

Synthesis and Spectral Study of New Mercerized Azodyes and their Complexes with Copper(II)

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Abstract: A new series of some mercerized azodyes, 2-(2-mercury chloride -4-X phenylazo)-4-acetamido phenol (where X = sulphonic acid [L₁], acetyl [L₂], carboxyl [L₃], nitro [L₄] and sulphamide [L₅]) were prepared. All these were characterized by melting points, FT IR-spectroscopy ¹H NMR and C H N analysis. The work involves a study of acid - base properties at different pH values, the ionization and protonation constants were calculated. The complexes of L₁ and L₅ with Cu(II) were prepared. These complexes have been concluding after fixing the optimum conditions (time, pH and sequence of addition effects). The spectra of the complexes solutions have been studied for a range of concentrations which Lambert - Beer's law obeyed. It was found that the complexes are 1: 2 (M:L) complexes and the overall stability constants were determined by the corresponding solutions method

Keywords: Mercerized azodyes, 4-Acetamido phenol, Mercerized aniline

Introduction

Azo compounds have been receiving much attention and have been widely used in many practical application such as coloring fiber¹ clothing², cosmetics³, plastics⁴, self-colored segmented polymeric dyes⁵. Anti corrosion⁶, azo metal chelates have also attracted increase attention due to their interesting electronic and geometrical features in connection with their application for molecular memory storages, nonlinear optical elements printing system⁷, drug, cosmetic and photochemical production⁸. Azo dyes of sulfa drugs are well known for their antiseptic activity⁹ and some are useful as chemotherapeutic agents¹⁰.

Organomercurials have been used extensively in organic synthesis as well as in mechanism investigation due to their ability to accommodate practically all of the important organic functional groups and their ease in undergoing transmetallation for the synthesis of other organ metallic compounds¹¹, organomercurials, coupled with heterocyclic compounds exhibit a wide range of pharmacological activities like fungicidal, bactericidal^{12,13}.

In the present investigation concerned with preparation five new mercerized azodyes by reaction of paracetamol (4-acetamido phenol) with 2-mercury chloride -4-X- aniline. The characterization of the azo compounds has been performed by IR, NMR and C H N and their complexes with copper.

Experimental

All the reagents and solvents were of reagent-grad quality. The progress of reaction was monitored by TLC using silica gel coated plates (0.5 mm thickness, Merck) and spots were visualized under UV radiation. Infrared spectra (in K Br pellets) were recorded on FT IR-8400S shimadzu. NMR spectra were recorded by Bruker Ultra Shield 300MHz spectrometer DMSO as solvent and TMS as internal reference. Melting point we determined on melting point apparatus. The elemental analysis (C, H, N) were carried out on a microanalysis unit of Perkin Elmer model 2400 and given in Table 1. UV-Vis. absorption spectra of the dyes in different buffer solutions at room temperature were recorded using Hitachi UL-1500 spectrophotometer.

2-Mercury chloride -4-X aniline (where X = sulphonic acid, acetyl, carboxyl, nitro and sulphamide) were prepared from 2-mercury chloride-4-X aniline and mercuric acetate according to literature method¹⁴.

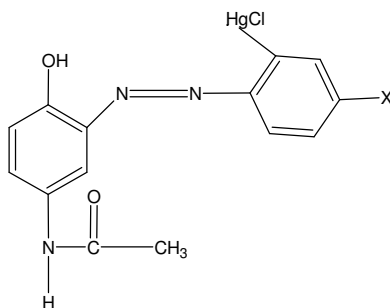
Synthesis of dyes

Diazotization

2-Mercury chloride -4-X aniline (0.02 mol) was dissolved in 50 mL of distilled water and 6 mL of concentrated hydrochloric acid was added the solution was then cooled to 0-5 °C in ice-bath and maintained at this temperature sodium nitrate (0.02 mol) solution in 5 mL water was then added drop wise with stirring for 30 min to produce diazonium salt.

