the sulphonic acid group in the diazotation component.

Physico-chemical analysis

The final products were isolated from the reaction mass and then purified by recrystallization from absolute ethanol. For the solubilization of azo chromium (1:1) complex dyes a mixture of distilled water and ammonia was used. Standard concentrations of these dyes were determined by chemical analysis of reductive cleavage with VSO_4 [2] and have values between 98.5 to 99 % . Purified compounds were subject to both spectrophotometric analysis (chromium content analysis) by atomic absorption spectrometry, with atomization in air - acetylene flame [3]. Purity determination of investigated dyes was carried out by using the thin layer chromatography method on silica gel on aluminum support by working with the eluent: n-BuOH: EtOH: sol. 25 % NH_3: Py = 4:1:3:2 (vol./vol.). For dissolving the samples of azo chromium (1:1) complex dyes was used as solvent, distilled water and ammonia.

Spectral parameters determination of investigated dyes was carried out by using spectrophotometric method in IR and UV-Vis ranges.

Results and discussions

The structure of the studied azo chromium (1:1) complex dyes containing one sulfonic group in the diazotation component was proven by spectrophotometric analysis (chromium content analysis), and their purity was proved by thin layer chromatography on silica gel on aluminum support.

This paper is a continuation of the [4] paper that explain the UV-Vis spectral parameters variation of pre-formed acid azo chromium (1:1) complex dyes, having benzene-azo-pyrazolone type structures, resulted from the same coupling component, depending on the nature and position of substituent in the diazotization component and taking into account the electronic effects (σ, π) of substituent.

Chromatographic analysis

In table 1, at **$CxII_{a-c}$** dyes type the chromatography revealed us that the approached way allowed to obtain uniform products.

In table 2, at **$CxIII_{a-f}$** dyes type the chromatography revealed us that the approached way allowed to obtain uniform products.

Chromium content analysis

In table 3, is presented the chromium content analysis of acid azo chromium (1:1) complex dyes of **$CxII_{a-c}$** type

Table 1

PRESENTATION OF R_f (RETENTION FACTOR) VALUES AT THIN LAYER CHROMATOGRAPHY OF ACID AZO CHROMIUM (1:1) COMPLEX DYES OF $CxII_{a-c}$ TYPE

Chromium (1:1) complex dye	**$CxII_a$** (AFS→AAA)	**$CxII_b$** (AFS→FMP)	**$CxII_c$** (AFS→2N)
B_i (i=1,2,3)	B_1	B_2	B_3
R_f	0.53	0.50	0.44

Table 2

PRESENTATION OF R_f (RETENTION FACTOR) VALUES AT THIN LAYER CHROMATOGRAPHY OF ACID AZO CHROMIUM (1:1) COMPLEX DYES OF $CxIII_{a-f}$ TYPE

Chromium (1:1) complex dye	**$CxIII_a$** (DO→AAA)	**$CxIII_b$** (NDO→AAA)	**$CxIII_c$** (DO→FMP)	**$CxIII_d$** (NDO→FMP)	**$CxIII_e$** (DO→2N)	**$CxIII_f$** (NDO→2N)
B_i (i=1,2,3)	B_1	B_1	B_2	B_2	B_3	B_3
R_f	0.56	0.69	0.54	0.61	0.58	0.68

Table 3

CHROMIUM CONTENT ANALYSIS BY ATOMIC ABSORPTION SPECTROSCOPY OF ACID AZO CHROMIUM (1:1) COMPLEX DYES OF $CxII_{a-c}$ TYPE

Chromium (1:1) complex dye		**$CxII_a$** (AFS→AAA)	**$CxII_b$** (AFS→FMP)	**$CxII_c$** (AFS→2N)
B_i (i=1,2,3)		B_1	B_2	B_3
Molecular weight (M)		481	476	448
Cr %	**Calc.**	10.8	10.9	11.6
	Exp.	10.1	10.2	11.1

