Spectral Studies of Azo Pyrazolone Derivatives Complexes with Some Transition Metals

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Abstract: The discharge of effluents from material ventures has been a noteworthy worry of the cutting edge world because of the colossal contamination that these effluents advance on the water assets. Among the engineered colors discharged in effluents from material ventures, azo dyes are a standout amongst the most unfavorable classes since it is exceedingly determined in the oceanic environment, because of its synthetic creations, involving aromatic rings, azoic linkages and amino groups. This review aimed to gather information on the importance of the production, what's more, mechanical utilization of azo dyes, and in addition exhibit a few studies that have been created to assess the harmfulness of such substance mixes and their metabolites on various living beings. This paper displays some new metal buildings of N-heterocyclic subordinates of azo-pyrazolone, spectrophotometric titration procedures of the complex arrangement of subsidiaries Azo pyrazolone contemplated in water-ethanol arrangements, the constants of ionization constants of ligands and complex mixes. The quantum-synthetic demonstrating (DFT/B3LYP) of natural ligands and complex mixes was performed and the structures of the metal edifices were proposed.

Keywords: Azo Pyrazolone, Metal Complexes, Electronic Absorption Spectra, Equilibrium in Solutions, Constant Education

1. Introduction

Azo exacerbates In light of 5-pyrazolone broad not main successful Concerning illustration a yellow-orange azo array shades as well as effectively utilized within biomedical examination Also for natural amalgamation [1-3]. Prosperity pyrazolone dyes because of the Straightforwardness about azo coupling reactions, more stupendous changes to structural transform and adjustment of the needs of Different provisions about dyes, and also generally secondary for The majority color molar elimination coefficient. The introduction of the structure for their metal cations modifies those spatial Furthermore electronic structure of natural atoms that determines the shades properties of the color. In this regard, the ponder from claiming their ghastly aspects What's more methods of complex subsidiaries: azo pyrazolone extremely critical Those point of the exhibit study were the spectrophotometric ponder of the forms of complexation of an amount from claiming subsidiaries azo pyrazolone

![Figure 1. It shows the chemical structures of (H₂L₁) and (H₂L₂).](image)

The present study is part of a cycle of the authors on the study of structure and properties of carbo- and heterocyclic azo compounds and metal complexes based on them [4-13].

2. Exploratory Part

Electronic absorption spectra of aqueous ethanol solutions of organic molecules in the pH range from 2 to 9, as well as
metal salts in the titration were recorded on a Varian Cary 50 spectrophotometer Scan in the wavelength range 200 - 750 nm in 1 cm cuvettes width. The concentrations were selected individually for each connection. The composition of the complexes and their formation constants in the solutions was determined by the saturation method [14, 15]. Statistical treatment of the results was performed by the method described in [16] For a 95% certainty level pH progressions were performed on the ER-potentiometer 74 during 21-23°C. Before you start the appliance set up by a freshly prepared buffer solutions.

3. Results and Its Discussion

Electronic absorption spectra of H$_2$L$^1$ and H$_2$L$^2$ ethanolic solutions are characterized by broad intense absorption bands in the orange-red part of the spectrum (401 nm, lg$\varepsilon$ 3.95 for H$_2$L$^1$ and 488 nm, lg$\varepsilon$ 4.31 for H$_2$L$^2$), that in alkaline solutions undergo small hypochromic shift falling on intensity (Fig. 1).

Figure 2. The electronic absorption spectra of the solutions at titration of H$_2$L$^1$ (a) and H$_2$L$^2$ (b) sodium hydroxide solution.

Changes in the spectra are not accompanied by the appearance of isopiestic points, making it difficult to interpret the processes and calculation of equilibrium constants.

To determine the amount of hydrogen cations formed during dissociation 1 mol of an organic molecule was performed potentiometric titration H$_3$L$^1$ aqueous ethanol solution. It is shown that, in the pH range from 6.7 to 12.2, the pH corresponding to the interval for recording the electronic absorption spectra observed a jump in the pH titration curve. The ratio of n (H$_2$L$^1$): n (NaOH) in the middle of the shock titration (at the equivalence point) is 1: 1, which corresponds to the dissociation of a proton of the carboxyl group. PKa1 (H$_2$L$^1$) = 9.8 ± 0.2. This value corresponds to the low acidity of the carboxyl group, which can be explained by its participation in the formation of strong intermolecular hydrogen bonds. This conclusion does not contradict the results of quantum chemical calculations [4], according to which the position of the absorption bands in the electronic spectra corresponds to the following structure H$_2$L$^1$ molecules:

Adding metal salts solutions to solutions H$_2$L$^1$ and H$_2$L$^2$ (Fig. 2) results in a bathochromic shift of the absorption wavelength band and the appearance of the spectra in the isobestic points, indicating that the complexation process is an equilibrium.

Figure 3. It shows the chemical structure of formation of strong intermolecular hydrogen bonds in H$_2$L$^1$.

Figure 4. Electronic absorption spectra when titrated solutions H$_2$L$^1$ (a) and H$_2$L$^2$ (b) a solution of NiCl$_2$. 
According to the results of spectrophotometric titration built saturation curves that are calculated composition of the complexes in solution and the overall formation constant.