Preparation of dyes

The diazonium solution was added portion wise to the coupling component solution prepared by dissolving 0.02 mol of paracetamol(4-acetaminophenol) in 100 mL of alkaline solution. The mixture was stirred for further 1 h at 0 °C and then the mixture was neutralized with dilute hydrochloric acid. The solid product was collected and washed with water until acid-free product and recrystallized from ethanol, dried at 50 °C in an oven to give azo dye (Scheme 1).



X: SO_3H (L_1), COCH_3 (L_2), COOH (L_3), NO_2 (L_4), SO_4NH_2 (L_5)

Scheme 1. Suggested molecular structure of dyes

A stock solutions of (0.8×10^{-4} M) of each dyes were prepared by dissolving an accurately weighted amount of the compounds in the required volume of ethanol, more dilute solution were obtained by accurate dilution.

For acid-base studies the ionization (for hydroxyl group) and protonation (of nitrogen) constants of a series of acetate and universal buffer solutions were prepared with different pH values (0.5-12) for each dyes¹⁵.

Results and Discussion

The physical properties and elemental analysis data of the prepared dyes are listed in the Table 1.

Table 1. The physical and analytical data of the dyes

Compd.	Molecular formula	M. Wt.	Color	M.P °C	Elemental analysis		
					Composition, Found (Calcd.)		
					%C	%H	%N
L ₁	C ₁₄ H ₁₂ O ₅ N ₃ SHgCl	570	Orange	331	36.21 (36.36)	4.25 (4.58)	6.46 (6.36)
L ₂	C ₁₆ H ₁₄ O ₃ N ₃ HgCl	532	RED	183	41.91 (42.58)	4.78 (4.87)	6.40 (6.77)
L ₃	C ₁₅ H ₁₂ O ₄ N ₃ HgCl	534	range	175	39.25 (39.41)	4.11 (4.47)	6.76 (6.89)
L ₄	C ₁₄ H ₁₁ O ₄ N ₄ HgCl	535	Dark Orange	159	37.02 (37.44)	4.01 (4.13)	8.98 (9.19)
L ₅	C ₁₄ H ₁₃ O ₄ N ₄ SHgCl	569	Orange	231	35.23 (35.46)	4.12 (4.23)	8.64 (8.71)

IR spectra

The structures of azo dyes were identified by IR spectra, it show intense bands appearing at (1770 and 1752 cm⁻¹) these peaks are attributed to carbonyl group abroad hydroxyl (-OH) peak observed with region 3200-3500 cm⁻¹, the low frequency and the broadening of these bonds suggest that these dyes having a strong hydrogen bonding (O-H.....N) in the solid state^{16,17}. The peak appearing in the region 1630-1625 cm⁻¹ are attributed to ν (C-N) stretching vibration. The band belonging to ν (N-H) stretching vibration is not observed probably due to overlapping with the broad hydroxyl peak. The other characteristic peaks of dyes are given in Table 2. These data are in agreement with those previously reported for similar compound¹⁸⁻²⁰.

Table 2. The IR spectral data of the azo-dyes (KBr disk)

Compd.	ν NH & OH str.	ν C-N str. cm ⁻¹	ν C=O str. cm ⁻¹	ν N=N str. cm ⁻¹	ν O=S=O Asy/Sym
L ₁	3500-3350 b	1325 w	1670 s	1429 w	1365 w 1195 s
L ₂	3300-3200 b	1355 w	1658 s	1415 (w)	-
L ₃	3450-3250 m	1332 w	1652 s	1406 s	-
L ₄	3350-3300 b	1323 w	1610 s	1432 w	-
L ₅	3500-3300 b	1375 w	1656 s	1433 w	1300 w 1137 w

b = board s = strong m = medium w = weak

NMR spectra

The structure of the compounds under study is investigated on the basis of ¹H NMR spectra (Table 3). The data shows two signals at 6.6-8.5 ppm which can assigned to the protons of benzene ring^{21,22}, compounds (Figure 1 & 2), shows signal at low field ($\delta \approx 10.5$ ppm) which can be assigned to the proton of NH or OH, since the proton signal of the hydrogen bonded NH must appear at low field. This supports the IR suggestion of the possibility for the structure of these compounds.

