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Research Article

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Study of Synthesis and Analysis Characterization and Solvatochromic Properties of Azo Chromogenic Reagents

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ABSTRACT

The reagent of Azo 4(4-Benzophenol Azo) pyrogallol [4-PABA] have been prepared. We have also prepared three Chelate complexes by the reaction this reagent with the metal ions of Co(II), Ni(II), Ag(I). The preparation was result after fixing the optimum conditions of concentration and (pH). UV-Visible spectra of these complex solution were studied for a range (pH) and concentration which obey Lambert-Beer Law. The structures of complexes are studied according to mole ratio methods which were obtained from the spectroscopic studies of the complex solutions. The ratio of metal: ligand obtained are (1:2) and (1:1) for complexes. Determined the reagent and its solid complexes were synthesized by analytical and spectroscopic methods available.

Keywords: Azo reagent; pyrogallol; [4-PABA]; Chelate complexes

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INTRODUCTION

Azo compounds are very important molecules and have received much attention in fundamental and applied chemistry [1-5]. Contain at least one nitrogen double bond (N=N), however many different structures are possible [6] and where the form of Azo dyes ratio ranging between (60%-70%) of the total dyes [7,8]. Have been prepared first type of Azo dyes in 1862 AD by Marty dye Bismarck Brown called [9] Azo dyes acquired wide interest in application to biological system and indicator in complexometric titration of analytical chemistry [10,11]. Over 50% of all colorants are Azo dyes [12] and they are the most widely used compounds in various areas, such as dyeing of textile fibers, coloring of different materials, in biological-medical studies and advanced applications in organic synthesis [13-19]. Color changes are caused by change in extent of delocalization of electrons more delocalization shifts the absorption max to longer wave lengths and makes the light absorbed redder, while less delocalization shifts the absorption max to shorter wave lengths [20,21].

MATERIALS AND METHODS

All the chemicals starting materials and reagents were of analytical grade and used further without purification. Melting points were taken in open glass capillary tubs using digital melting point-SMP3 apparatus. Thin layer chromatography was done with silica gel G, as purified. IR spectra of compounds were recorded on shimadzu FTIR 8400S spectrophotometer. UV spectra of compounds were recorded on UV-1650 PC UV-Visible spectrophotometer shimadzu. PH was taken by using pH meter.

Synthesis reagent 4(3-benzophenol Azo) pyrogallol

Synthesis of diazonium salt: In a 500 ml round bottom flask, 2.7428 gm (0.02 mol) of PABA was dissolved in a mixture of 10 ml of conc. HCl and 80 ml of distilled water and the temperature of solution was maintained below 5°C. Further, ice cold solution of 1.38 gm (0.02 mol) of sodium nitrite ($NaNO_3$) in 20 ml water and added to it in a small volume, while shaking the mixture well for 30 min.

Conversion of diazonium salt to azo compound: Dissolve 2.52 gm (0.02 mol) of pyrogallol in a 4 gm sodium hydroxide solution. The mixture was cooled below 5°C. Now the cold solution was added to cold diazonium solution synthesized in above step. PH of the mixture controlled within range of (6-6.5). The resulting solution formed a colored precipitate. The mixture was diluted with appropriate amount of deionized water and allowed to stand in ice bath for 1 h with constant stirring, left overnight then filtered and allowed to dry. The product was purified with absolute ethanol and monitored by TLC on silica gel plates using 2:3 methanols: toluene as solvent. yield of the product was 43% and m.p of the reagent was (290-300).

Preparation of solid complexes: Prepared solid complexes depending on the appropriate conditions of concentration, PH and molar ratio (metal:ligands) [1:1] and [1:2]. Prepared Cobalt complex by added (0.002 mol) (0.274 gm) from reagent was dissolved in ethanol gradually with continuous stirring to (0.001 mol) (0.237 gm) of aqueous cobalt chloride (II) was dissolved in PH equal to 7. The mixture was heated to 60°C for 30 min to complete the reaction, and a brown precipitate was observed. Then filtered and allowed to dry. While nickel complex was prepared by added (0.137 gm) (0.001 mol) from reagent was dissolved in ethanol gradually with continuous stirring to (0.238 gm) (0.001 mol) of aqueous nickel chloride (II) was dissolved in pH equal to 7. The mixture was heated to 60°C for 30 min to complete the reaction, and dark green precipitate was observed. Then filtered and allowed to dry. Also prepared silver complex by added (0.137 gm, 0.001 mol) from reagent was dissolved in ethanol gradually with continuous stirring to (0.170 gm, 0.001 mol) from silver nitrate (I) solution was dissolved in pH equal to 7. The mixture was heated to 60°C for 30 min to complete the reaction, and reddish-brown precipitate was observed. Then filtered and allowed to dry.

