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Voltammetric, Potentiometric and Spectrophotometric Studies of Some Hydrazones and Their Metal Complexes in Ethanolic-Aqueous Buffered Solutions

Mohammed M. Ghoneim*, **Ibrahim S. El-Hallag**, **Kamal Y. El-Baradie**, **Hanaa S. El-Desoky**, and **Mona A. El-Attar**

Chemistry Department, Faculty of Science, Tanta University, 31527 Tanta, Egypt

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Summary. The electrochemical behavior of some hydrazones derived from 6-chloro-2-hydrazinopyridine in the *Britton-Robinson* universal buffer of *pH* 2–11 containing 35% ethanol was investigated at the mercury electrode using dc-polarography, controlled-potential coulometry, and cyclic voltammetry techniques. The examined hydrazones were reduced in solutions of $pH<9$ in a single 4-electron diffusion-controlled irreversible step corresponding to both the saturation of –N=C< double bond and cleavage of the –HN–NH– single bond of the hydrazone molecule *via* the consumption of two electrons for each center. Whereas the starting compound, 6-chloro-2-hydrazinopyridine, was reduced in a single 2-electron diffusion-controlled irreversible step corresponding to cleavage of its $-NH-NH_2$ single bond. The mechanistic pathway of the electrode reaction of the studied compounds was elucidated and discussed. The pK_a values of the examined hydrazones and the stoichiometry of their complexes in solution with some transition metal ions were determined spectrophotometrically. The dissociation constants and the thermodynamic parameters of the investigated hydrazones, and the stability constants of their metal complexes in solution were determined potentiometrically.

Keywords. Hydrazones; 6-Chloro-2-hydrazinopyridine; Polarography; Coulometry; Cyclic voltammetry.

Introduction

Hydrazones and their metal complexes are of current interest for their physicochemical properties and applications in many important chemical processes that include sensors, non-linear optics, medicine, and others [1–7]. Here we report the electrochemical behavior of seven hydrazones derived from 6-chloro-2-hydrazinopyridine and their electrode reaction pathway at the mercury electrode in

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* Corresponding author. E-mail: mmghoneim@usa.net

ethanolic-aqueous buffered solutions of *pH* 2–11. The pK_a values, dissociation constants, and the thermodynamic parameters of the examined hydrazones, and the stoichiometry of their complexes in solution with some transition metal ions and stability constants of these metal complexes were determined.

Results and Discussion

DC-Polarograhic Studies

Polarograms of the examined hydrazones (L1–L7) in the *Britton-Robinson* (*B-R*) universal buffer of $pH < 9$ containing 35% (v/v) ethanol exhibited a single 4-electron irreversible cathodic wave (*e.g.* Fig. 1), whereas those of the starting compound 6-chloro-2-hydrazinopyridine (L0) showed a single 2-electron irreversible cathodic wave. The limiting current (i_l) of the studied hydrazones was *pH*-independent in solutions of $pH < 9$ (Fig. 2). At higher *pH* values the limiting current decreases on the increase of *pH* with the formation of a large minimum at more negative potentials which is a behavior usually observed in alkaline media for hydrazones [8–12]. This behavior was attributed to the protonation that occurs as a heterogeneous process at the electrode surface, where the amount of adsorbed conjugate base decreases with increasing negative potential and the limiting current is controlled by the rate of protonation [9–13].

Logarithmic analysis of the irreversible polarographic waves [14] of the investigated compounds by plotting $E_{d.e}$ *versus* $\log(i/i_l - i)$ at various *pH* values displayed straight lines with slope values $S_1 = 55 - 84\,\text{mV}$ ($S_1/\text{mV} = 59/\alpha n_a$), from which values of αn_a and the symmetry coefficient α at the *pH* values < 8 were

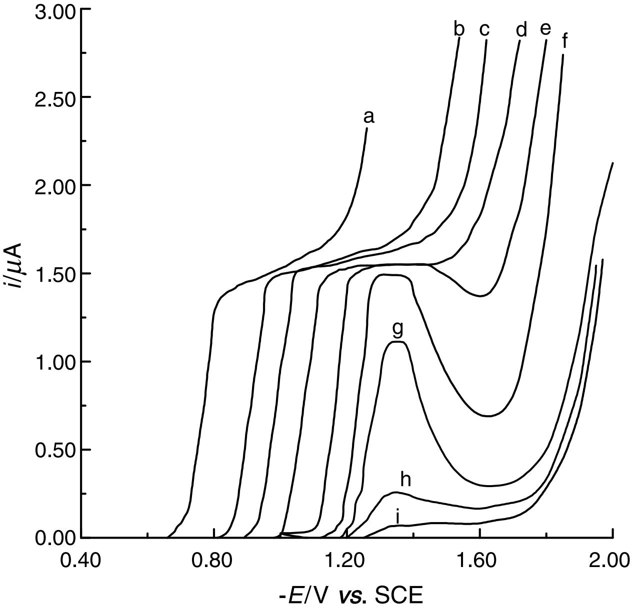


Fig. 1. *Dc*-polarograms of $1 \times 10^{-4}\,M$ solution of compound (L1) in the *Britton-Robinson* universal buffer of various *pH* values: (a) 2.0, (b) 3.6, (c) 4.2, (d) 5.2, (e) 6.4, (f) 8.6, (g) 9.2, (h) 10.2, and (i) 11.2