Table 3. ^1H NMR spectra of azo compounds

Compd.	δ , ppm
L ₁	2.02 (S, 3H, CH ₃), 6.9-7.9(m, 6H, Ar-H), 7(S, 1H, SO ₃ H), 9.8 (S, 1H, NH), 10.7 (S, 1H, OH)
L ₂	2.02(S, 3H, NH-C(=O)-CH ₃), 6.5-8.2(m, 6H, Ar-H), 2.4(S, 3H, COCH ₃), 9.65 (S, 1H, NH), 9.9(S, 1H, OH)
L ₃	2.03 (S, 3H, CH ₃), 6.6-8(m, 6H, Ar-H), 9.8(S, 1H, NH), 10.1 (S, 1H, OH)
L ₄	2.02 (S, 3H, CH ₃), 6.6-8.5(m, 6H, Ar-H), 6.7(S, 1H, NH), 9.9(S, 1H, OH)
L ₅	2.02 (S, 3H, CH ₃), 6.6-7.9(m, 6H, Ar-H), 7.31(S, 2H, SO ₂ NH ₂), 9.67 (S, 1H, NH), 9.9(S, 1H, OH)

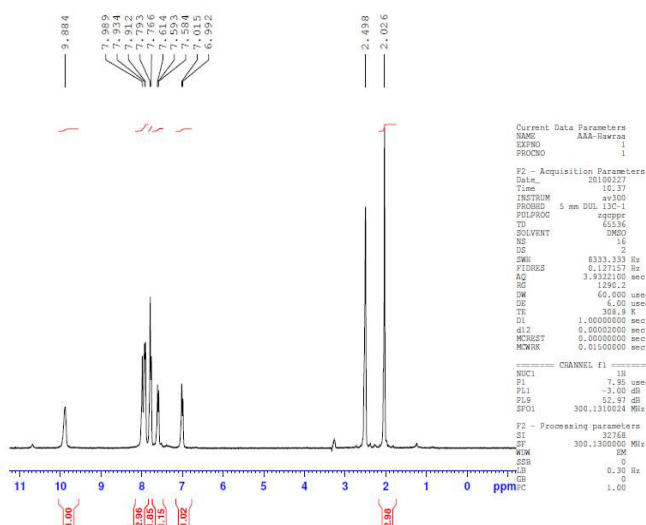


Figure 1. NMR spectra of L_1

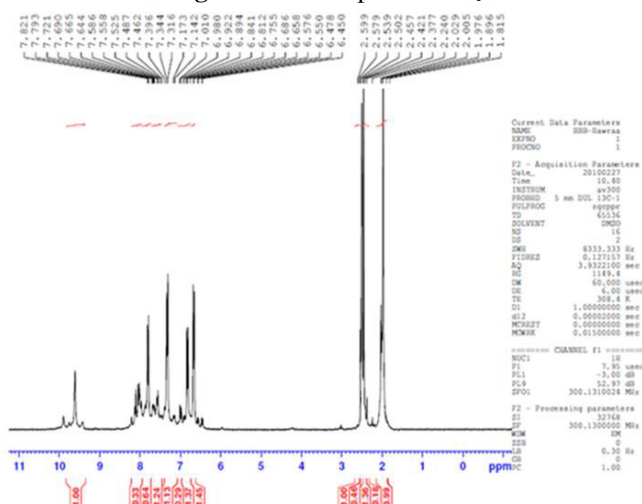


Figure 2. ^1H NMR spectra of L_2

Electronic absorption spectra

The electronic absorption spectral of new dyes involve the absorption band due various electronic transitions liable to occur within the molecules such as bands due to localized excitation of the in π -electron within the aromatic moieties attached to azo group which lie at 240-260 nm, may be attributed to $\pi \rightarrow \pi^*$ transition of benzenoid moiety of compounds. The second band observed in the region of 290-295 nm is attributed to $n \rightarrow \pi^*$ electronic transition of $N=N$ - group. The third band appearing in the visible region at (515,330, 480. 390 & 500 nm) for dyes L_1 - L_5 respectively can be assigned to $\pi \rightarrow \pi^*$ transition involving the whole electronic system of the azo dyes influenced by inter-molecular charge transfer character²³.

