Stereochemistry of New Nitrogen-Containing Heterocyclic Compounds
XIV. Potentiometric and Thermodynamic Studies of 5-(Phenylazo)-8-hydroxyquinolines and their Metal Complexes

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A series of 5-(phenylazo)-8-hydroxyquinolines (HL_1—HL_6) have been prepared and characterized by elemental analysis and IR spectra. Proton-ligand dissociation constants of 5-(phenylazo)-8-hydroxyquinoline derivatives and metal—ligand stability constants of their complexes with metal ions (La^{3+}, Ce^{3+}, Pr^{3+}, Zr^{4+}, Hf^{4+}, and Th^{4+}) have been determined potentiometrically in 0.1 M-KCl and 40 vol. % CH_3OH—water mixture. The influence of substituents on the dissociation and stability constants was examined on the basis of the electron-repelling property of the substituent. The stability constants of the formed complexes increase in the order La^{3+}, Ce^{3+}, Pr^{3+}, Zr^{4+}, Hf^{4+}, Th^{4+}. The effect of temperature was studied and the corresponding thermodynamic parameters (ΔG, ΔH, and ΔS) were derived and discussed.

The chemistry of 8-hydroxyquinoline and its derivatives has attracted special interest due to their therapeutic properties [1] and the fact that they are well-known bidentate ligands. Quinoline sulfonamides have been used in treatment of cancer, turberculosis, and malaria [2]. Azo compounds based on 8-hydroxyquinoline play a central role as chelating agents for a large number of metal ions, as they form a stable six-membered ring after complexation with the metal ion, and can also be used as analytical reagents [3, 4].

In continuation of our earlier work [5—9], we report herein the synthesis of 5-(phenylazo)-8-hydroxyquinolines (Table 1 and Scheme 1).

The following intramolecular and intermolecular association through hydrogen bonds processes could be assumed to exist in 5-(X-phenylazo)-8-hydroxyquinoline derivatives (Scheme 1).

The stability constants of La^{3+}, Ce^{3+}, Pr^{3+}, Zr^{4+}, Hf^{4+}, and Th^{4+} complexes with 5-(phenylazo)-8-hydroxyquinolines were studied at different temperatures. Ionization potential and substituent effects on the dissociation and stability constants are also investigated. Furthermore, the corresponding thermodynamic functions of complexation are evaluated and discussed.

The average number of protons associated with the ligands at different pH values, $\bar{n}_A$, was calculated from the titration curves of the acid in the absence and presence of a ligand. 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 ligands HL_1, HL_2, HL_3, and HL_6 have one ionizable proton (the enolized hydrogen ion of the hydroxyl group in the 8-hydroxyquinoline moiety, pK_1^H). But the ligands HL_4 and HL_5 have two ionizable protons (the enolized hydrogen ion of the hydroxyl group in the 8-hydroxyquinoline moiety, pK_1^H and in the sulfonic (HL_4) or carboxylic groups (HL_5), pK_2^H). It can be seen that for the same volume of NaOH 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 respect to the acid titration curve is an indication of proton dissociation. The proton-ligand stability constants were calculated using the method of *Irving* and *Rossotti* [10].

The phenolic —OH group is known to be weakly acidic, indicating a stronger bonding between the proton and the oxygen donor. This means that the proton-ligand stability constant of 5-(phenylazo)-8-hydroxyquinolines should be high due to the dissociation of the —OH group [11].

An inspection of the results in Table 2 reveals that the pK_1^H values of HL_3 and its substituted derivatives are influenced by the inductive or mesomeric effect of the substituents. The *p*-OCH_3 and *p*-CH_3 derivatives (HL_1 and HL_2) have a lower acidic character (higher