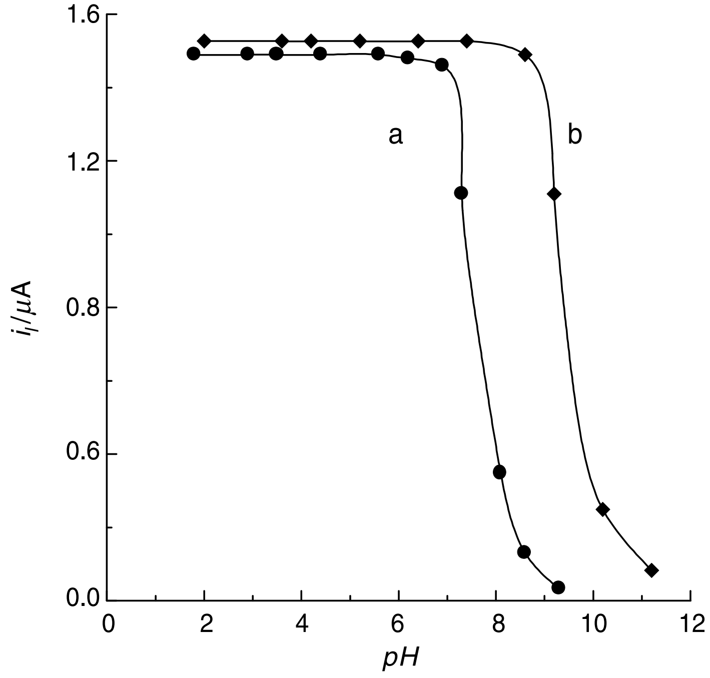


Fig. 2. Limiting current (i_l) *vs. pH* plots for 1×10^{-4} *M* solutions of the hydrazones L3 (a) and L1 (b) in the *B-R* universal buffer

estimated (Table 1). The most probable values (0.3–0.5) of the symmetry coefficient α revealed that the number of electrons n_a involved in the rate-determining step (the slowest step of the electrode reaction) of the reduction process equals two.

The half-wave potential ($E_{1/2}$) of the polarographic waves of the examined compounds shifted to more negative values with the increase of *pH* indicating the involvement of protons in the electrode reaction and that the proton-transfer reaction precedes the electrode process properly [15]. The $E_{1/2} - pH$ plots of the reduction waves of the examined compounds were straight lines with slope values $\mathrm{d}E_{1/2}/\mathrm{d}pH = S_2 = 57\text{–}89\,\mathrm{mV}$, $\{S_2/\mathrm{mV} = (59/\alpha n_a)\ P\}$. The number of protons *P* participating in the rate-determining step of the reduction process was calculated from Eq. (1) [14] which was expressed in the form of Eq. (2) [14, 16] and was found to equal one (Table 1).

$$\mathrm{d}E_{1/2}/\mathrm{d}pH/mV = (59/\alpha n_a)P \tag{1}$$

$$P = (\mathrm{d}E_{1/2}/\mathrm{d}pH)/(59/\alpha n_a) = S_2/S_1 \tag{2}$$

The obtained data indicated that the rate-determining step of the reduction processes of the examined compounds involved the transfer of one proton ($P = 1$) and two electrons ($n_a = 2$), *i.e.* the ratio $P/n_a = 0.5$.

Controlled-Potential Electrolysis and TLC Studies

The number of electrons *n* transferred in the overall electrode reduction of each of the investigated hydrazones was determined by means of controlled-potential

Table 1. Dc-polarographic results of the investigated hydrazones in the ethanolic-aqueous *B-R* universal buffer

pH	$\frac{-E_{1/2}}{V}$	$\frac{S_1}{mV}$	$\frac{S_2}{mV}$	$p\ (S_2/S_1)$	$\frac{\alpha}{P/n_a}$		
					2.0	1.0	0.5
Compound L0							
4.0	1.00	55	57	1.0	2.1	1.0	0.5
6.5	1.28	71		0.8			
Compound L1							
2.0	0.78	56	89	1.6	1.3	0.7	0.3
6.4	1.17	58		1.5			
Compound L2							
2.0	0.90	62	87	1.4	1.4	0.7	0.3
6.6	1.30	74		1.3			
Compound L3							
1.8	0.84	67	75	1.1	1.6	0.8	0.4
6.2	1.19	64		1.2			
Compound L4							
2.0	0.98	67	70	1.0	1.7	0.8	0.4
7.7	1.40	65		1.1			
Compound L5							
2.0	0.85	60	77	1.3	1.5	0.8	0.4
6.2	1.18	66		1.2			
Compound L6							
2.0	0.65	74	72	1.0	1.6	0.8	0.4
6.7	0.99	65		1.1			
Compound L7							
1.7	0.75	80	66	0.8	1.8	0.9	0.4
6.8	1.10	84		0.8			