RESULTS AND DISCUSSION

Characterized of (4-PABA) and its metallic complexes

Determination of the complex formation by mole ratio method: In the molar ratio method, a series of solutions should be provided in a way that concentration of a reactant is constant (metal) while that of the other reactant is changed. Then, the absorbance of each solution is determined and the absorption diagrams are plotted versus molar ratio of reactants (21). The considered molar ratios are shown in Table 1. In this study three cations were used including cobalt, nickel, and silver (Figures 1-3).

Table 1. The molar ratio of ligand and metal cation

M/L	CO(II)	Ni(II)	Ag(I)	M/L	CO(II)	Ni(II)	Ag(I)
0.000697338	0.19	0.136	0.05	0.000714699	0.447	0.384	0.246
0.000700231	0.291	0.213	0.096	0.043055556	0.465	0.372	0.251
0.000703125	0.342	0.26	0.149	0.000720486	0.46	0.382	0.269
0.042361111	0.359	0.305	0.187	0.00072338	0.471	0.403	0.278
0.000708912	0.403	0.344	0.209	0.000726273	0.478	0.41	0.273
0.000711806	0.435	0.361	0.222	0.04375	0.484	0.418	0.289

Figure 1. Molar ratio curve for cobalt complex with ligand 4-PABA

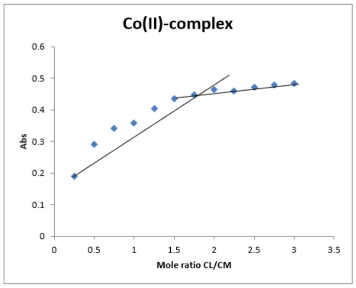


Figure 2. Molar ratio curve for Nickel complex with ligand 4-PABA

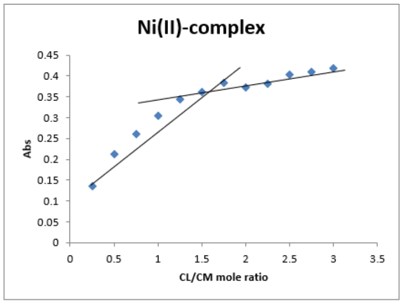
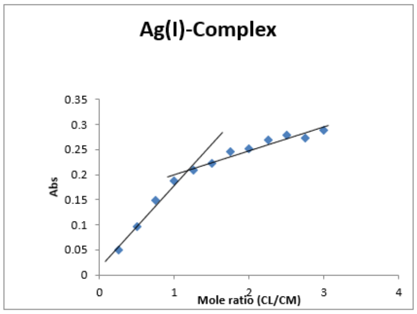


Figure 3. Molar ratio curves for silver complex with ligand 4-PABA



Study the effect of solvent: The effect of solvent was studied in order to know the role of polarity and its effect on the displacement of absorption sites from the spectrum (max ג) and also to find out the best and suitable solvent for the process of preparing the reagent and its metal complexes and to be adopted in the preparation process. This study using various solvents and different polarity, and these solvents are ethanol, methanol, acetone, Tetrahydrofuran, Dimethyl formamide, Dimethyl sulfo-oxide, cyclohexane, gasoline, propanol, and ethyl acetate, where the reagent solutions were prepared in these solvents with a At the laboratory temperature of all the above mentioned solvents, the spectra of the rays of the azo reagent (4-PABA) showed. For this study, the solvent polarity and its difference from one solvent to another are important role in changing the location of maximum absorption values (max ג) and have a fundamental role in changing the shape and intensity of the beams. Absorption as shown below concentration of $(1 \times 10)^{-3M}$) where this study was conducted using UV-visible rays (Figures 4-7).