Chromium (1:1) complex dye		CxIII$_a$ (DO→AAA)	CxIII$_b$ (NDO→AAA)	CxIII$_c$ (DO→FMP)	CxIII$_d$ (NDO→FMP)	CxIII$_e$ (DO→2N)	CxIII$_f$ (NDO→2N)
B$_i$ (i=1,2,3)		B$_1$	B$_1$	B$_2$	B$_2$	B$_3$	B$_3$
Molecular weight (M)		531	576	528	573	498	543
Cr %	Calc.	9.8	9.0	9.8	9.1	10.4	9.6
	Exp.	9.1	8.5	9.3	8.4	9.7	9

Table 4

Determinations attest a good agreement between the real and the assigned structures.

Crt.	Vibration nature	CxII$_b$ (AFS→FMP)	CxII$_c$ (AFS→2N)	CxIII$_e$ (DO→2N)
1	**Deformation vibration γ_{OH} (cm^{-1})**	3450 (i)	3450 (i)	3450 (i)
2	**Aromatic ring deformation vibration $\gamma_{C=C}$ (cm^{-1})**	1590-1630 (i)	1600 (i)	1600 (i)
3	**Valence vibration $\nu^s_{S=O}$ (cm^{-1})**	1150-1250 (i)	1150-1250 (i)	1150-1250 (i)
4	**Valence vibration $\nu^{as}_{S=O}$ (cm^{-1})**	1040 (i)	1040 (i)	1040 (i)
5	**Valence vibration at 5-membered heterocycles**	1590 (m) 1490 (m) 1400 (m)	- - -	- - -
6	**Deformation vibration of 1,2,4-tri-substituted benzene ring γ_{C-H} (cm^{-1})**	805-825 (i) 870-885 (i)	805-825 (i) 870-885 (i)	- -
7	**Mono-substituted aromatic ring deformation vibration γ_{C-H} (cm^{-1})**	735-765(i) 685-710 (i)	- -	- -

Table 5

in which: (i) = intense band; (m) = medium band.

by atomic absorption spectroscopy with ionization in air – acetylene flame.

This is an instrumental analysis method based on the wavelength radiation absorption characteristic to each element for chromium atom: $\lambda_{\lambda Cr}$ =357.9nm.

In table 4, is presented the chromium content analysis of acid azo chromium (1:1) complex dyes of **CxIII**$_{a-f}$ type by atomic absorption spectroscopy with ionization in air – acetylene flame.

IR spectrophotometric analysis

Synthesized compounds containing a sulfonic group in the diazo component were characterized in the IR spectrum, presenting the bands displacement value characteristic to the studied chemical bonds and functional groups, for **CxII**$_b$, **CxII**$_c$ andi **CxIII**$_e$ dyes.

In table 5, are presented the (UV-Vis) spectral data on the behaviour of **CxII**$_b$, **CxII**$_c$ and **CxIII**$_e$ dyes, in aqueous solutions.

UV-Vis spectrophotometric analysis

Table 6, presents the (UV-Vis) spectral data on the behavior of **CxII**$_{a-c}$ type dyes, in aqueous solutions.

λ_{max} – represents the maximum absorption wavelength value of chromium (1:1) complex dye;

$\dot{\varepsilon}_{max}$. 10^{-3} – represent the molar extinction coefficient value of investigated chromium (1:1) complex dye*10^{-3}, by respecting the Lambert-Beer law;

$\Delta\lambda_{max}$– represents the difference between the maximum absorption wavelength value of investigated chromium (1:1) complex dye and that of the chromium (1:1) complex dye, considered as the reference structure, CxII$_a$;

$\Delta\dot{\varepsilon}_{max}$. 10^{-3} – represents the difference between the molar extinction coefficient of the investigated chromium (1:1) complex dye*10^{-3} and that of the chromium (1:1) complex dye*10^{-3}, considered as the reference structure, **CxII**$_a$.