electrolysis of various concentrations of the reactant in buffered solutions of *pH* values <9 at a mercury pool working electrode and was found to equal four *per* hydrazone molecule (L1–L7), whereas it was two electrons in case of their starting compound (L0). The transfer of four electrons may be attributed to both the reductive saturation of the –N=C< double bond (E_1) and cleavage of the –HN–NH– single bond (E_2) *via* the consumption of two electrons for each center ($E_1 = E_2 = E_{1/2}$). Azo-test for the completely electrolyzed solutions of the examined hydrazones (L1–L7) in the *B-R* universal buffer of *pH* values <9, at a potential corresponding to the plateau of their polarographic waves revealed the cleavage of the –HN–NH– single bond with the formation of 2-amino-6-chloropyridine (iii, Scheme 2). Thin layer chromatographic (TLC) analysis of the extracted product of the hydrazones (L1–L7) confirmed the presence of two products in their electrolyzed solutions. The UV-spectra of the completely electrolyzed solutions of the examined hydrazones (L1–L7) indicated the disap-

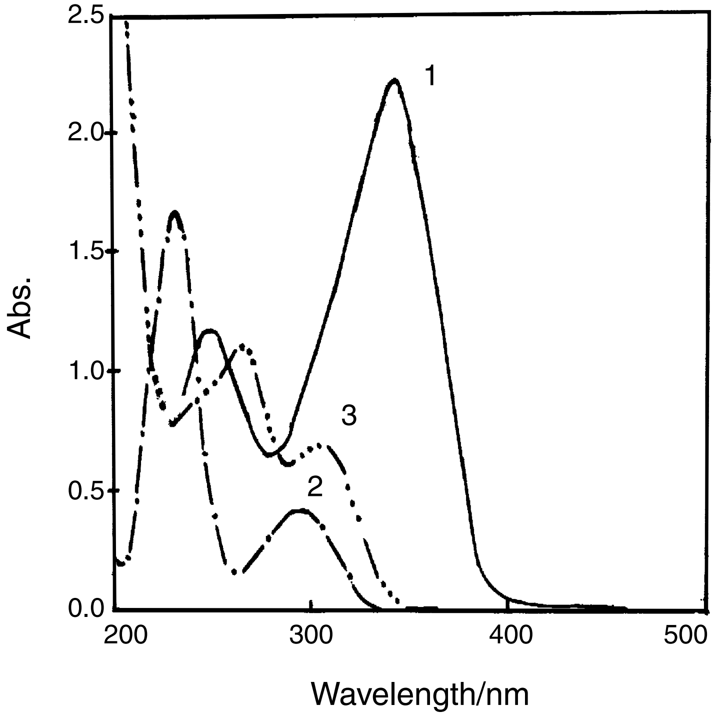


Fig. 3. UV-spectra in an ethanolic-aqueous *B-R* universal buffer of $pH = 5.3$ for: $1 \times 10^{-4} M$ hydrazone (L1) solution before (1) and after (2) complete electrolysis, and $1 \times 10^{-4} M$ solution of the starting compound L0 (3)

pearance of the band due to the n → π^* transition of the –HN–NH– single bond (Fig. 3, curve 2) compared to that of the analyte before electrolysis (Fig. 3, curve 1, $\lambda = 343.5$ nm). This confirms the reductive cleavage of the –HN–NH– single bond (Scheme 2). In case of the starting compound (L0), the transfer of two electrons may be attributed to the reductive cleavage of the $-HN-NH_2$ single bond leading to formation of 2-amino-6-chloropyridine and the release of ammonia (Scheme 1). The latter was confirmed by adding *Nessler*'s reagent to the completely electrolyzed solution of compound L0 where a reddish brown precipitate was formed [17].

Cyclic Voltammetric Studies

Cyclic voltammograms of the studied hydrazones in the *B-R* universal buffer of *pH* values < 9 at various scan rates (20–500 mV/s) exhibited a single irreversible cathodic peak (Fig. 4). The peak potentials (E_p) of the examined compounds shifted to more negative values with the increase of scan rate. The extent of the cathodic shift of the peak potential (E_p) and the difference between peak potential and the half-peak ($E_p - E_{p/2}$) as a function of the scan rate (Table 2) confirmed the irreversible nature of the reduction process of the investigated hydrazones [18]. The peak potential (E_p) varies with scan rate according to Eq. (3) [19] where $k^{\circ}_{f,h}$ is