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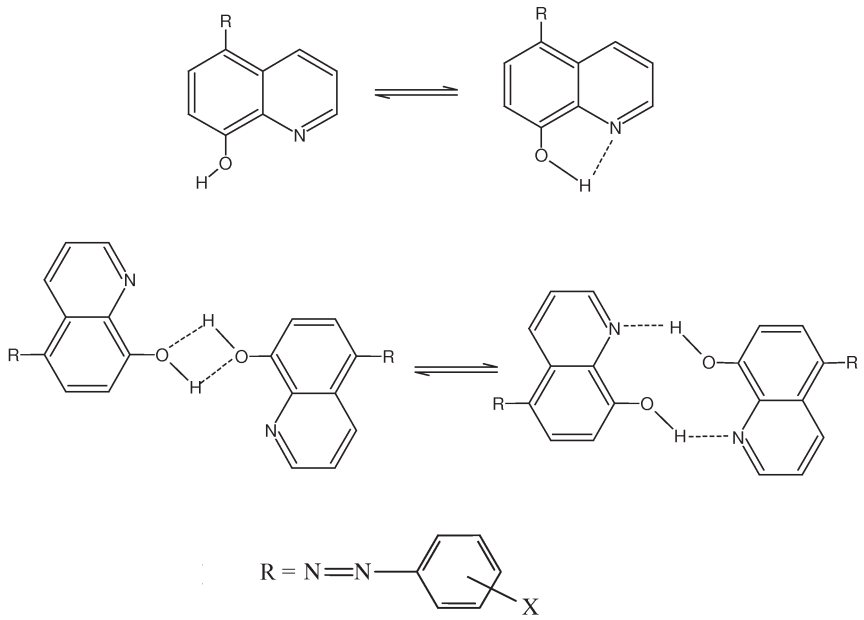

X = *p*-OCH_3 (HL_1), *p*-CH_3 (HL_2), H (HL_3), *p*-SO_3H (HL_4), *o*-COOH (HL_5), *p*-NO_2 (HL_6)

Scheme 1. General formula of the 5-(X-phenylazo)-8-hydroxyquinoline (HL_n).

Table 1. Analytical Data of 5-(Phenylazo)-8-hydroxyquinolines (HL_n)

Compound	Formula	M_r	w_i(calc.)/% w_i(found)/%			M.p.
			C	H	N	°C
HL_1	$C_{16}H_{13}N_3O_2$	279.28	68.81 68.62	4.69 4.59	15.05 14.95	202
HL_2	$C_{16}H_{13}N_3O$	263.28	72.99 72.85	4.98 4.94	15.96 15.80	212
HL_3	$C_{15}H_{11}N_3O$	249.26	72.27 71.99	4.45 4.50	16.86 16.82	210
HL_4	$C_{16}H_{11}N_3O_3$	293.27	65.52 65.28	3.78 3.55	14.33 13.98	160
HL_5	$C_{15}H_{11}N_3O_4S$	329.32	54.70 53.65	3.37 3.26	12.76 12.40	190
HL_6	$C_{15}H_{10}N_4O_3$	294.26	61.22 61.70	3.43 3.50	19.04 18.85	220

pK^H values) than the *p*-SO_3H, *o*-COOH, and *p*-NO_2 derivatives (HL_4, HL_5, and HL_6). This is quite reasonable because the presence of *p*-OCH_3 and *p*-CH_3 groups (*i.e.* an electron-donating effect) will enhance the electron density by their high positive inductive or mesomeric effect, whereby a stronger O—H bond is formed. The presence of *p*-SO_3H, *o*-COOH, and *p*-NO_2 groups (*i.e.* an electron-withdrawing effect) will lead to the opposite effect.

The results are also in accordance with Hammett's *para*-substituent constant values σ^X [12]. Straight lines are obtained on plotting pK_1^H values at different temperatures *vs.* σ^X (Fig. 1). The *para*-substituents in the 8-hydroxyquinoline moiety have a direct influence on the pK_1^H values of the investigated compounds, revealing the coplanarity of the molecule and thus affording a maximum resonance *via* delocalization of its π-system.

The formation curves for the metal complexes were obtained by plotting the average number of ligands

Table 2. Thermodynamic Functions for the Dissociation of 5-(Phenylazo)-8-hydroxyquinolines in 40 vol. % CH_3OH—Water Mixture and 0.1 M-KCl at Different Temperatures

Compound	T	Dissociation constant		ΔG_1	ΔG_2	ΔH_1	ΔH_2	$-\Delta S_1$	$-\Delta S_2$
	K	pK_1^H	pK_2^H	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}	J mol^{-1} K^{-1}
HL_1	298	9.98		56.9		33.6		78.4	
	308	9.79		57.7				74.2	
	318	9.61		58.5				72.1	
HL_2	298	9.85		56.2		35.4		69.8	
	308	9.65		56.9				69.9	
	318	9.46		57.6				69.8	
HL_3	298	9.65		55.1		39.0		53.8	
	308	9.43		55.6				53.9	
	318	9.22		56.1				53.8	
HL_4	298	9.30	5.25	53.1	30.0	39.9	24.5	44.1	18.3
	308	9.07	5.11	53.5	30.1			44.0	18.3
	318	8.86	4.98	54.0	30.3			44.1	18.3
HL_5	298	9.10	5.61	51.9	32.0	39.0	27.2	43.3	16.1
	308	8.89	5.46	52.4	32.2			43.5	16.2
	318	8.67	5.31	52.8	32.3			43.3	16.1
HL_6	298	8.59		49.0		38.1		36.6	
	308	8.37		49.4				36.5	
	318	8.17		49.8				36.6	

