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



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#### ARTICLE INFO

# ABSTRACT

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Keywords: Quinoline azodyes Potentiometry Stability constants Thermodynamics parameters Quantum chemical parameters A series of ligands of quinoline azodye derivatives (H<sub>L</sub>–HL<sub>VI</sub>) have been prepared and characterized by elemental analysis, X-ray diffraction analysis, <sup>1</sup>H NMR and IR spectra. The proton–ligand dissociation constant of the ligands (H<sub>L</sub>–HL<sub>VI</sub>) and the metal stability constant of their Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, La<sup>3+</sup>, UO<sub>2</sub><sup>2+</sup> and Th<sup>4+</sup> 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<sup>2+</sup> Co<sup>2+</sup> Ni<sup>2+</sup> Cu<sup>2+</sup> La<sup>3+</sup> UO<sub>2</sub><sup>2+</sup> Th<sup>4+</sup>. The effect of temperature was studied and the corresponding thermodynamic parameters ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ) 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.

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#### 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<sup>+2</sup> < Co<sup>+2</sup> < Ni<sup>2+</sup> < Cu<sup>2+</sup>. The corresponding thermodynamic parameters ( $\Delta G$ ,  $\Delta H$ ,  $\Delta S$ ) were also derived. The stoichiometrically 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<sub>1</sub>-HL<sub>VI</sub>) 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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HLI	X = H
HL <sub>II</sub>	X = o-Cl
HL <sub>III</sub>	X = o-CH <sub>3</sub> and $p$ -OCH <sub>3</sub>
HL <sub>IV</sub>	X = m-NO <sub>2</sub> and $p$ -CH <sub>3</sub>
$HL_V$	$X = o-OCH_3$ and $p-NO_2$
HL <sub>VI</sub>	$X = o-NO_2$ and $p-OCH_3$
HL <sub>VI</sub>	$X = o-NO_2$ and $p-OCH_3$



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

Table 1		
Analytical data of	auinoline	azodves <sup>a</sup> .

Compound <sup>b</sup>	Empirical	M.p.(°C)	Formula	Calc. (ex	Calc. (exp.) %		
	formula	ula weight (g/mol)		С	Н	Ν	
HL	$C_{15}H_{11}N_3O$	267	249.27	72.30 (72.20)	4.50 (4.40)	16.90 (16.60)	
HLII	$C_{15}H_{10}CIN_{3}O$	273	283.05	63.50 (63.40)	3.60 (3.40)	14.80 (14.70)	
HLIII	$C_{17}H_{15}N_3O_2$	276	293.12	69.61 (69.53)	5.15 (5.05)	14.33 (14.20)	
HL <sub>IV</sub>	$C_{16}H_{12}N_4O_4$	287	324.29	59.26 (59.15)	3.73 (3.64)	17.28 (17.15)	
$\mathrm{HL}_{\mathrm{V}}$	$C_{16}H_{12}N_4O_3$	281	308.29	62.33 (63.19)	3.92 (3.80)	18.17 (18.15)	
HL <sub>VI</sub>	$C_{16}H_{12}N_4O_3$	279	308.29	62.33 (63.15)	3.92 (3.82)	18.17 (18.07)	

<sup>a</sup> Further studies with title ligands, using different metals, are in progress and will be published in due coarse.

<sup>b</sup> The analytical data agrees satisfactory with the expected formulae represented as

given in Scheme 1 (see experimental).  $H_{I}$ – $H_{VII}$  are the ligand as given in Scheme 1. Airstable, high melting temperature, colored, insoluble in water, but soluble in hot ethanol, and coordinate solvent. Decomposition near 275 °C.

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



Fig. 1. X-ray diffraction pattern of HL<sub>1</sub> powder form.



Fig. 2. The optimized structures of ligands (HL<sub>I</sub> and HL<sub>II</sub>) within numbering of atoms.

# (iii) 5 ml 0.001 M HC1 + 5 ml 1.0 M KC1 + 15 ml EtOH + 5 ml 0.001 M ligand + 1 ml 0.001 M metal chloride

For each mixture, the volume was made up to 50 ml with doubly distilled water before titration. These titrations were repeated at temperatures 308 and 318 K. A constant temperature was maintained at  $\pm 0.05$  K by using an ultra-thermostat (Neslab 2 RTE 220). The pH-meter readings in 40% (v/v) EtOH–water mixture were corrected according to the Van Uitert and Hass relation [19].