Ionization and protonation constants of dyes

Figure 3 show the electronic spectra of L_1 at varying pH values (0.7-12).

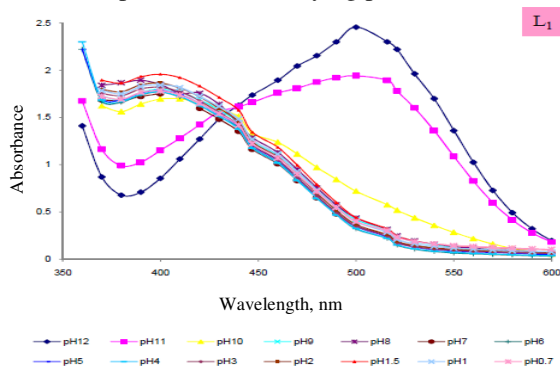
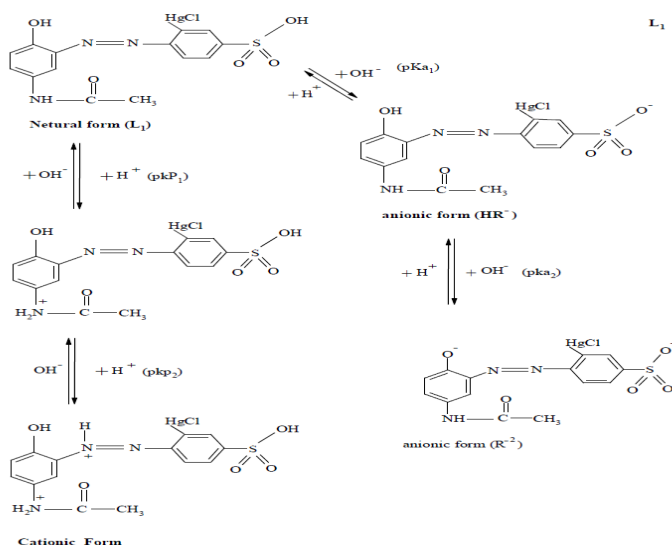


Figure 3. Absorbance pH for L_1

Scheme 2 show the suggested mechanism for ionization and protonation of dyes, which show two isopiestic points are due to ionization and two isopiestic points are due to protonation of dyes in acidic and basic medium



Scheme 2. The suggested mechanism for ionization and protonation of dyes

The protonation and ionization constants (pK_p and pK_a) of dyes were determined from their spectral behavior in buffer solution of varying pH from the absorbance-pH curves at fix λ (Figure 4). The pK_a and pK_p values were determined by using of half height method²⁴ as shown in Table 4.

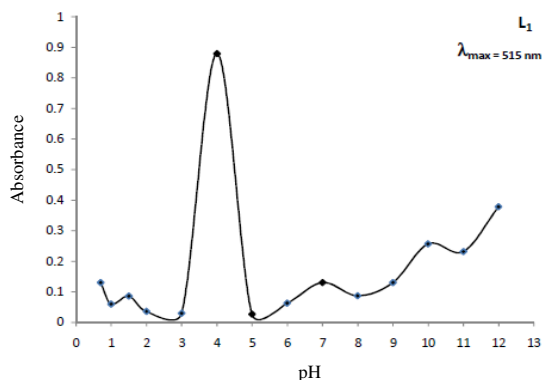


Figure 4. Absorbance pH for L_1

Table 4. The ionization and protonation constants of dyes

	λ_{\max} , nm	$pKp1$	$pKp2$	$pKp3$	$pKa1$	$pKa2$
L_1	515	1.4	3.5	-	6.2	9.3
L_2	330	3.5	-	-	7.8	10.5
L_3	480	4.5	-	-	6.5	9.8
L_4	390	3.2	5.6	-	7.7	-
L_5	500	1.4	3.5	6	9.2	-