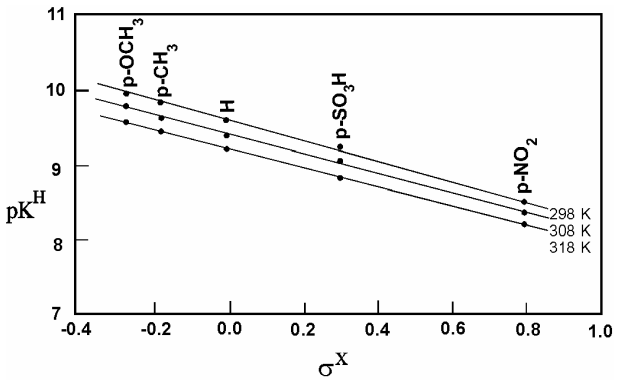

Fig. 1. Correlation of pK_1^H with the Hammett's constant σ^X at 298 K, 308 K, and 318 K.

attached per metal ions ($\bar{n}$) *vs.* the free ligand exponent (pL), according to *Irving* and *Rossotti* [13]. These curves were analyzed and the successive stability constants were determined using different computational methods [14, 15] which agree within 1 % error. Accordingly the average values are presented in Table 3. The following general remarks can be pointed out:

i) The maximum value of $\bar{n}$ was ≈ 2, indicating the formation of 1 : 1 and 1 : 2 (n(metal) : n(ligand)) complexes only.

ii) The metal ion solution used in the present study was very dilute (1×10^{-5} mol dm^{-3}), hence there was no possibility of formation of polynuclear complexes [16].

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 [17].

iv) In most cases, the colour of the solution after complex formation was observed to be different from the colour of the ligand at the same pH.

v) For the same ligand at constant temperature, the stability of the chelates increases in the order La^{3+}, Ce^{3+}, Pr^{3+}, Zr^{4+}, Hf^{4+}, Th^{4+} [8, 18]. 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 ion [19, 20] and the crystal-field stabilization energies [21].

An inspection of the results in Table 3 reveals that the stability constant values of the complexes of HL_3 and their substituted derivatives are influenced by the inductive or mesomeric effect of the substituents. This behaviour correlates with the effect of substitution on the phenyl ring as follows:

i) The high stability of HL_1 and HL_2 complexes can be attributed to the presence of the —OCH_3 and —CH_3 groups in the *p*-position relative to the azo group, respectively. This is quite reasonable because the presence of *p*-OCH_3 and *p*-CH_3 groups (*i.e.* an electron-donating effect) will enhance the electron density by their high positive inductive or mesomeric

Table 3. Stepwise Stability Constants for the Complexation of 5-(Phenylazo)-8-hydroxyquinolines in 40 vol. % CH_3OH—Water Mixture and 0.1 M-KCl at Different Temperatures