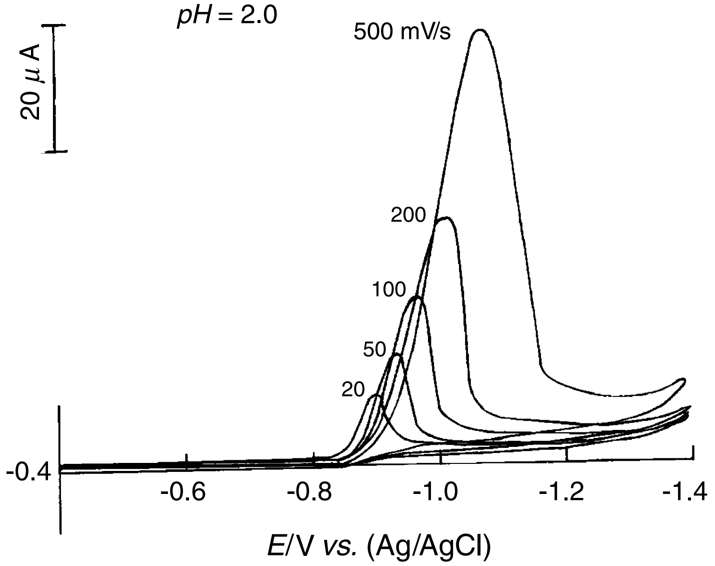


Fig. 4. Cyclic voltammograms of $5\times10^{-5}\,M$ of hydrazone (L1) at different scan rates in an ethanolic-aqueous *B-R* universal buffer of *pH* 2

Table 2. Electrochemical parameters extracted from cyclic voltammetric data of the investigated hydrazones in the ethanolic-aqueous *B-R* universal buffer

Compound	*pH*	α		$D^0\times10^5$	$k_{f,h}$
		E_p *vs* ln ν	E_p–$E_{p/2}$	$\mathrm{cm^2/s}$	$\mathrm{cm/s}$
L1	2.0	0.2	0.2	2	2×10^{-6}
	7.4	0.2	0.2	2	2×10^{-8}
L2	2.0	0.3	0.3	5	4×10^{-7}
	7.5	0.4	0.3	4	2×10^{-10}
L3	2.3	0.3	0.3	5	1×10^{-6}
	7.0	0.4	0.3	2	7×10^{-10}
L4	2.2	0.2	0.3	8	9×10^{-7}
	7.3	0.3	0.2	5	4×10^{-9}
L5	2.2	0.3	0.3	3	1×10^{-7}
	7.9	0.4	0.4	1	1×10^{-10}
L6	1.7	0.3	0.3	1	3×10^{-5}
	7.2	0.3	0.3	9	3×10^{-7}
L7	1.7	0.3	0.3	2	7×10^{-7}
	7.7	0.4	0.4	1	1×10^{-10}

the standard heterogeneous rate constant and the other terms have their usual meanings.

$$E_p = -1.14(RT/\alpha n_a F) + (RT/\alpha n_a F)\ln k^{\circ}_{f,h}/D^{1/2} - RT/2\alpha n_a F \ln(\alpha n_a \nu) \qquad (3)$$

Values of αn_a and the cathodic symmetry coefficient α at various *pH* values were calculated from slope values of the obtained linear plots of E_p *versus* ln ν (Table 2). Values of the symmetry coefficient α were also determined using Eq. (4) [18] and were found to be less than 0.5 when $n_a = 2$ (Table 2) which confirmed the irreversible nature of the electrode process of the investigated hydrazones.

$$E_p - E_{p/2} = 1.857(RT/\alpha n_a F) \tag{4}$$

The peak current of an irreversible electrode process (i_{pirr}) was expressed by Eq. (5) [18] where C_0 is the bulk concentration of reactant species and the other terms have their usual meanings.

$$i_{pirr} = 2.99 \times 10^5 n(\alpha n_a)^{1/2} A D^{1/2} C_0 \nu^{1/2} \tag{5}$$

The diffusion-controlled reduction process of the examined hydrazones was identified from the linearity of the i_{pirr} *versus* $\nu^{1/2}$ plots with slight deviation from the origin [20]. The plots of E_p *versus pH* for the investigated hydrazones were straight lines with slope values of 66–90 mV/*pH* which agree well with those obtained from dc-polarograhic measurements.

The diffusion coefficients D^0 of the examined hydrazones were calculated using Eq. (5) and then the heterogeneous rate constant ($k^{\circ}_{f,h}$) of their irreversible electrode reactions was calculated (Table 2) from cyclic voltammetric data using Eq. (3). It seems that the higher the *pH* values the lower is the value of ($k^{\circ}_{f,h}$) denoting a more difficult electron transfer.

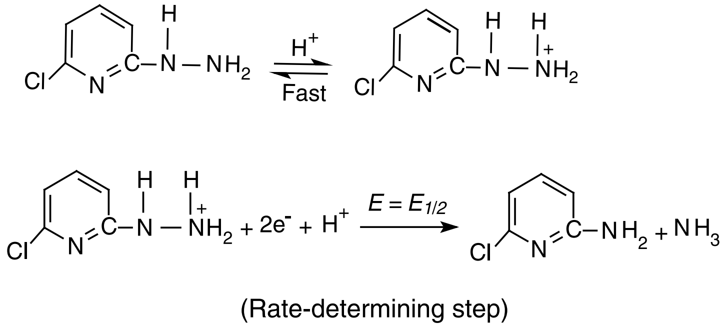
The Electrode Reaction

Reduction pathway of 6-chloro-2-hydrazinopyridine: This compound was reduced at the mercury electrode surface in the *B-R* universal buffer of $pH < 9$ through a single 2-electron irreversible step corresponding to the reductive cleavage of the –HN–NH$_2$ single bond with the release of ammonia as shown in Scheme 1. The released ammonia was confirmed by *Nessler*'s reagent test [17].