K_a = Ionization constant of $-OH$ group pKp = Protonation constants

Complex formation studies

Complex dyes L_1 & L_5 with copper(II) (C_1 & C_2) were identified optimum conditions for the composition of these complexes (time, pH and sequence of addition effects).

Time effect

It was found the two complexes C_1 & C_2 are of high stability because of stable absorbance measurements. The more intense color was for in the region of (1- 40 min) and (1-120 min) with respect of C_1 & C_2 . The color is stable over night for both two complexes.

pH effect

By using of acetate and universal buffer solution (pH =1-13). The spectra of C_1 & C_2 were studied in wavelength range of (360-600 nm). It was found that the (pH= 8) of buffer solution is the suitable for forming both C_1 & C_2 complexes (Figure 5).

Sequence of addition

The best sequence of addition for giving highest absorbance for both C_1 & C_2 complexes is Metal + pH₈ + Dye.

The acid-base properties of the ligands (L_1 & L_5) facilitate the investigation of the coordinating behavior of these ligands toward the copper ion (Cu^{II}). Therefore the mechanism of complexation is based on hydrogen ion liberation.

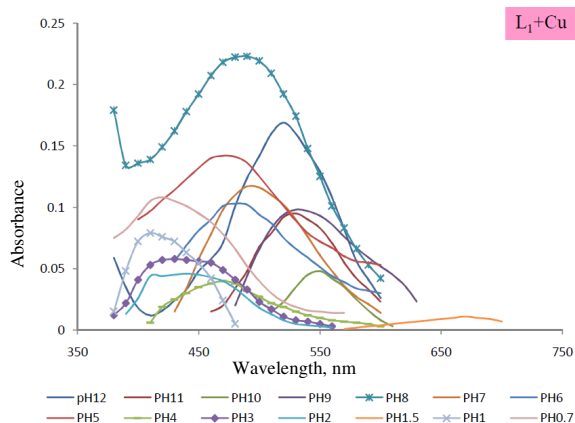


Figure 5. Absorbance pH for C_1

The composition (stoichiometry) of the complexes was determined by the continuous variation and molar ratio methods. Both showed that the ratio of 1:1 and 1:2 (M:L) for both complexes.

The calibration curve shows that Beers law is obeyed in the concentration range of ($0-15.25 \mu\text{g mL}^{-1}$) and ($0-11.43 \mu\text{g mL}^{-1}$) for complex of L_1 and L_5 with Cu(II) (C_1 and C_2) respectively. Table 5 shows the values obtained that represented by λ_{max} (nm), the molar absorptivity coefficient ($\epsilon \text{ L.mol}^{-1}\text{.cm}^{-1}$) and sensitive index ($s \mu\text{g.cm}^{-2}$), with higher precision that represented by the results of standard deviation (S.D), with high linearity of Beer's law which represented by the correlation coefficient R which is nearly unity and the detection limit (DL $\mu\text{g.mL}$) of the complexes C_1 and C_2 .