Correlating the spectral parameters in table 6 with azo structures, results the following findings:

- replacement of the acetoacetanilide residue with pyrazolone respectively naphthalene residue leads to conjugation expansion and give rise to bathochromic and hypochromic effect, lower or higher. In the first case we are dealing with longitudinal conjugation extension and in the second with expansion of both longitudinal and lateral conjugation.

- at **CxII** dyes type the molecule transition from the ground state (CxII$_{a-c}$) in the excited state (**CxII**$_{a-c}$*) takes place by electrons moving from left to right from the phenolic-**O-** atom to the azo group.

UV-Vis spectral data interpretation

In the category of dyes with the general structure **CxIII**$_{a-f}$ were studied the next compounds: **CXIII**$_a$ and **CxIII**$_b$ (CxIII$_{a-f}$, when B$_1$ is a acetoacetanilidic residue), **CxIII**$_c$ and **CxIII**$_d$ (CxIII$_{a-f}$, when B$_2$ is a pyrazolone residue), **CxIII**$_e$ and **CxIII**$_f$ (CxIII$_{a-f}$, when B$_3$ is a naphthalene residue).

In table 7 are presented the (UV-VIS) spectral data on the behavior of these complexes in aqueous solutions.

Correlating the spectral parameters in table 7 with azo structures can be drawn the next findings:

- the introduction of the $-NO_2$ group in **CxIII**$_{a,c,e}$ dyes, in a conjugate position to the naphthol **-O-** atom, is giving rise to an hipsochromic effect of lower or higher value, in Vis spectrum;

The explanation is that the $-NO_2$ group situated in this position causes a strong acceptor ð effect, which leads to emergence of quinone-imine structures (**CxIII**$_{b,d,f}$), in the ground state of dyes molecules. These structures cause the conjugation decreasing and polarity increasing of **O$^+$%Cr** bond, which gets a strong ionic character. The two effects tend to lower dye molecules planarity, implicitly absorption intensity.

In **CxIII**$_{b,d,f}$ dyes, the molecule transition from the ground state to the excited state (**CxIII**$_{b,d,f}$*) takes place by electrons moving from right to left, from acetoacetanilidic, pyrazolone or naphthalene **-O-** atom directly linked by Cr (III) ion to the azo group, while in **CxIII**$_{a,c,e}$ this transition occurs in reverse, by electrons moving from the naphthol **-O-** atom to the azo group;

- The bathochromic effect which appears by replacing the acetoacetanilidic residue with pyrazolone respectively

Table 6
(UV-Vis) SPECTRAL ANALYSIS IN ACID AZO CHROMIUM (1:1) COMPLEX DYES OF CxII$_{a-c}$ TYPE

Chromium (1:1) complex dye	CxII$_a$ (AFS→AAA)	CxII$_b$ (AFS→FMP)	CxII$_c$ (AFS→2N)
B$_i$ (i=1,2,3)	B$_1$	B$_2$	B$_3$
λ_{max}(nm)	443.2 (yellow)	473.5 (orange)	550.7 (violet)
$\acute{\varepsilon}_{max}$* 10^{-3} $M^{-1}cm^{-1}$	21	11,7	3.76
Conc.*10^2 g/L	2.7	3.25	3.14
$\Delta\lambda_{max}$ (nm)	0	+30.3	+107.5
$\Delta\acute{\varepsilon}_{max}$* 10^{-3} $M^{-1}cm^{-1}$	0	-9.3	-17.3