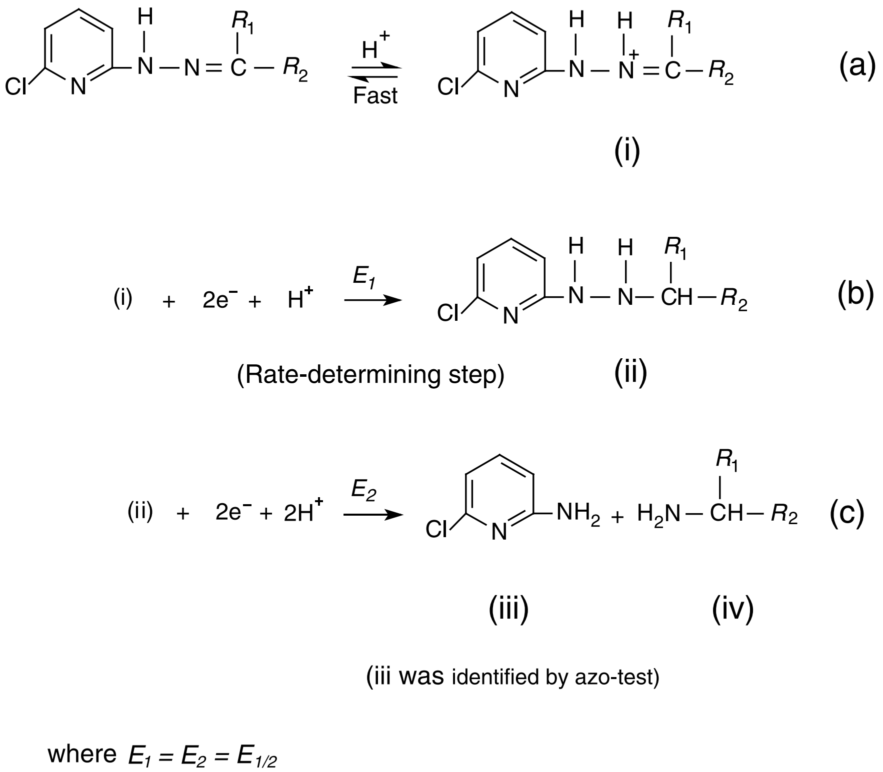
Reduction pathway of hydrazones: The examined hydrazones L1–L7 were reduced at the mercury surface in the *B-R* universal buffer of $pH < 9$ through a single 4-electron irreversible step corresponding to both the saturation of –N=C< double bond and cleavage of the –HN–NH– single bond as shown in Scheme 2.

Spectrophotometric Studies

pK$_a$ values: The absorbance-wavelength spectra of the hydrazones L1–L7 in the *B-R* universal buffer of *pH* values 2–11 containing 35% (*v*/*v*) ethanol were recorded within the wavelength range 200–600 nm. Compounds L1 and L2 showed a single band at $\lambda_{\max} = 346$ and 340 nm, respectively, and the absorbance of each is *pH*-independent indicating that the species of the compound in the acidic and alkaline solutions are similar. Whereas the absorption spectra of compounds L3–L7 exhibited two bands with the appearance of an obvious isosbestic point. The first band may be due to the non-ionized form whereas the second band that developed with the increase of *pH* may be due to the ionized species. The observed isosbestic point indicates an acid-base equilibrium. The spectra of compounds L6 and L7 in acidic solutions of $pH < 5$ exhibited absorption bands at $\lambda_{\max} = 385$ and 380 nm, respec-



Scheme 1



Scheme 2

tively, whereas at higher *pH* values these bands were blue shifted to $\lambda_{max} = 341$ and 330 nm, respectively (Fig. 5). This behavior can be explained on the basis that protonation takes place in acidic solutions on the nitrogen of the unsubstituted pyridine ring which enhances the charge transfer from the hydrazone moiety. However, with the increase of *pH* this effect disappears, thus the absorption bands were blue shifted. The pK_a values of the investigated compounds were estimated from the typical Z or S-shaped absorbance-*pH* curves at two different wavelengths using the half-height [21], the limiting absorbance [22], and the modified limiting absorbance [23, 24] methods. The obtained pK_a values are reported in Table 3.