2.3. Measurements

All the compounds and solvents used were purchased from Aldrich and Sigma and were used as received without further purification. The IR spectra were recorded as KBr discs using a Perkin-Elmer 1340 spectrophotometer. The <sup>1</sup>H-NMR spectra was performed using a JEOL FX90 Fourier transform spectrometer with DMSO-d<sup>6</sup> as the solvent and TMS as an internal reference. X-ray diffraction analysis of the ligand (HL) powder form was recorded on X-ray diffractometer in the range of diffraction angle  $2\theta^{\circ} = 4-70^{\circ}$ . This analysis was carried out using Cu

Table 2					
Calculated of	quantum chemical	parameters	for HL	and HL <sub>II</sub>	ligands

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Compound	$E_{HOMO}\left( eV ight)$	$E_{LUMO}$ (eV)	$\Delta E (eV)$	X (eV)	η (eV)	$\sigma (eV)^{-1}$	Pi (eV)	$S (eV)^{-1}$	ω (eV)	$\Delta N_{\text{max}}$
HL	-5.021	-2.030	2.991	3.525	1.495	0.669	- 3.525	0.334	4.156	2.358
HLII	-4.643	-1.136	3.507	2.889	1.754	0.570	-2.889	0.285	2.381	1.648

Selected geometrical parameters for ligand (HL<sub>I</sub>).

Bond lengths (	۲Å)	Bond angles (°)		Bond angles (°)	
C(10) U(20)	1 1 0 0		120.021		124.000
C(18) - H(30) C(17) H(20)	1.103	H(29)-C(17)-C(18) H(20)-C(17)-C(16)	120.031	U(12)-U(3)-U(4) V(10) C(2) C(2)	134.668
C(17) = H(23)	1.103	C(18) = C(17) = C(16)	120 325	N(10) - C(2) - C(3) N(10) - C(2) - C(1)	130 758
C(15) - H(27)	1 103	H(28) - C(16) - C(17)	120.323	C(3) - C(2) - C(1)	127 655
C(14) - H(26)	1.105	H(28) - C(16) - C(15)	120.291	C(2)-C(1)-C(6)	114.414
C(9) - H(25)	1.102	C(17)-C(16)-C(15)	119.388	C(2)-C(1)-C(7)	110.416
C(8)-H(24)	1.103	H(27)-C(15)-C(16)	119.897	C(6)-C(1)-C(7)	135.144
C(7)-H(23)	1.099	H(27)-C(15)-C(14)	120.117		
C(5)-H(22)	1.106	C(16)-C(15)-C(14)	119.985		
C(4)-H(21)	1.101	H(30)-C(18)-C(13)	121.88		
C(13)-C(18)	1.348	H(30)-C(18)-C(17)	117.031		
C(17)-C(18)	1.343	C(13)-C(18)-C(17)	121.088		
C(16) - C(17)	1.341	H(26)-C(14)-C(15)	118.158		
C(15) - C(16)	1.341	H(26)-C(14)-C(13)	120.362		
C(14) - C(15)	1.342	C(15)-C(14)-C(13)	121.48		
U(13) - U(14)	1.348	C(18) - C(13) - C(14)	117./34		
N(10) - C(2)	1,230	C(16) - C(13) - N(19) C(14) - C(13) - N(19)	125,610		
C(3) - C(2)	1 3 3 2	C(13) = N(19) = N(11)	110.45		
C(6) - C(1)	1 355	N(10) - H(20) - O(12)	147 701		
C(7) - C(1)	1.35	H(10) H(20) O(12) H(25)-C(9)-C(8)	122.571		
C(8) - C(7)	1.354	H(25)-C(9)-N(10)	119.611		
C(9) - C(8)	1.35	C(8)-C(9)-N(10)	117.721		
N(10)-C(9)	1.262	H(24)-C(8)-C(7)	119.654		
H(20)-N(10)	1.035	H(24)-C(8)-C(9)	119.052		
O(12)-H(20)	1.003	C(7)-C(8)-C(9)	121.272		
C(3)-O(12)	1.238	N(19)-N(11)-C(6)	121.4		
C(4) - C(3)	1.335	H(23)-C(7)-C(1)	122.839		
C(5) - C(4)	1.35	H(23)-C(7)-C(8)	116.753		
C(6) - C(5)	1.361	C(1)-C(7)-C(8)	120.015		
C(13) - N(19)	1.269	C(1) - C(6) - C(5)	118.296		
N(11) - N(19)	1.249	C(I) - C(b) - N(II)	128.234		
C(0) = N(11)	1.27	U(3) - U(0) - N(11) U(32) - C(5) - C(4)	115,431		
		H(22) = C(5) = C(4) H(22) = C(5) = C(6)	110.002		
		C(4) = C(5) = C(6)	125 001		
		H(20)=O(12)=C(3)	90.02		
		H(21)-C(4)-C(3)	121.286		
		H(21)-C(4)-C(5)	122.441		
		C(3)-C(4)-C(5)	116.261		
		C(2)-N(10)-C(9)	118.015		
		C(2)-N(10)-H(20)	92.722		
		C(9)-N(10)-H(20)	139.312		
		C(2)-C(3)-O(12)	107.584		
		C(2)-C(3)-C(4)	117.659		