Compound	M^{n+}	298 K		308 K		318 K	
		log K_1	log K_2	log K_1	log K_2	log K_1	log K_2
HL_1	La^{3+}	6.24	5.41	6.40	5.57	6.57	5.73
	Ce^{3+}	6.28	5.45	6.43	5.61	6.61	5.76
	Pr^{3+}	6.33	5.48	6.48	5.64	6.64	5.79
	Zr^{4+}	6.40	5.53	6.55	5.70	6.70	5.85
	Hf^{4+}	6.46	5.57	6.62	5.74	6.78	5.90
	Th^{4+}	6.50	5.61	6.68	5.79	6.85	5.96
HL_2	La^{3+}	6.14	5.20	6.30	5.36	6.47	5.51
	Ce^{3+}	6.19	5.24	6.34	5.41	6.51	5.57
	Pr^{3+}	6.24	5.28	6.40	5.44	6.56	5.61
	Zr^{4+}	6.30	5.33	6.45	5.50	6.60	5.66
	Hf^{4+}	6.36	5.38	6.53	5.55	6.69	5.71
	Th^{4+}	6.42	5.44	6.59	5.61	6.76	5.78
HL_3	La^{3+}	6.05	5.02	6.21	5.19	6.38	5.35
	Ce^{3+}	6.08	5.06	6.24	5.23	6.41	5.39
	Pr^{3+}	6.12	5.10	6.29	5.27	6.46	5.43
	Zr^{4+}	6.16	5.15	6.33	5.31	6.49	5.48
	Hf^{4+}	6.20	5.21	6.37	5.38	6.53	5.55
	Th^{4+}	6.23	5.27	6.41	5.44	6.58	5.60
HL_4	La^{3+}	5.95	4.84	6.11	5.00	6.26	5.16
	Ce^{3+}	5.98	4.87	6.14	5.03	6.28	5.19
	Pr^{3+}	6.02	4.91	6.18	5.07	6.33	5.22
	Zr^{4+}	6.06	4.96	6.22	5.12	6.37	5.28
	Hf^{4+}	6.10	5.01	6.27	5.18	6.43	5.34
	Th^{4+}	6.15	5.07	6.32	5.24	6.48	5.40
HL_5	La^{3+}	5.80	4.67	5.95	4.83	6.09	5.00
	Ce^{3+}	5.88	4.70	6.04	4.86	6.19	5.03
	Pr^{3+}	5.92	4.74	6.08	4.89	6.23	5.05
	Zr^{4+}	5.96	4.80	6.12	4.97	6.29	5.13
	Hf^{4+}	6.00	4.84	6.17	5.00	6.33	5.18
	Th^{4+}	6.05	4.90	6.23	5.07	6.40	5.25
HL_6	La^{3+}	5.62	4.48	5.79	4.64	5.95	4.80
	Ce^{3+}	5.66	4.52	5.83	4.67	5.99	4.83
	Pr^{3+}	5.70	4.55	5.86	4.71	6.02	4.87
	Zr^{4+}	5.75	4.60	5.92	4.77	6.09	4.93
	Hf^{4+}	5.79	4.65	5.95	4.82	6.12	4.99
	Th^{4+}	5.85	4.71	6.02	4.89	6.19	5.06

effect, whereby stronger chelation was formed and therefore the greater stability of the complexes.

ii) The low stability of HL_4, HL_5, and HL_6 complexes can be attributed to the presence of the *p*-SO_3H, *o*-COOH, and *p*-NO_2 groups in the *p*-position relative to the azo group, respectively. This is caused by the negative inductive effect of these groups which decreases their ability for chelation and therefore the stability of the complexes.

iii) For the ligands with the same metal ion at constant temperature, the stability of the chelates increases in the order HL_1, HL_2, HL_3, HL_4, HL_5, HL_6 [8].

The dissociation constants (pK^H) for 5-(phenylazo)-8-hydroxyquinoline and its substituted derivatives, as well as the stability constants of their complexes with La^{3+}, Ce^{3+}, Pr^{3+}, Zr^{4+}, Hf^{4+}, and Th^{4+} have been evaluated at 298, 308, and 318 K, and are given in Tables 2 and 4. The slope of the plot (pK^H or log K *vs.* $1/T$) was utilized to evaluate the enthalpy change (ΔH) for the dissociation or complexation process, respectively. From the free energy change ΔG and ΔH values one can deduce the entropy changes ΔS using the well-known relationships

$$\Delta G = -2.303RT \log K \qquad (1)$$

$$\Delta S = (\Delta H - \Delta G)/T \qquad (2)$$

All thermodynamic parameters of the dissociation process of HL_3 and its derivatives are recorded in Table 2. From these results the following conclusions can be drawn:

a) The pK^H values decrease with increasing tem-

Table 4. Thermodynamic Functions for the Complexation of 5-(Phenylazo)-8-hydroxyquinolines in 40 vol. % CH_3OH—Water Mixture at 298 K