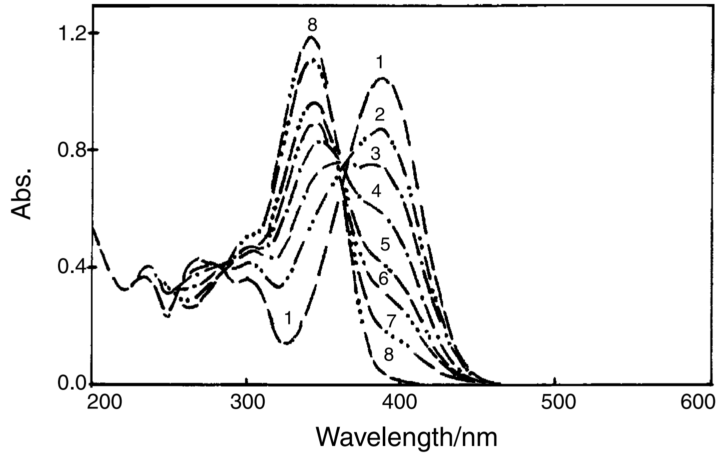


Fig. 5. Absorption spectra of $4 \times 10^{-5} M$ solution of hydrazone L6 in the ethanolic-aqueous *B-R* universal buffer of various *pH* values: (1) 1.8, (2) 3.6, (3) 4.0, (4) 4.2, (5) 4.5, (6) 4.7, (7) 5.1, and (8) 6.3

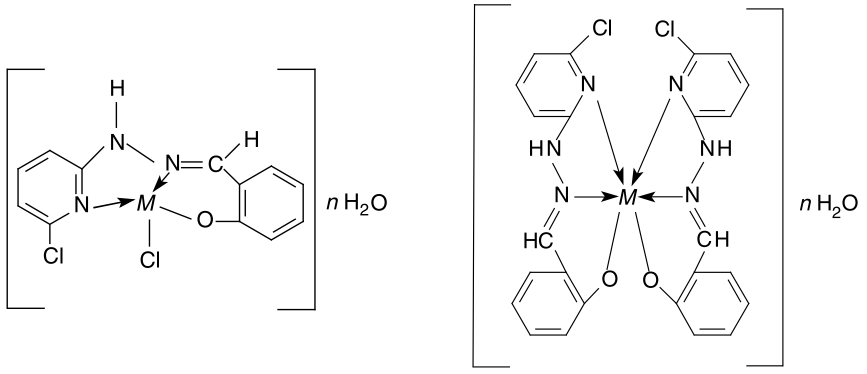
Table 3. The ionization constants (pK_a) of the investigated hydrazones in the ethanolic-aqueous *B-R* universal buffer using the half-height (1), limiting-absorbance (2), and modified limiting-absorbance (3) methods

Compound	$\frac{\lambda}{\text{nm}}$	pK_a			
		(1)	(2)	(3)	Mean value
L0	304	3.4	3.1	3.5	3.3
L3	337	9.4	10.3	9.4	9.7
	370	9.6	9.3	9.6	9.5
L4	289	10.1	10.4	10.1	10.2
	337	10.4	10.7	10.4	10.5
L5	370	10.5	10.9	10.5	10.6
	406	10.4	10.2	10.3	10.3
L6	341	4.3	3.9	4.4	4.2
	385	4.2	4.4	4.3	4.3
L7	330	4.9	4.6	5.0	4.9
	380	4.7	4.8	4.7	4.7

Stoichiometry of hydrazone-metal complexes: The complexes formed in solution for the investigated hydrazones L3–L7 with the metal ions Mn(II), Co(II), Cu(II), Zn(II), and Cd(II) were studied. The stoichiometry of the formed complexes was determined by the molar ratio [25] and continuous variation [26–29] methods. The results indicated formation of complexes of stoichiometric ratios 1:1 and 1:2 (*M*:*L*) (Scheme 3).

Potentiometric Studies

Dissociation constant: The average number of protons, $\overline{n_A}$, associated with the reagent molecule at different *pH* values was calculated from the titration curves