 $K_{\alpha}$  radiation ( $\lambda = 1.541874$  Å). The applied voltage and the tube current are 40 kV and 30 mA, respectively.

The calculations of geometry optimization were performed using Perkin Elmer ChemBio 3D software by HF method with 3-21G basis set [20]. Geometry optimization option was employed to obtain the most stable structure.

The pH measurements were carried out using VWR Scientific Instruments Model 8000 pH-meter accurate to  $\pm 0.01$  units. The pH-meter readings in the non–aqueous medium were corrected [21]. The electrode system was calibrated according to the method of Irving et al. [22]. Titrations were performed in a double walled glass cell in an inert atmosphere (nitrogen) at ionic strength of 0.1 M KCl. Potentiometric measurements were carried out at different temperatures. The temperatures were controlled to within  $\pm 0.05$  K by circulating thermostated water (Neslab 2 RTE 220) through the outer jacket of the vessel.

#### 3. Results and discussion

#### 3.1. Structural determination of the ligands

The <sup>1</sup>H NMR spectra of the ligands showed a signal in the region 9.3–9.7 ppm assigned to  $C_8$ –OH of the hydroxy quinoline ring. This

value favors the formation of an intramolecular hydrogen bond between  $C_8$ –OH and the N in quinoline moiety. Electron-withdrawing substituents reduce considerably the intramolecular hydrogen bond as indicated by the marked shift of the hydroxyl signal to a higher field in the NO<sub>2</sub> compound. Electron-donating substituents give the opposite effect, arising from the increasing basicity of the azo-nitrogen.

It is known that 8-hydroxyquinoline exists in solution in a monomer–dimer equilibrium [23]. In the monomeric form, intramolecular H-bond is present whereas the strong 950 cm<sup>-1</sup> band indicates the existence of this ligand in a dimeric structure through intermolecular hydrogen bonding. This is in agreement with previous results [24]. The 2800–3550 cm<sup>-1</sup> region is characteristic for the vibrational frequency of the –OH group. The bands in the 3400–3500 cm<sup>-1</sup> region are assigned to intramolecular hydrogen bonding. Thus, HL<sub>n</sub> ligands can exist as a five-membered chelate skeleton with hydrogen bonding classified into two types:

- (a) An intramolecular hydrogen bond (O–H.....N) formed between hydrogen of (C<sub>8</sub>–OH) and nitrogen of quinoline ring.
- (b) An intermolecular hydrogen bonding (O–H....O) formed between the two C<sub>8</sub>–OH groups of two different hydroxyl–quinoline groups or OH of one ring and quinoline N of the other.

The band within the 1100 cm<sup>-1</sup> could be due to vC–OH [26]. The high frequency value of the  $\delta$ OH may account for the existence of hydrogen bonding.