Compound	M^{n+}	$-\Delta G_1$	$-\Delta G_2$	ΔH_1	ΔH_2	ΔS_1	ΔS_2
		kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}	J mol^{-1} K^{-1}
HL_1	La^{3+}	35.6	30.9	30.0	29.0	220.0	201.0
	Ce^{3+}	35.8	31.1	30.0	28.1	220.7	198.8
	Pr^{3+}	36.1	31.3	28.1	28.1	215.6	199.3
	Zr^{4+}	36.5	31.6	27.2	29.0	213.9	203.3
	Hf^{4+}	36.9	31.8	29.0	30.0	221.13	207.1
	Th^{4+}	37.1	32.0	31.8	31.8	231.0	214.0
HL_2	La^{3+}	35.0	29.7	30.0	28.1	218.0	194.0
	Ce^{3+}	35.3	29.9	29.0	30.0	216.0	200.8
	Pr^{3+}	35.6	30.1	29.0	30.0	216.9	201.6
	Zr^{4+}	36.0	30.4	27.2	30.0	212.0	202.5
	Hf^{4+}	36.3	30.7	30.0	30.0	222.3	203.5
	Th^{4+}	36.6	31.0	30.9	30.9	226.5	207.7
HL_3	La^{3+}	34.5	28.6	30.0	30.0	216.3	196.6
	Ce^{3+}	37.7	28.9	30.0	30.0	216.9	197.4
	Pr^{3+}	34.9	29.1	30.9	30.0	220.7	198.1
	Zr^{4+}	35.2	29.4	30.0	30.0	218.4	199.1
	Hf^{4+}	35.4	29.7	30.0	30.9	219.2	203.3
	Th^{4+}	35.6	30.1	31.8	30.0	225.9	201.4
HL_4	La^{3+}	34.0	27.6	28.1	29.0	208.3	190.1
	Ce^{3+}	34.1	27.8	27.2	29.0	205.9	190.7
	Pr^{3+}	34.4	28.0	28.1	28.1	209.7	188.4
	Zr^{4+}	34.6	28.3	28.1	29.0	210.4	192.4
	Hf^{4+}	34.8	28.6	30.0	30.0	217.3	196.4
	Th^{4+}	35.1	28.9	30.0	30.0	218.2	197.6
HL_5	La^{3+}	33.1	26.7	26.3	30.0	199.4	189.9
	Ce^{3+}	33.6	26.8	28.1	30.0	207.0	190.5
	Pr^{3+}	33.8	27.1	28.1	28.1	207.8	185.2
	Zr^{4+}	34.0	27.4	30.0	30.0	214.6	192.4
	Hf^{4+}	34.2	27.6	30.0	30.9	215.4	196.2
	Th^{4+}	34.5	28.0	31.8	31.8	222.4	200.4
HL_6	La^{3+}	32.1	25.6	30.0	29.0	208.1	183.2
	Ce^{3+}	32.3	25.8	30.0	28.1	208.9	181.0
	Pr^{3+}	32.5	26.0	29.0	29.0	206.6	184.6
	Zr^{4+}	32.8	26.3	30.9	30.0	213.6	188.6
	Hf^{4+}	33.0	26.5	30.0	30.9	211.4	192.6
	Th^{4+}	33.4	26.9	30.9	31.8	215.5	196.8

perature, *i.e.* the acidity of the ligands increases, independently of the nature of the substituent [8].

b) A positive value of ΔH indicates that the process is endothermic.

c) A large positive value of ΔG indicates that the dissociation process is not spontaneous.

d) The dissociation processes for HL_3 and its derivatives have negative values of ΔS, indicating increased order as a result of the solvation processes.

All the thermodynamic parameters of the stepwise stability constants of complexes are recorded in Table 4. It is known that the divalent metal ions exist in solution as octahedrally hydrated species and the obtained values of ΔH and ΔS can then be considered as the sum of two contributions: *a*) release of H_2O molecules and *b*) metal—ligand bond formation. Examination of these values shows that:

i) The stepwise stability constants (log K_1 and log K_2) for ligand complexes increase with increasing temperature, *i.e.* their stability constants increase with increasing the temperature.

ii) The negative value of ΔG for the complexation process indicates the spontaneous nature of such process.

iii) The ΔH values are positive, meaning that these processes are endothermic and favourable at higher temperature.

iv) The ΔS values for the ligand complexes are positive, confirming that the complex formation is entropically favourable.

EXPERIMENTAL

The standard chemical aniline and aniline deriva-

tives (*p*-OCH_3, *p*-CH_3, *o*-COOH, *p*-SO_3H, and *p*-NO_2; Aldrich) were used as received. The experimental technique has been described previously [8, 9].

5-(X-Phenylazo)-8-hydroxyquinolines (HL_n) were prepared from aniline or its *o*- or *p*-substituted derivatives (10 mmol) dissolved in hydrochloric acid (20 mmol; 25 cm^3 of distilled H_2O). The hydrochloric compound was diazotized below −5 °C with a solution of sodium nitrite (10 mmol, 30 cm^3 of distilled H_2O). The diazonium chloride was coupled with an alkaline solution of oxine (10 mmol) in 20 cm^3 of ethanol. The crude dye was collected by filtration and crystallized from ethanol, then dried in a vacuum desiccator over P_2O_5.