Table 7
(UV-Vis) SPECTRAL ANALYSIS IN ACID AZO CHROMIUM (1:1) COMPLEX DYES OF CxIII$_{a-f}$ TYPE

Chromium (1:1) complex dye	CxIII$_a$ (DO→AAA)	CxIII$_b$ (NDO→AAA)	CxIII$_c$ (DO→FMP)	CxIII$_d$ (NDO→FMP)	CxIII$_e$ (DO→2N)	CxIII$_f$ (NDO→2N)
B$_i$ (i = 1,2,3)	B$_1$	B$_1$	B$_2$	B$_2$	B$_3$	B$_3$
D$_i$ (i = 1,2,3)	-	D$_1$	-	D$_2$	-	D$_3$
Conc.*10^2 g/L	3.5	3.65	2.94	1.75	3.38	2.4
λ_{max}(nm)	485.4 (reddish brown)	481.7 (reddish brown)	525.2 (cyclam claret)	513.3 (reddish claret)	591 (blue)	544.7 (dark gray)
$\acute{\varepsilon}_{max}$* 10^{-3} $M^{-1}cm^{-1}$	11.3	11	14.9	14.6	8.9	8.25
$\Delta\lambda_{max}$ (nm)	0	-3.7	0	-11.9	0	-46.3
$\Delta\acute{\varepsilon}_{max}$* 10^{-3} $M^{-1}cm^{-1}$	0	-0.3	0	-0.3	0	-0.65

naphthalene residue at CxII type dyes, is maintained at CxIII type dyes;

- If we compare **CxII$_{a,b,c}$** dyes with **CxIII$_{a,c,e}$** dyes, a remarkable bathochromic effect is observed to those that include the same component coupling (acetoacetanilide, 1-phenyl-3-methyl-5-pyrazolone or 2-naphthol), which is due to the lateral conjugation expansion by annealing at the diazotation component;

$\Delta\lambda^1_{max}$ = + 42.7 nm; $\Delta\lambda^2_{max}$ = + 51.7 nm;

$\Delta\lambda^2_{max}$ = + 40.3 nm.

By comparing the spectral effects we're observing a great approximation of $\Delta\lambda_{max}$ values, so it can be concluded that in most cases to the azo chromium (1:1) complex dyes, to annealing the value of bathochromic effect is approx. 40-50 nm, depending on the chemical structure.

Conclusions

A number of pre-formed acid azo chromium (1:1) complex dyes with the sulphonic group in the diazotation component, having aryl-azo-acetoacethanilide, aryl-azo-pyrazolone and aryl-azo-naphtaline, (aryl = benzene, naphtaline) type structures, have been synthesized by methods described in the literature (1, 3 and 4 structures). The structure of the synthesized compounds was proved by spectrophotometric analysis and their purity by thin layer chromatography. These chromium (1:1) complex dyes were characterized by (IR, UV-Vis) spectral analysis. Determinations attest a good agreement between the real and the assigned structures.

Interpretation of (UV-Vis) spectral parameters variation of the studied acid azo chromium (1:1) complex dyes led to the following conclusions:

Introduction of –NO$_2$ group in the CxIII$_{a,c,e}$ dyes, in a conjugable position to -O- naphtolic atom is giving rise to a lower or higher hypsocrome effect in the Vis spectrum.

1) In the acid azo chromium (1:1) complex dyes to annealing at the diazotization component, the batochrome effect is about 40-50 nm, depending on the chemical structure.

2) Replacement of the acetoacetanilidic coupling component with pyrazolone respectively naphthalene residue in the acid azo chromium (1:1) complex dyes, is giving rise to a remarkable batochrome effect.

3) In acid azo chromium (1:1) complex dyes, the change of sulfonic group place from the coupling component in the diazotization component, is not changing the position of maximum absorption in the VIS spectrum.

This paper explains the variation of UV-Vis spectral parameters of pre-formed acid azo chromium (1:1) complex dyes having aryl-azo-acetanilide, aryl-azo-pyrazolone and aryl-azo-naphthalene (aryl = benzene, naphthalene) type structures, containing one sulphonic group in the diazotization component, depending on the nature of diazotization and coupling components, the nature and position substituent and considering the electronic effects (σ, π) of substituent.

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