IR spectra exhibited also a medium to strong band in the region 1540–1570 cm<sup>-1</sup> range assigned to  $\upsilon N = N$  stretching vibrations [8,9,25] and a very strong band at 1585  $\pm$  10 cm<sup>-1</sup> assignable to  $\upsilon C = C$  of the phenyl ring.

Analytical data (Table 1) are in agreement with the proposed formulae.

# 3.2. X-ray diffraction analysis

Single crystals of the ligands could not be prepared, hence powder diffraction data were used for structural characterization. Structural determination by X-ray powder diffraction data has gone through a recent surge so as to become important to get to the structural information of materials that do not yield good quality single crystals.

The X-ray diffraction (XRD) patterns of HL<sub>I</sub> ligand in the powder form is shown in Fig. 1. The XRD pattern shows many diffraction peaks indicating a polycrystalline phase for this ligand. The average crystallite size ( $\xi$ ) can be calculated from the XRD patterns according to Debye–Scherrer equation:

$$\xi = \frac{K\lambda}{\beta_{1/2}\cos\theta}.$$

The equation uses the reference peak width at angle ( $\theta$ ), where  $\lambda$  is wavelength of X-ray radiation (1.540598 Å), K is constant taken as 0.95 for organic compounds [16] and  $\beta_{1/2}$  is the width at half maximum of the reference diffraction peak measured in radians. The dislocation density ( $\delta$ ) is the number of dislocation lines per unit area of the crystal. The value of  $\delta$  is related to the average particle diameter ( $\xi$ ) by the relation [27]:

 $\delta = \frac{1}{\xi^2}.$ 

The values of  $\xi$  and  $\delta$  for HL<sub>1</sub> ligand were calculated and found to be 24.3 nm and  $1.69\times10^{-3}$  nm<sup>-2</sup>, respectively.



Fig. 3. HOMO and LUMO molecular orbital of ligands (HL<sub>I</sub> and HL<sub>II</sub>).

#### 3.3. Geometrical structures

The optimized structures of the ligands (HLI and HLII) are presented in Fig. 2. Selected geometric parameter bond lengths and bond angles of ligands (HL<sub>I</sub> and HL<sub>II</sub>) are tabulated in Tables 2 and 3. Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the main orbitals that take part in chemical stability. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. Molecular orbital structures (HOMO & LUMO) for ligands (HL<sub>I</sub> and  $HL_{II}$ ) are presented in Fig. 3. Electronic absorption corresponds to the transition from the ground state to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. Recently, the energy gap between HOMO and LUMO has been used to prove the activity and stability of the compounds [18]. Quantum chemical parameters of the ligands (HL<sub>I</sub> and HL<sub>II</sub>) were obtained from calculations including the energies of the highest occupied molecular orbital ( $E_{HOMO}$ ) and the lowest unoccupied molecular orbital  $(E_{IIIMO})$  as listed in Table 4. Additional parameters such as HOMO–LUMO energy gap,  $\Delta E^*$ , absolute electronegativities,  $\chi$ , chemical potentials, Pi, absolute hardness,  $\eta$ , absolute softness,  $\sigma$ , global electrophilicity,  $\omega$ , global softness, *S*, and additional electronic charge,  $\Delta N_{\text{max}}$ , were calculated using the following equations [17,28]:

$$\Delta E = E_{LUMO} - E_{HOMO} \tag{1}$$

$$\chi = \frac{-(E_{HOMO} + E_{LUMO})}{2} \tag{2}$$

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} \tag{3}$$

$$\sigma = \frac{1}{\eta} \tag{4}$$

$$Pi = -\chi \tag{5}$$

$$S = \frac{1}{2\eta} \tag{6}$$

$$\omega = \frac{P i^2}{2\eta} \tag{7}$$

$$\Delta N_{\rm max} = -\frac{Pi}{\eta}.\tag{8}$$

The value of  $\Delta E$  for HL<sub>1</sub> and HL<sub>11</sub> ligands was found to be 2.991 and 3.507 eV, respectively. The calculations indicated that the HL<sub>1</sub> ligand is more stable and highly reactive than HL<sub>11</sub> ligand.