Analytical data (Table 1) are in agreement with the proposed formulae. The IR spectra exhibit a medium to strong band in the region $\tilde{\nu}$ = 1540—1570 cm^{-1}, which could be assigned to ν(N═N) stretching vibration [1]. The investigation of *Rossmey* and *Mecke* [22] on deuterated phenolic derivatives showed that the higher frequency band is related to δ(OH), whereas the band within 1100 cm^{-1} can be due to ν(C—OH). The higher value for the δ(OH) may result from hydrogen bonding. *Califan* and *Luttke* [23] found that the —OH in hydroxy compounds undergoes a blue shift while this group is involved in a hydrogen bond.

Coggeshall [24] and *Diab* and *El-Sonbati* [25] found three kinds of bonded —OH structures on the basis of the frequencies: i) only the oxygen is in the bridge while the hydrogen is free, ii) a polymer chain is formed in which both hydrogen and oxygen atoms participate in the hydrogen bond, iii) dimer associates are formed.

The IR spectral data exhibit a very strong band at (1585 ± 10) cm^{-1} which is assignable to ν(C═C) mode of the phenyl ring. A very interesting region is the frequency range 2800—3550 cm^{-1}. This is a characteristic region for the vibrational frequency of the —OH group where vibrational bands at 2900 cm^{-1} of medium appearance and a broad one at 3400—3550 cm^{-1} are apparent.

Metal ion solutions (1×10^{-4} mol dm^{-3}) were prepared from Analar metal chlorides in bidistilled water and were standardized with EDTA [26]. The ligand solutions (5×10^{-4} mol dm^{-3}) were prepared by dissolving the accurate mass of the solid in methanol (Analar). Solutions of 5×10^{-4} M-HCl and 1 M-KCl were also prepared in bidistilled water. A carbonate-free sodium hydroxide solution in 40 vol. % CH_3OH—water mixture was used as titrant and standardized against oxalic acid (Analar).

The apparatus, general conditions, and methods of calculation were the same as in our previous works [7, 8]. The following mixtures were prepared and titrated potentiometrically at 298 K against standard 2×10^{-3} M-NaOH in 40 vol. % CH_3OH—water mixture:

a) 5 cm^3 5×10^{-4} M-HCl + 5 cm^3 1 M-KCl + 20 cm^3 CH_3OH;

b) 5 cm^3 5×10^{-4} M-HCl + 5 cm^3 1 M-KCl + 15 cm^3 CH_3OH + 5 cm^3 5×10^{-4} M-ligand;

c) 5 cm^3 5×10^{-4} M-HCl + 5 cm^3 1 M-KCl + 15 cm^3 CH_3OH + 5 cm^3 5×10^{-4} M-ligand + 5 cm^3 1 $\times 10^{-4}$ M-metal chloride.

For each mixture, the volume was made up to 50 cm^3 with bidistilled water before the titration. These titrations were repeated for temperatures of 308 K and 318 K. A constant temperature was maintained at ± 0.05 K by using an ultrathermostat (Neslab 2 RTE 220). The pH-meter readings in 40 vol. % CH_3OH—water mixture are corrected according to the *Van Uitert* and *Hass* relation [27].

CONCLUSION

Proton-ligand dissociation constants of 5-(phenylazo)-8-hydroxyquinoline derivatives, and metal-ligand stability constants of their complexes with metal ions (La^{3+}, Ce^{3+}, Pr^{3+}, Zr^{4+}, Hf^{4+}, and Th^{4+}) have been determined potentiometrically in 0.1 M-KCl and 40 vol. % CH_3OH—water mixture. The pK_1^H values are influenced by the inductive or mesomeric effect of the substituents. The *p*-OCH_3 and *p*-CH_3 derivatives (*i.e.* an electron-donating effect) have a lower acidic character (higher pK_1^H values) than the *p*-SO_3H, *o*-COOH, and *p*-NO_2 derivatives (*i.e.* an electron-withdrawing effect). The *para*-substituents in the 8-hydroxyquinoline moiety have a direct influence on the pK_1^H values of the investigated compounds, revealing the coplanarity of the molecule and thus affording a maximum resonance *via* delocalization of its π-system. For the ligands with the same metal ion at constant temperature, the stability of the chelates increases in the order HL_1, HL_2, HL_3, HL_4, HL_5, HL_6. The dissociation processes are nonspontaneous, endothermic, and entropically unfavourable. The formation of the complexes is spontaneous, endothermic, and entropically favourable.

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