Figure 4. The reagent in ethyl acetate solvent

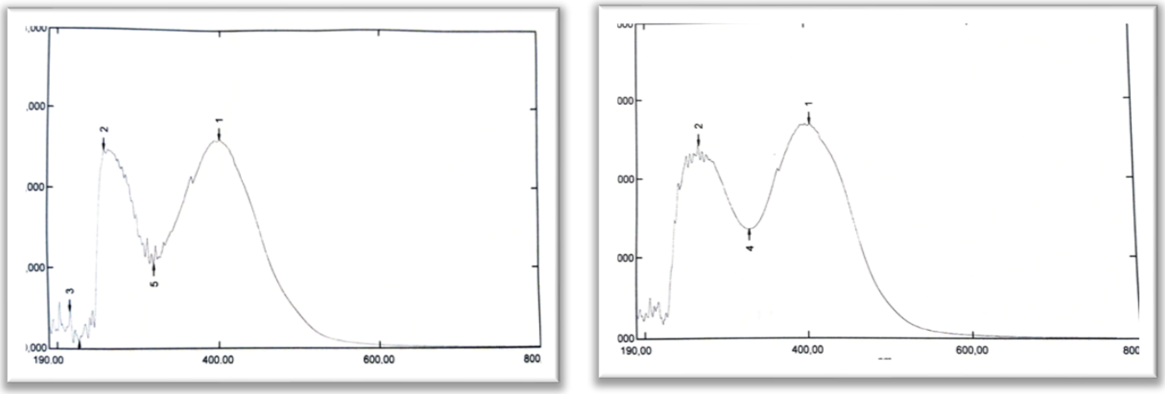


Figure 5. The reagent in propanol solvent

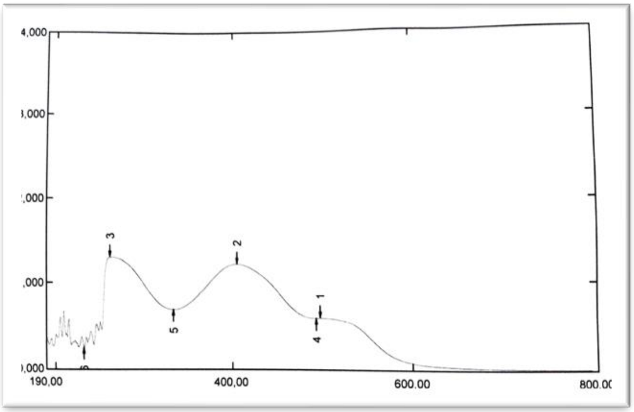


Figure 6. The reagent in DMSO solvent

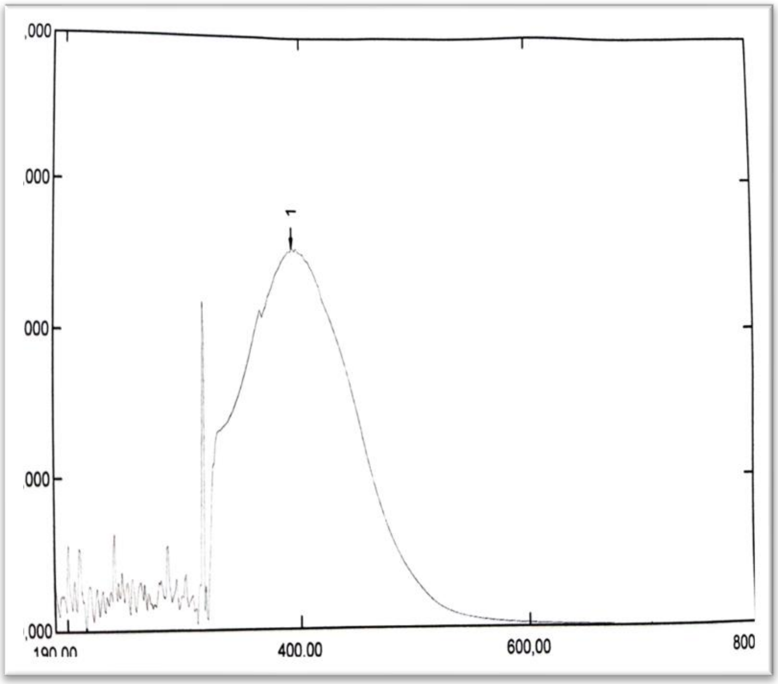


Figure 7. The reagent in acetone solvent

Spectral analysis for 4-PABA

The synthesized compounds were characterized by their consistent IR and UV spectral characteristics. The appearance of IR bands in the region 3433 cm^{-1} depicted the presence of phenol O-H stretch. The IR bands in the region 3074 cm^{-1} marked the presence of C-H stretching (aromatic). The IR bands in the region 2540 cm^{-1} marked the presence of O-H stretch (carboxylic acid). 1425 cm^{-1} (N=N Azo linkage), 1600 cm^{-1} (C=C aromatic), 1280 cm^{-1} (C-N stretch aromatic amines), 1045 cm^{-1} (C-O stretch carboxylic acid), 927, 945 cm^{-1} (O-H bend carboxylic acid), 775 cm^{-1} (C-H bending aromatic), 694 cm^{-1} (C-H oop aromatics), 1687 cm^{-1} (C=O stretch carboxylic acid) (Table 2) (Figures 8,9).