#### 3.4. Potentiometric studies

#### 3.4.1. Proton–ligand stability constants

The average number of the protons associated with ligands ( $HL_I$ – $HL_{VI}$ ) at different pH values,  $\overline{n}_A$ , was calculated from the titration curves of the acid in the absence and presence of ligands ( $HL_I$ – $HL_{VI}$ ) by applying the following equation:

$$\bar{n}_A = Y \pm \frac{(V_1 - V_2)(N^o + E^o)}{(V^o - V_1)TC_L^o}$$
(9)

where Y is the number of available protons in ligands (Y = 1) and V<sub>1</sub> and V<sub>2</sub> are the volumes of alkali required to reach the same pH on the titration curve of hydrochloric acid and reagent, respectively, V° is the initial volume (50 cm<sup>3</sup>) of the mixture, TC°<sub>L</sub> is the total concentration of the reagent, N° is the normality of sodium hydroxide solution and E° is the initial concentration of the free acid. Thus, the formation curves ( $\bar{n}_A$  vs. pH) for the proton–ligand systems were constructed and found to extend between 0 and 1 in the  $\bar{n}_A$  scale. This means that each ligand has one ionizable proton (the enolized hydrogen ion of the hydroxyl group in the quinoline moiety). It can be seen that for the same volume of KOH added, the ligand titration curves had a lower pH value than the acid titration curve. The displacement of a ligand titration curve along the volume axis with

Table 4	ļ
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Selected geometrical parameters for ligand (HL  $_{\rm II}).$ 

Bond lengths (	(Å)	Bond angles (°)		Bond angles (°)	
C(17)-H(30)	1.104	H(30)-C(17)-C(18)	121.063	N(10)-C(2)-C(3)	115.818
C(16)-H(29)	1.103	H(30)-C(17)-C(16)	117.653	C(1)-C(2)-C(3)	121.274
C(15)-H(28)	1.103	C(18)-C(17)-C(16)	121.285	C(2)-C(1)-C(6)	120.679
C(14)-H(27)	1.106	H(29)-C(16)-C(17)	120.589	C(2)-C(1)-C(7)	116.597
C(9)-H(26)	1.103	H(29)-C(16)-C(15)	120.329	C(6)-C(1)-C(7)	122.724
C(8)-H(25)	1.102	C(17)-C(16)-C(15)	119.082		
C(7)-H(24)	1.1	H(28)-C(15)-C(16)	120.025		
C(5)-H(23)	1.103	H(28)-C(15)-C(14)	120.418		
C(4) - H(22)	1.103	C(16)-C(15)-C(14)	119.557		
C(13)-C(18)	1.354	C(13)-C(18)-C(17)	120.472		
C(17) - C(18)	1.346	C(13)-C(18)-Cl(21)	125.001		
C(16) - C(17)	1.34	C(17)-C(18)-Cl(21)	114.527		
C(15)-C(16)	1.338	H(27)-C(14)-C(15)	116.817		
C(14) - C(15)	1.341	H(27)-C(14)-C(13)	120.611		
C(13) - C(14)	1.352	C(15)-C(14)-C(13)	122.572		
C(9) - N(10)	1.263	C(18)-C(13)-C(14)	117.032		
C(2) - N(10)	1.269	C(18)-C(13)-N(19)	130.429		
C(1) - C(2)	1.352	C(14) - C(13) - N(19)	112.539		
C(3) - C(2)	1.347	C(13) - N(19) - N(11)	123.567		
C(4) - C(3)	1.341	H(26)-C(9)-N(10)	116.689		
C(5) - C(4)	1.34	H(26)-C(9)-C(8)	120.338		
C(6) - C(5)	1.349	N(10) - C(9) - C(8)	122.973		
C(1) - C(6)	1.355	H(25)-C(8)-C(7)	121.39		
C(7) - C(1)	1.349	H(25) - C(8) - C(9)	121.039		
C(8) - C(7)	1.34	U(7) - U(8) - U(9)	11/.5/1		
C(9) - C(8)	1.339	N(19) - N(11) - C(6)	120.172		
C(18) - C(21)	1./33	H(24) - C(7) - C(1)	122.951		
O(12) - H(20)	0.971	H(24) - C(7) - C(8)	117.036		
C(13) - N(19)	1.271	C(1) - C(7) - C(8)	120.013		
N(11) - N(19)	1.25	C(5) - C(6) - C(1)	122.255		
C(0) = N(11)	1.272	C(3) - C(0) - N(11)	123.233		
C(3) = O(12)	1.302	U(1) - U(0) - IN(11)	115.02		
		H(23) - C(5) - C(4)	110.82		
		H(23) - U(3) - U(6)	122.518		
		U(4) - U(5) - U(6)	121.002		
		H(20) = O(12) = C(3)	110.046		
		H(22) - C(4) - C(3) H(22) - C(4) - C(5)	119.040		
		$\Gamma(22) = C(4) = C(5)$	119.72		
		C(3) = C(4) = C(3) C(3) = N(10) = C(3)	121,234		
		C(3) = N(10) = C(2) C(2) = C(3) = C(4)	117.33/		
		C(2) = C(3) = C(4) C(2) = C(3) = O(12)	121 //24		
		C(2) = C(3) = O(12) C(4) = C(3) = O(12)	121,445		
		N(10) = C(2) = C(12)	120.751		
		11(10) - C(2) - C(1)	122,300		