**Table 1. The complex formation constants and calculated by spectrophotometric titration.**

<table>
<thead>
<tr>
<th>Ligands</th>
<th>Cation metal</th>
<th>Lmax, nm</th>
<th>n</th>
<th>MLα</th>
<th>lgβ</th>
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<tbody>
<tr>
<td>H2L1</td>
<td>Mn2+</td>
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<td>1</td>
<td>3.00±0.15</td>
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<tr>
<td></td>
<td>Co2+</td>
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<td>1</td>
<td>3.17±0.21</td>
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<tr>
<td></td>
<td>Ni2+</td>
<td>420</td>
<td>1</td>
<td>3.55±0.08</td>
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<tr>
<td></td>
<td>Cu2+</td>
<td>403</td>
<td>1</td>
<td>3.62±0.13</td>
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<tr>
<td></td>
<td>Zn2+</td>
<td>412</td>
<td>1</td>
<td>3.24±0.11</td>
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<tr>
<td></td>
<td>Fe3+</td>
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<td>1</td>
<td>3.11±0.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn2</td>
<td>524</td>
<td>1</td>
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<tr>
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<td>H2L2</td>
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<td></td>
<td>Fe3+</td>
<td>492</td>
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<td>3.40±0.19</td>
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</tr>
</tbody>
</table>

Due to the fact that to obtain single crystals of compounds failed to offer schemes of their structure using spectroscopic methods.

IR absorption spectra of uncoordinated \( H_2L_1 \) and \( H_2L_2 \) are characterized by several absorption bands in the region of stretching vibrations of carboxyl and carboxyl groups. Medium intensity band 1705 cm\(^{-1}\) present in the \( H_2L_1 \) and \( H_2L_2 \) and maintain its position in the transition to complex compounds has been attributed to the vibrations of the carboxyl group benzo [4, 5] imidazo [1, 2] quinazoline fragments of organic molecules. Such an absorption band at 1725 - 1690 cm\(^{-1}\) is also present in the IR spectra of model compounds - derivatives Benzimidazole pyrimidine. The absorption band of the average intensity of 1667 cm\(^{-1}\) in \( H_2L_1 \) can be attributed to fluctuations in the carboxyl group imidazole fragment of the molecule, and intense bands 1635 and 1640 cm\(^{-1}\) in \( H_2L_1 \) spectra and \( H_2L_2 \), respectively - to the stretching vibrations of the C = O communication aromatic carboxylic group linked by strong intramolecular hydrogen bonds [2]. The broad absorption band with a maximum at 3310 cm\(^{-1}\) in the IR spectrum \( H_2L_2 \) due to stretching vibrations of OH groups of 8- hydroxyquinoline fragment of the molecule, and its shift to lower frequencies can be attributed to a strong involvement in hydrogen bonding.

In the transition from uncoordinated \( H_2L_1 \) to its metal 1, the following changes take place in the IR spectrum. Band 1705 cm\(^{-1}\) maintains its position, which indicates that the carboxyl group is benzo [4, 5] imidazo [1, 2] quinazoline moiety does not participate in coordination. The band 1667 cm\(^{-1}\) fragment imidazolone shifted to lower frequencies in the 12 cm\(^{-1}\), which can be explained by its participation in the coordination. The appearance in the IR spectrum of the complex compound intense absorption bands at 1650 and 1350 cm\(^{-1}\) due to the ionization of the carboxyl groups and the appearance of bands ant symmetric and symmetric vibrations carboxyl anion involved in the coordination with the metal cation.

Based on the ratio of metal: ligand complex 1, a 2: 1 as well as the fact that based on the results of qualitative analysis of anions are chloride inner-character, the following scheme may be a complex compound of the structure:

The IR absorption spectra of complexes of 2 - 6, containing the organic ligand \( H_2L_2 \), just as in the case of compound 1 is observed preservation absorption band 1705 cm\(^{-1}\) and appearance of absorption bands \( \nu_\text{as} \) (COO\(^{-}\)), \( \nu_\text{s} \) (COO\(^{-}\)) in the low frequency region with respect to the corresponding sodium salt bands ("free" carboxyl anion), we can explain the participation of the carboxyl group in coordination with metal cations \( \Delta \nu \text{as} \) (COO\(^{-}\)) \( \nu \text{s} \) (COO\(^{-}\)). The disappearance of the absorption band of hydroxyl group 3310 cm\(^{-1}\) in IR spectra of complexes due to the ionization of the hydroxyl group of 8- hydroxyquinoline fragment at the transition from \( H_2L_2 \) to its metal complexes, and broad unresolved absorption band in the region 3600 - 3400 cm\(^{-1}\), we refer to the stretching vibrations of crystallization water molecules.

According to the results of chemical analysis of \( H_2L_2 \) part of the coordination compounds in double deprotonated form. The ratio of metal: ligand ratio of 1: 1 in the case of complex compounds of 2 - 5, and a large number of organic electron-donor centers molecules suggests the formation of polymer structures in which the anion (L2) 2- is directly bridged and implements two metal chelate cycle.

Compounds \( H_2L_1 \) and \( H_2L_2 \) have an extended conjugated system and a set of functional groups (carboxyl, carboxyl, hydroxyl, azo group, heterocyclic nitrogen atoms) capable of reacting with the functional groups of natural and synthetic fibers. In this regard, data organic molecules and their metal complexes can be considered as promising dyes or pigments.

Should test trial. was conducted dyeing cotton, polyester and polyamide fibers. The samples taken for testing \( H_2L_1 \), \( H_2L_2 \), \( Na_2L_2 \) sodium salt and complex compound 2. As shown by the experiment, cotton and polyester fibers hardly stained selected compounds in the given conditions. Polyamide fibers stained \( H_2L_1 \) compound in a golden yellow color, and \( H_2L_2 \), its sodium salt and a copper complex of 2 - bright red color of various shades.

Resistance to staining and washable dry friction visually
estimated at maximum score 5. It is noted that the dyeing process is accompanied by the almost complete transfer of the dye solution to the fiber. This is a valuable property from an environmental perspective, as it prevents the contamination of waste water dyes.

4. Conclusions

1. The processes of complexation: Azo pyrazolone metals in water-ethanol solutions, defined constants of complex compounds.
2. The correlation dependence of the constants formation of metal on the physical characteristics of the complexing ions.

References