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 → acetocetanilide and (B): 1-diazo-2-naphthol-4-sulphonic acid → acetocetanilide, 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 sulfonic 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 → acetocetanilide;
(B). 1-diazo-2-naphthol-4-sulphonic acid → acetocetanilide.

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-acetilidene, aryl-azo-pyrazolone and aryl-azo-naphtalene type structures (aryl = benzene, naphtalene), which were purified and analyzed. From the dyes category with general structure CxIIIa-f were studied the next compounds: CxIIIa and CxIIIb (CxIIIa when B1 represents an acetocetanilide residue), CxIIIc and CxIIIc (CxIIIc when B2 represents a pyrazolone residue), CxIIIe and CxIIIe (CxIIIe when B3 represents a naphtaline residue). Chemical structures of the compounds CxIIIa, CxIIIb, CxIIIc, CxIIIe, CxIII, CxIII are presented, both in the ground and excited state:

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Materials, methods and equipment

**Diazotization components:** 2-aminophenol-4-sulphonic acid (AFS), 1-diazot-2-naphthol-4-sulphonic acid (diazoxid) (DO), 6-nitro-1-diazot-2-naphthol-4-sulphonic acid (nitrodiazoxid) (NDO).

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

The (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) DO→AAA; 4) DO→AAA; 5) DO→FMP; 6) DO→FMP; 7) NDO→AAA; 8) NDO→FMP; 9) NDO→FMP.

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%.

**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.

**Chromatographic analysis**

In table 1, at CxIIa-c dyes type the chromatography revealed us that the approached way allowed to obtain uniform products.

In table 2, at CxIIIa-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 CxIIa-c type.
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: \( \lambda_{Cr} = 357.9 \text{nm} \).

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 \( CxII_b, CxII_c \) and \( CxIII_e \) 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**

In table 6, presents the (UV-Vis) spectral data on the behavior of \( CxII_a, CxII_b \) and \( CxII_c \) dyes, in aqueous solutions.

<table>
<thead>
<tr>
<th>Crt.</th>
<th>Vibration nature</th>
<th>( \chi_{BO} ) (cm(^{-1}))</th>
<th>( \chi_{C-C} ) (cm(^{-1}))</th>
<th>( \chi_{S=O} ) (cm(^{-1}))</th>
<th>( \chi_{C-H} ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Deformation vibration</td>
<td>3450 (i)</td>
<td>1590-1650 (i)</td>
<td>1150-1250 (i)</td>
<td>735-765(i)</td>
</tr>
<tr>
<td>2</td>
<td>Aromatic ring deformation vibration</td>
<td>1600 (i)</td>
<td>1600 (i)</td>
<td>1150-1250 (i)</td>
<td>685-710 (i)</td>
</tr>
<tr>
<td>3</td>
<td>Valence vibration</td>
<td>1040 (i)</td>
<td>805-825 (i)</td>
<td>1590 (m)</td>
<td>1490 (m)</td>
</tr>
<tr>
<td>4</td>
<td>Valence vibration at 5-membered heterocycles</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Deformation vibration of 1,2,4-tri-</td>
<td>1400 (m)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>methylated benzene ring</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>Mono-substituted aromatic ring</td>
<td>735-765(i)</td>
<td>805-825 (i)</td>
<td>870-885 (i)</td>
<td>-</td>
</tr>
</tbody>
</table>

**UV-Vis spectral data interpretation**

In the category of dyes with the general structure \( CxIII_a-f \) were studied the next compounds: \( CxIII_a \) (when \( B_1 \) is a acetoacetanilidic residue), \( CxIII_c \) (when \( B_2 \) is a pyrazolone residue), \( CxIII_e \) (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 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 to the azo group and give rise to bathochromic and hypochromic effect, lower or higher.

This means that 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 \( (CxII_a) \) in the excited state \( (CxII_a^*) \) takes place by electrons moving from left to right from the phenolic-O- atom to the azo group.
naphthalene residue at CxII type dyes, is maintained at CxIII type dyes; 

- If we compare CxIIa,b,c dyes with CxIIIa,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; 

$\Delta \lambda_{\text{max}}^1 = +42.7 \text{ nm}$; 

$\Delta \lambda_{\text{max}}^2 = +40.3 \text{ nm}$. 

By comparing the spectral effects we’re observing a great approximation of $\Delta \lambda_{\text{max}}$ 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-acetanilide, aryl-azo-pyrazolone and aryl-azo-naphthalene, (aryl = benzene, naphthalene) 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:

1) In the acid azo chromium (1:1) complex dyes to annealing at the diazotization component, the bathochrome 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 bathochrome 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 ($\sigma$, $\pi$) of substituent.

Aknowledgements: The work was funded by Executive Agency for Higher Education, Research, Development and Innovation (UEFISCDI) under the Ministry of Education from Romania.

References


Manuscript received: 7.01.2015