respect to the acid titration curve is an indication of proton dissociation. The proton-ligand stability constants were calculated using the method of lrving and Rossotti [29]. The phenolic –OH group is known to be weakly acidic, indicating a stronger bonding between the proton and the oxygen atom. This means that the proton–ligand stability constant of quinoline azo dyes should be high due to the dissociation of the –OH group [30].

An inspection of the results in Table 5 reveals that the pK<sup>H</sup> values of HLI and its substituted derivatives are influenced by the inductive or mesomeric effect of the substituents [31]. The o-OCH<sub>3</sub> and o-CH<sub>3</sub> derivatives (HL<sub>III</sub> and HL<sub>V</sub>) have a lower acidic character (higher  $pK^{H}$  values) than the o-Cl and o-NO2 derivatives (HL<sub>II</sub> and HL<sub>VI</sub>). This is quite reasonable because the presence of o-OCH<sub>3</sub> and p-CH<sub>3</sub> groups (i.e. an electron donating group) will enhance the electron density by its high positive inductive or mesomeric effect, whereby a stronger O-H bond is formed. The presence of o-Cl and o-NO<sub>2</sub> groups (i.e. electron withdrawing groups) will lead to the opposite effect. The high acidic character found in the HL<sub>IV</sub> ligand (*m*-NO<sub>2</sub> and *p*-CH<sub>3</sub> groups) is due to the enhancement of the electron density by the high positive inductive or mesomeric effect, whereby a stronger O-H bond is formed. The ortho and para substituents in the quinoline moiety have a direct influence on the pK<sup>H</sup> values of the investigated compounds, revealing the coplanarity of the molecule and thus affording a maximum resonance via delocalization of its  $\pi$ -system.

#### 3.4.2. Metal-ligand stability constants

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ion ( $\overline{n}_A$ ) vs. the free ligand exponent (pL), according to Irving and Rossotti [32]. These curves were analyzed and the successive stability constants were determined using different computational methods [33,34] which agree within 1% error. The average number of the reagent molecules attached per metal ion,  $\overline{n}$ , and free ligand exponent, pL, can be calculated using Eqs. (10) and (11):

$$\overline{n} = \frac{(V_3 - V_2)(N^o + E^o)}{(V^o - V_2) \cdot \overline{n}_A \cdot TC_M^o}$$

$$\tag{10}$$

and

$$pL = log_{10} \frac{\sum_{n=0}^{n=J} \beta_n^H \left(\frac{1}{[H^+]}\right)^n}{TC_L^0 - \overline{n} \cdot TC_M^0} \cdot \frac{V^0 + V_3}{V^0}$$
(11)

where  $TC_M^{\circ}$  is the total concentration of the metal ion present in the solution, and  $\beta^H_n$  is the overall proton-reagent stability constant. V<sub>1</sub>, V<sub>2</sub> and V<sub>3</sub> are the volumes of alkali required to reach the same pH on the

Table 5

Thermodynamic function of azoquinoline in 40% (v/v) EtOH-water mixture and 1 M KCl at different temperatures.