Scheme 3

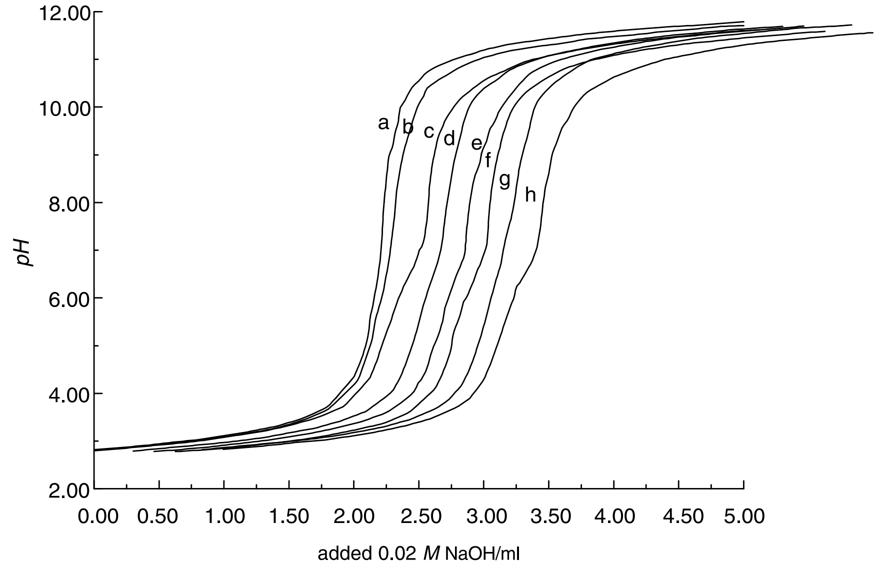


Fig. 6. Potentiometric titration curves using 0.02 *M* NaOH ethanolic-aqueous (40% *v*/*v*) solution at 293 K for the solutions: (a) 5 cm^3 0.1 *M* HCl + 5 cm^3 1 *M* KCl + 20 cm^3 H_2O + 20 cm^3 *Et*OH; (b) 5 cm^3 0.1 *M* HCl + 5 cm^3 1 *M* KCl + 5 cm^3 1×10^{-3} *M* hydrazone L4 + 20 cm^3 H_2O + 15 cm^3 *Et*OH; 5 cm^3 0.1 *M* HCl + 5 cm^3 1 *M* KCl + 5 cm^3 1×10^{-3} *M* hydrazone L4 + 10 cm^3 H_2O + 15 cm^3 *Et*OH + 10 cm^3 1×10^{-4} *M* (c) Mn^{2+}; (d) Co^{2+}; (e) Ni^{2+}; (f) Cu^{2+}; (g) Zn^{2+}; and (h) Cd^{2+}

of hydrochloric acid in the absence and presence of hydrazone compound (Fig. 6). As shown in Fig. 6, the metal- titration curves (curves c–h) are well separated from that of free ligand (curve b), along the axis of added volume of NaOH solution, which attributed to liberation of H^+ ions as a result of the complexation process. Thus, the formation curves ($\overline{n_A}$ *versus pH*) for the proton-hydrazone systems were constructed and found to extend between 0 and 2 on the $\overline{n_A}$ scale. This means that there are two dissociable protons one may be from the enolized –HN–N– moiety and the second from the phenolic –OH. The proton-ligand dissociation constants of the examined hydrazones in a mixture of 40% (*v*/*v*) ethanol-water and 0.1 *M* KCl at 293, 303, and 313 K were calculated [30] and reported in Table 4. From values of

Table 4. Dissociation constants and thermodynamic parameters for the dissociation process of the investigated hydrazones L3 and L4 in a mixture of 40% (v/v) ethanol-water and 0.1 M KCl at different temperatures

Temperature	pK_1^H	pK_2^H	ΔG_1	ΔG_2	ΔH_1	ΔH_2	ΔS_1	ΔS_2
K			$\mathrm{kJmol^{-1}}$		$\mathrm{kJmol^{-1}}$		$\mathrm{Jmol^{-1}\,K^{-1}}$	
Compound L3								
293	5.4	10.6	30.3	59.5	60.9	87.0	140.0	95.1
303	5.1	9.9	29.6	57.4				
313	4.7	9.6	28.2	57.5				
Compound L4								
293	5.9	11.0	33.1	61.7	121.8	130.5	304.4	236.1
303	4.9	10.0	28.4	58.0				
313	4.5	9.5	27.0	56.9				

dissociation constants pK^H of free ligands L3 and L4 estimated at 293, 303, and 313 K the thermodynamic parameters ΔG, ΔH, and ΔS of the dissociation process were calculated (Table 4) using Eqs. (6)–(8) [31–33], where, R is the gas constant, pK^H is the dissociation constant of the ligand and T is the temperature (in K).

$$\Delta G = -2.303\,RT \log K = 2.303\,RT\,pK^H \tag{6}$$

$$-2.303\,RT \log K = \Delta H - T\Delta S \tag{7}$$

$$\log K = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303R} \cdot \frac{1}{T} \tag{8}$$

Values of ΔH were estimated from plotting log K *vs.* $\frac{1}{T}$ while those of the entropy change (ΔS) were estimated from the intercept of Eq. (8). From the obtained results (Table 4) the following information can be concluded: (i) values of the stepwise dissociation constants pK_1^H and pK_2^H of both the compounds L3 and L4 decreased with the increase of temperature revealing that the acidity of ligands increases with increasing temperature; (ii) the positive values of ΔG indicated that the dissociation process of the ligand is thermodynamically unfavorable [34, 35]; (iii) the positive values of ΔH of the dissociation process of the ligand indicated its endothermic nature and that the process enhances with rising temperature; and (iv) the positive values of ΔS confirmed that the dissociation process is entropically favorable.

