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# Potentiometry and geometrical structure of some azodye compounds and their metal complexes

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ABSTRACT

A series of ligands of quinoline azodye derivatives ($HL_I$–$HL_{VI}$) have been prepared and characterized by elemental analysis, X-ray diffraction analysis, $^1H$ NMR and IR spectra. The proton–ligand dissociation constant of the ligands ($HL_I$–$HL_{VI}$) and the metal stability constant of their $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $La^{3+}$, $UO_2^{2+}$ and $Th^{4+}$ complexes have been determined potentiometrically in 1 M KC1 and 40% (V:V) EtOH–water mixture. The molecular structure of each ligand was optimized theoretically and the quantum chemical parameters were calculated. The influence of derivatives on the dissociation and stability constants was examined on the basis of the electron repelling property of the derivatives. Order of the stability constant of the formed complexes was found to be $Mn^{2+}$ $Co^{2+}$ $Ni^{2+}$ $Cu^{2+}$ $La^{3+}$ $UO_2^{2+}$ $Th^{4+}$. The effect of temperature was studied and the corresponding thermodynamic parameters (ΔG, ΔH and ΔS) were derived and discussed. The dissociation process was found to be non-spontaneous, endothermic and entropically unfavorable. On the other hand the formation of the metal complexes was found to be spontaneous, endothermic and entropically favorable.



## 1. Introduction

Azo compounds containing heterocyclic moieties have drawn the attention of many researchers. The chemistry of quinoline and its derivatives has attracted special interest due to their electrical and optical properties [1–5]. The electrical conductivities of quinoline compounds have received considerable attention [6] because of their physiological activity, analytical and industrial applications. Some of 8-hydroxyquinoline and azo derivatives found numerous applications in analytical chemistry as chromophoric and metallochromic indicators [7].

Moreover, azo compounds based on quinolone, play a central role as chelating agents for a large number of metal ions, as they form a stable six and/or five-membered ring after complexation with the metal ion [8–10]. The azo compounds are used in dyeing processes and some of them are used in the analytical separation of many metal ions present in a mixture [11]. The effect of temperature on the proton–ligand dissociation constants of a series of azo dyes was previously studied potentiometrically [12–15] and the stability constants of their complexes were found to be in the order $Mn^{+2} < Co^{+2} < Ni^{2+} < Cu^{2+}$. The corresponding thermodynamic parameters (ΔG, ΔH, ΔS) were also derived. The stoichiometries of the complexes were determined conductometrically and indicated the formation of 1:1 and 1:2 (metal:ligand) complexes.

In the present paper the potentiometric studies were used to determine the dissociation constants of quinoline azo dye derivatives ($HL_I$–$HL_{VI}$) and the stability constants of their $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $La^{3+}$, $UO_2^{2+}$ and $Th^{4+}$ complexes at different temperatures.

The molecular structures of the investigated ligands were optimized theoretically and the quantum chemical parameters were calculated. Moreover, the corresponding thermodynamic functions were also calculated and discussed.

## 2. Materials and methods

### 2.1. Preparation of quinoline azodye derivatives ($HL_I$–$HL_{VI}$)

Ligands of quinoline azo dye derivatives ($HL_I$–$HL_{VI}$) were prepared according to the following procedure. In a typical preparation, 25 ml of distilled water containing 0.01 mol hydrochloric acid was added to aniline (0.01 mol) or aniline derivatives. A solution of 0.01 mol sodium nitrite in 20 ml of water was added drop-wise to the resulting mixture then stirred and cooled to 0 °C. The formed diazonium chloride was consecutively coupled with an alkaline solution of 0.01 mol quinolin-8-ol, in 10 ml of pyridine. The preparation of ligands ($HL_I$–$HL_{VI}$) is summarized in Scheme 1. The colored precipitates, which formed immediately, were filtered through sintered glass crucible, washed several times with water. The crude products were purified by recrystallization from hot ethanol, (yield ~75%) then dried in a vacuum desiccator over $P_2O_5$.

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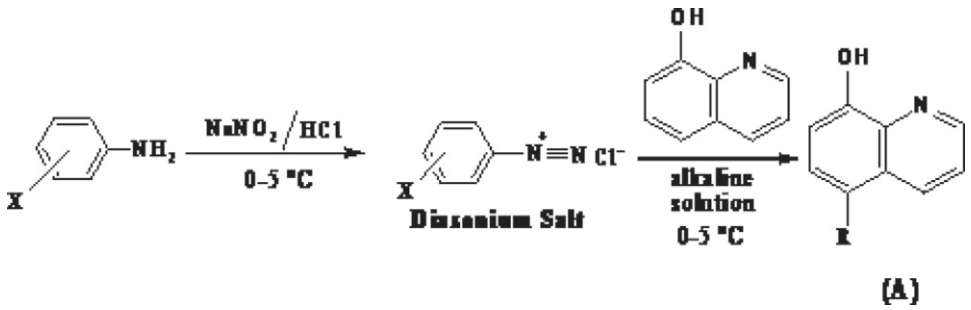
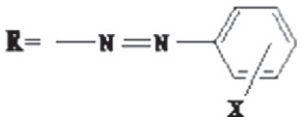