Table 5. Some results obtained from Beer's law

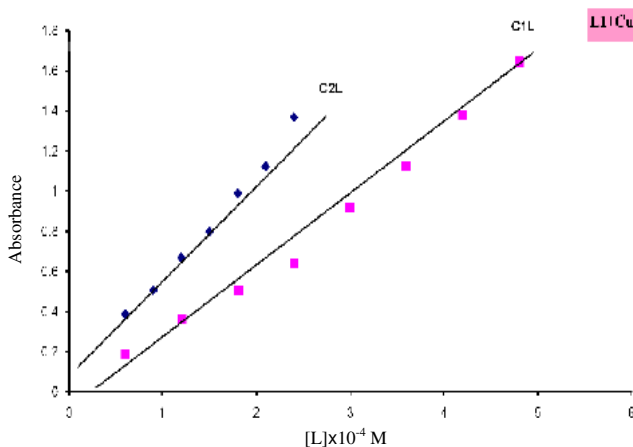
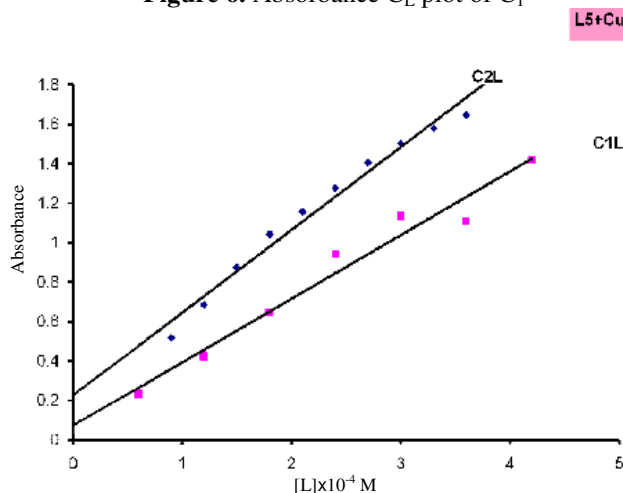
Compd.	λ_{max}	ϵ $\text{L.mol}^{-1}\text{.cm}$	S.D	S $\mu\text{g.cm}^{-2}$	DL $\mu\text{g.mL}^{-1}$	r	Beer's law limit
C_1	520	7302.3	0.021	0.0087	0.76	0.9946	15.25 ppm Cu
C_2	530	6097.3	0.026	0.0104	0.56	0.9929	11.43 ppm Cu

The stability of the complexes

The stability constants of complexes of copper with azodyes ligand were calculated using corresponding solutions method (by aid of half- value method)²⁴. This method required two series of solutions of total metal ion concentration C_{1M} (concentrated series) and C_{2M} (diluted series) and varying ligand concentrations C_{1L} and C_{2L} , then the diluted series was multiplied by the factor (C_{1M}/C_{2M}) . The corresponding solutions are those which have the same absorbance at different ligand concentration. From the absorbance – C_L plots (Figures 6 & 7) from many pairs of C_{1L} and C_{2L} values, n (complex formation function) and $[L]$ free ligand concentration can be determined.

$$n = (C_{1L} - C_{2L}) / (C_{1M} - C_{2M}), [L] = (C_{1M} C_{2L} - C_{2M} C_{1L}) / (C_{1M} - C_{2M})$$

By using the half value method the $\log \beta_1$ and $\log \beta_2$ are obtained from a plot of n against pL , when $n = 0.5$ gives $\log \beta_1$ ($\log K_1$) and $n = 1.5$ gives $\log \beta_2$ ($\log K_1 + \log K_2$). It was found that $\log \beta_1$ values of C_1 & C_2 are 5.55 & 3.79 respectively and $\log \beta_2$ values of C_1 & C_2 are 9.4 & 6.81 respectively.

Figure 6. Absorbance C_L plot of C_1 Figure 7. Absorbance C_L plot of C_2

Conclusion

In this study we have reported the synthesis of new mercerized azodyes by reaction of paracetamol (4-acetamido phenol) with 2-mercury chloride-4-X-aniline. The structural characterization of the azo compounds were made by using the elemental analysis, NMR, IR and UV spectral techniques. Ionization and protonation constants of dyes were calculated from electronic absorption spectral. The stability constants of complexes of copper with azodyes ligand were calculated using Corresponding Solutions method (by aid of half- value method).

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