Comp.	Temp. (K)	Dissociation constant pK <sup>H</sup>	Enthalpy change (kJ mol <sup>−1</sup> ) ΔG	Free energy change (kJ mol <sup>−1</sup> ) ∆H	Entropy change (J mol <sup><math>-1</math></sup> K <sup><math>-1</math></sup> ) $-\Delta$ S
HL	298	9.40	53.63	27.21	88.658
	308	9.25	54.55		88.766
	318	9.10	55.41		88.679
$HL_{II}$	298	8.30	47.36	27.19	67.684
	308	8.16	48.12		67.955
	318	8.00	48.71		67.673
HLIII	298	9.60	54.78	25.41	98.557
	308	9.45	55.73		98.442
	318	9.32	56.75		98.553
HLIV	298	9.80	55.92	26.29	99.430
	308	9.66	56.97		99.610
	318	9.51	57.90		99.403
HLv	298	9.70	55.27	27.21	94.161
	308	9.55	56.25		94.286
	318	9.40	57.16		94.182
HL <sub>VI</sub>	298	8.50	48.50	25.39	77.550
	308	8.36	49.30		77.630
	318	8.22	50.05		77.547



Fig. 4. The relation between stability constant (log  $\beta$ ) and atomic number of metal complexes for ligands a) HL\_I and b) HL\_I.

titration curves of hydrochloric acid, organic ligand and complex, respectively. The following general remarks may be pointed out:

- (i) The maximum value of n was  $\approx 2$  indicating the formation of 1:1 and 1:2 (metal:ligand) complexes only.
- (ii) The metal ion solution used in the present study was very dilute  $(2 \times 10^{-4} \text{ M})$ ; hence there was no possibility for the formation of polynuclear complexes [35].
- (iii) The metal titration curves were displaced to the right-hand side of the ligand titration curves along the volume axis, indicating proton release upon complex formation of the metal ion with the ligand. The large decrease in pH for the metal titration curves relative to ligand titration curves points to the formation of strong metal complexes [36].
- (iv) In most cases, the color of the solution after complex formation was observed to be different from the color of the ligand at the same pH.
- (v) For the same ligand at constant temperature, the stability of the chelates increases in the order  $Mn^{2+} Co^{2+} Ni^{2+} Cu^{2+} La^{3+} UO_2^{2+} Th^{4+} [14,37]$ . This order largely reflects the changes in the heat of complex formation across the series from a combination of the influence of both the polarizing ability of the metal



Fig. 5. The relation between stability constant (log  $\beta$ ) and atomic number of metal complexes for ligands a) HL\_{III} and b) HL\_{IV}.



Fig. 6. The relation between stability constant (log  $\beta$ ) and atomic number of metal complexes for a) HLv and b) HLvI.



Fig. 7. The relation between free energy change ( $\Delta G_{\beta}$ ) and atomic number of metal complexes for ligands a) HL and b) HL<sub>II</sub>.

ion [38] and the crystal field stabilization energies [39]. The greater stability of  $Cu^{2+}$  complexes is produced by the well-known Jahn–Teller effect.



Fig. 8. The relation between free energy change ( $\Delta G_{\beta}$ ) and atomic number of metal complexes for ligands a) HL<sub>III</sub> and b) HL<sub>IV</sub>.



Fig. 9. The relation between free energy change ( $\Delta G_{\beta}$ ) and atomic number of metal complexes for ligands a) HL<sub>v</sub> and b) HL<sub>vl</sub>.

An inspection of the results reveals that the stability constant values of the complexes of  $HL_{IV}$ ,  $HL_{V}$  and  $HL_{VI}$  are influenced by the inductive or mesomeric effect of the substituents. This behavior correlates with the effect of substitution on the phenyl ring as follows:

- (i) The high stability of HL<sub>v</sub> complexes can be attributed to the presence of the *p*-CH<sub>3</sub> group relative to the azo group. This is quite reasonable because of the presence *p*-CH<sub>3</sub> group (i.e. an electron donating effect), whereby stronger chelation was formed and therefore the stability of the complexes.
- (ii) The stability of HL<sub>V</sub> complexes can be attributed to the presence of the *p*-NO<sub>2</sub> and *o*-OCH<sub>3</sub> groups relative to the azo group.
- (iii) The low stability of  $HL_{VI}$  complexes can be attributed to the presence of the NO<sub>2</sub> group in the o-position relative to the azo group. This is caused by the negative indicative effect of the NO<sub>2</sub> group, which decreases its ability for chelation, and therefore the stability of the complexes.
- (iv) For the ligands with the same metal ion at constant temperature, the stability of the chelates increases in the order  $H_L > H_{L_{II}} > H_{L_{III}}$  [36].
- (v) The stability constants of  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$  and  $Cu^{2+}$  complexes were increased with increasing atomic number in the order  $Cu^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$  at constant temperature as shown in Figs. 4–6.

#### 3.4.3. Effect of temperature

The dissociation constant (pK<sup>H</sup>) for azoquinoline and its substituted derivatives, as well as the stability constants of their complexes with  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $La^{3+}$ ,  $UO_2^{2+}$  and  $Th^{4+}$  have been evaluated at 298, 308 and 318 K. The enthalpy ( $\Delta$ H) for the dissociation and complexation process was calculated from the slope of the plot pK<sup>H</sup> or log K vs.  $^{1}/_{T}$  using the graphical representation of Van't Hoff Eqs. (12) and (13):

$$\Delta G = -2.303 RT \log K = \Delta H - T\Delta S \tag{12}$$

or

$$\log K = \left(\frac{-\Delta H}{2.303R}\right) \left(\frac{1}{T}\right) + \frac{\Delta S}{2.303R}$$
(13)

where R is the gas constant  $= 8.314 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$ , K is the dissociation constant for the ligand stability and T is the temperature (K).

From the values of free energy change ( $\Delta G$ ) and enthalpy change ( $\Delta H$ ), we can deduce the entropy ( $\Delta S$ ) using the well-known relationships (12) and (14):

$$\Delta S = (\Delta H - \Delta G)/T. \tag{14}$$

All thermodynamic parameters of the dissociation process of ligands  $(HL_I-HL_{VI})$  are recorded in Table 5. From these results the following conclusions can be made:

- (i) The pK<sup>H</sup> values decrease with increasing temperature, i.e., the acidity of the ligands increases, independent of the nature of the substituent [17,36].
- (ii) A positive value of  $\Delta H$  indicates that the process is endothermic.
- (iii) A large positive value of △G indicates that the dissociation process is not spontaneous.
- (iv) The dissociation processes for the compounds have negative values of  $\Delta S$  due to the increased order as a result of the solvation processes.

It is known that the divalent metal ions exist in solution as octahedral hydrated species and the obtained values of  $\Delta H$  and  $\Delta S$  can then be considered as the sum of two contributions: (a) release of H<sub>2</sub>O molecules and (b) metal-ligand bond formation. Examination of these values shows that:

- (i) The stepwise stability constant (log K<sub>1</sub> and log K<sub>2</sub>) for ligand complexes increases with increasing temperature, i.e., its stability constants increase with increasing the temperature.
- (ii) The negative value of  $\Delta G$  for the complexation process suggests the spontaneous nature of such process.
- (iii) The values of free energy change of formed complexes were increased with increasing atomic number as shown in Figs. 7–9.
- (iv) The  $\Delta$ H values are positive, meaning that these processes are endothermic and favorable at higher temperature,
- (v) The  $\Delta S$  values for the ligand complexes are positive, confirming that the complex formation is entropically favorable.

### 4. Conclusion

The proton–ligand dissociation constant of quinoline azo-dye derivatives (HL<sub>I</sub>–HL<sub>VI</sub>) and metal–ligand stability constants of their complexes with metal ions (Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, La<sup>3+</sup>, UO<sub>2</sub><sup>2+</sup> and Th<sup>4+</sup>) at different temperatures were determined. At constant temperature the stability constants of the formed complexes decreases in the order Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup> and Mn<sup>2+</sup>. The dissociation process is nonspontaneous, endothermic and entropically unfavorable. The formation of the metal complexes has been found to be spontaneous, endothermic and entropically favorable. The values of stability constants of quinoline azodye derivatives (HL<sub>I</sub>–HL<sub>VI</sub>) complexes increase with increasing temperature.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.molliq.2015.05.059.

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