(A)

Where R =




| | |
|---|---|
| $HL_I$ | X = H |
| $HL_{II}$ | X = *o*-Cl |
| $HL_{III}$ | X = *o*-$CH_3$ and *p*-$OCH_3$ |
| $HL_{IV}$ | X = *m*-$NO_2$ and *p*-$CH_3$ |
| $HL_V$ | X = o-$OCH_3$ and *p*-$NO_2$ |
| $HL_{VI}$ | X = *o*-$NO_2$ and *p*-$OCH_3$ |

**Scheme 1.** Synthesis of azo 8-hydroxyquinoline dyes $HL_I$–$HL_{VI}$.

The ligands were characterized by elemental analysis (Table 1) and IR spectroscopy.

### 2.2. Potentiometric studies

The ligand solution (0.001 M) was prepared by dissolving an accurately weighted amount of the solid in DMF. Metal ion solutions (0.001 M) were prepared from metal chlorides in doubly distilled water and standardized with EDTA [16]. Solutions of 0.001 M HCl and 1 M KCl were also prepared in doubly distilled water. A carbonate-free NaOH solution in 40% (by volume) EtOH–water mixture was used as titrant and standardized against oxalic acid.

The apparatus, general conditions and methods of calculations were the same as in previous works [17,18]. The following mixtures (i)–(iii) were prepared and titrated potentiometrically at 298 K against standard 0.004 M NaOH in a 40% (by volume) DMF–water mixture:

(i) 5 ml 0.001 M HC1 + 5 ml 1.0 M KC1 + 20 ml EtOH
(ii) 5 ml 0.001 M HC1 + 5 ml 1.0 M KC1 + 15 ml EtOH + 5 ml 0.001 M ligand

**Table 1**
Analytical data of quinoline azodyes[a].

| Compound[b] | Empirical formula | M.p.(°C) | Formula weight (g/mol) | Calc. (exp.) % | | |
|---|---|---|---|---|---|---|
| | | | | C | H | N |
| $HL_I$ | $C_{15}H_{11}N_3O$ | 267 | 249.27 | 72.30 (72.20) | 4.50 (4.40) | 16.90 (16.60) |
| $HL_{II}$ | $C_{15}H_{10}ClN_3O$ | 273 | 283.05 | 63.50 (63.40) | 3.60 (3.40) | 14.80 (14.70) |
| $HL_{III}$ | $C_{17}H_{15}N_3O_2$ | 276 | 293.12 | 69.61 (69.53) | 5.15 (5.05) | 14.33 (14.20) |
| $HL_{IV}$ | $C_{16}H_{12}N_4O_4$ | 287 | 324.29 | 59.26 (59.15) | 3.73 (3.64) | 17.28 (17.15) |
| $HL_V$ | $C_{16}H_{12}N_4O_3$ | 281 | 308.29 | 62.33 (63.19) | 3.92 (3.80) | 18.17 (18.15) |
| $HL_{VI}$ | $C_{16}H_{12}N_4O_3$ | 279 | 308.29 | 62.33 (63.15) | 3.92 (3.82) | 18.17 (18.07) |

[a] Further studies with title ligands, using different metals, are in progress and will be published in due coarse.
[b] The analytical data agrees satisfactory with the expected formulae represented as given in Scheme 1 (see experimental). $HL_I$–$HL_{VII}$ are the ligand as given in Scheme 1. Air-stable, high melting temperature, colored, insoluble in water, but soluble in hot ethanol, and coordinate solvent. Decomposition near 275 °C.

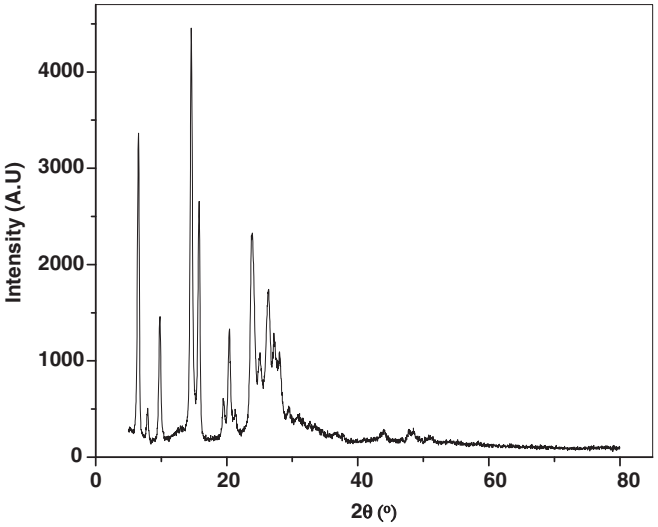



**Fig. 1.** X-ray diffraction pattern of $HL_I$ powder form.