Table 2. The famous IR frequencies of important bands of 4-PABA

υ O-H	**υ C-H**	**υ N=N**	**υ C=C**	**υ C-N**	**υ C-O**	**υ C=O**
3433cm^{-1}	3074cm^{-1}	1425cm^{-1}	1600cm^{-1}	1280cm^{-1}	1045cm^{-1}	1687cm^{-1}
2540cm^{-1}	694cm-^{1}	…………….	………………………	…………….	………………	……………….
927cm^{-1}	775cm^{-1}	……………. .	……………….	……………. .	……………….….	………………. .
945cm^{-1}						

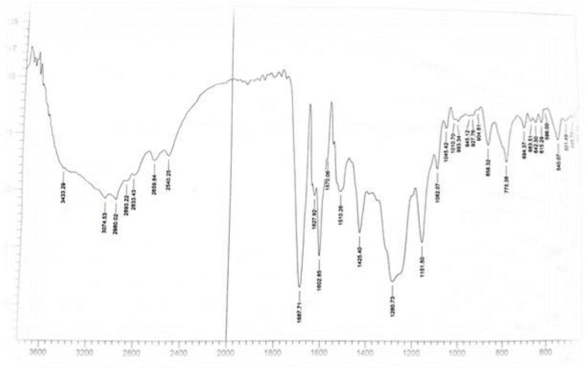


Figure 8. The FTIR spectral for 4-PABA

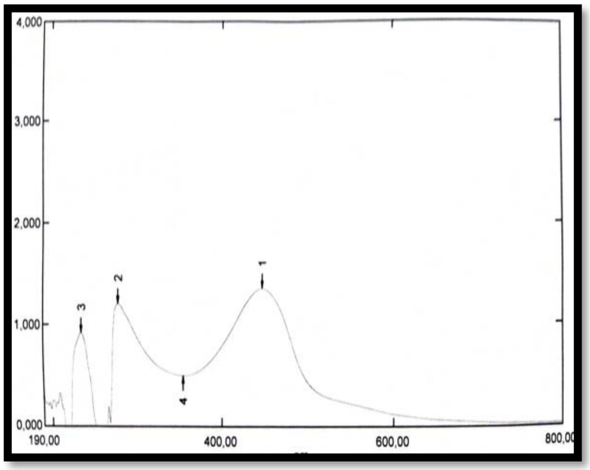
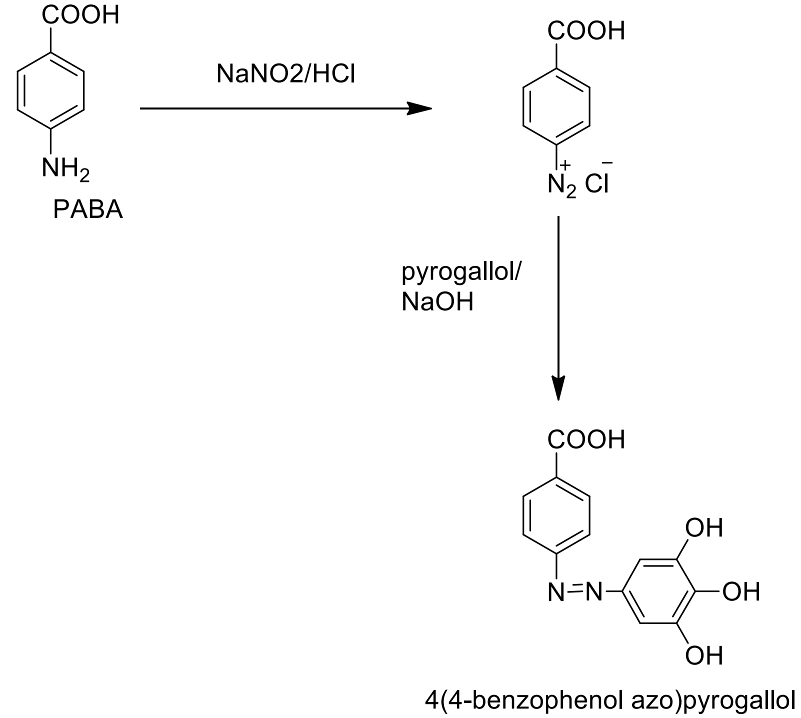


Figure 9. The UV-VIS spectral analysis for 4-PABA

The UV spectra of synthesized 4-PABA showed three transitions at 446 nm, 278 nm and 235 nm absorb at visible area, because of its orange color but also gives transitions at far UV back to the shift towards short wavelengths (Blue shift), back to pulling groups.

Scheme 1. Synthetic route for 4-PABA



CONCLUSION

The studies confirm 4-PABA was prepared from react diazonium salts Para amino benzoic acid with pyrogallol. And its complexes were prepared. The products; 4-PABA was characterized by FTIR and UV-Visible spectrophotometer. Azo and its complexes were studied in solutions of different pH and determination molar ratio for complexes and measurement UV-VIS spectra to know effect the solvent on ligand.

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