Stability constant of hydrazone-metal complexes: The formation curves for the metal complexes of the two investigated hydrazones L3 and L4 with the metal ions Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+}, Fe^{3+}, La^{3+}, Ce^{3+}, Th^{4+}, and UO_2^{2+} were obtained by plotting the average number ($\bar{n}$) of ligands attached per metal ion *versus* the free ligand exponent (pL). By analysis of the formation curves, the successive stability constants log K_1 and log K_2 of the studied metal complexes ML and ML_2, respectively, were determined (Table 5) using different computational methods [36, 37]. The obtained results can be summarized as follows: (i) the maximum $\bar{n}$ value of all the studied metal complexes was found to equal $\cong 2$,

Table 5. Stability constants of the hydrazone L4-metal complex in a mixture of 40% (v/v) ethanol-water and 0.1 M KCl at different temperatures

	293 K		303 K		313 K	
M^{n+}	log K_1	log K_2	log K_1	log K_2	log K_1	log K_2
Mn^{2+}	10.1	8.5	9.8	8.2	9.7	8.0
Co^{2+}	10.3	8.5	10.1	8.4	10.0	8.1
Ni^{2+}	10.5	9.0	10.4	8.9	10.3	8.8
Cu^{2+}	10.9	9.3	10.7	9.2	10.6	9.1
Zn^{2+}	10.6	9.2	10.6	8.9	10.5	8.9
Cd^{2+}	10.4	8.8	10.2	8.7	10.1	8.6
Cr^{3+}	11.0	9.4	10.9	9.3	10.9	9.2
Fe^{3+}	11.9	10.3	11.7	10.3	11.0	9.7
La^{3+}	11.3	9.9	11.2	9.8	10.9	9.6
Ce^{3+}	11.5	10.0	11.4	9.9	11.0	9.6
Th^{4+}	12.3	10.8	11.85	10.7	11.14	10.2
UO_2^{2+}	11.9	10.6	11.80	10.3	11.03	9.8

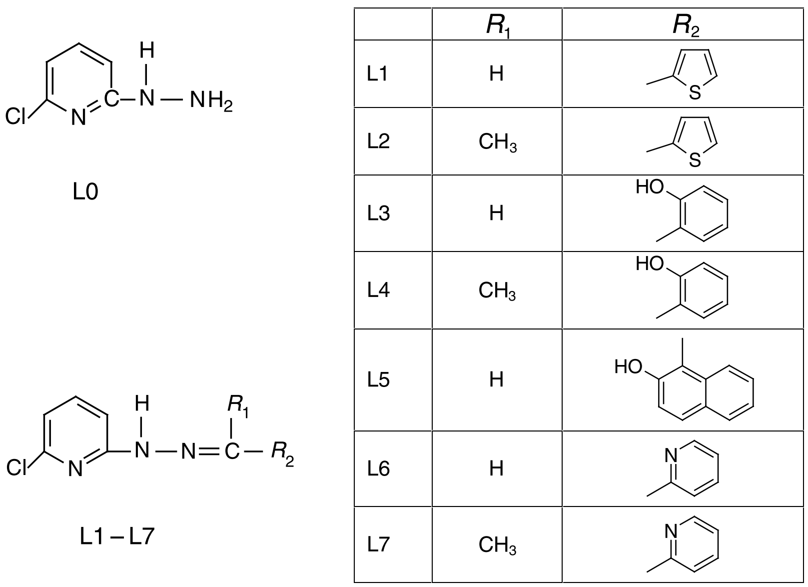
revealing the formation of two types of metal complexes, ML and ML_2, in solution. No precipitate was observed in the titration vessel, thus the formation of metal hydroxide is excluded; (ii) values of log K_1 were always found higher than those of log K_2. This may be due to the fact that the vacant sites of the metal ions are easier available for binding of the first ligand molecule than for the second one [38, 39]; and (iii) the order of stability constants of metal complexes of compound L3 and L4 with the transition metal ions was found as: $Cr^{3+} > Fe^{3+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Cd^{2+} > Co^{2+} > Mn^{2+}$ which agrees will with that reported by *Irving* and *Williams* [40, 41].

For actinides and lanthanides, the stability of the formed complexes increases in the order: $Th^{4+} > UO_2^{2+} > Ce^{3+} > La^{3+}$. A similar order was previously reported [42–45]. The Th^{4+} complexes are more stable than those of the other metal complexes as a result of increasing both the oxidation state and the ionization potential. The stability constant of the divalent oxygenated cation complex (UO_2^{2+}) has a higher value than that of the other divalent cation complexes, which may be attributed to the bonded oxygen atoms that increases the electrostatic attraction between the metal ion and the coordinated ligand and overcomes any steric hindrance offered by the oxygen of the oxygenated cations [46, 47].

Experimental

Preparation of the Investigated Hydrazones

The examined hydrazones L1–L7 were synthesized [48] by the condensation of 6-chloro-2-hydrazinopyridine (L0) with 2-thiophen-aldehyde (L1), methyl-2-thienylketone (L2), salicylaldehyde (L3), 2-hydroxy-acetophenon (L4), 2-hydroxy-1-naphthaldehyde (L5), α-formyl-pyridine (L6), or α-acetylpyridine (L7) in 1:1 molar ratio in absolute ethanol. The prepared hydrazones were purified by recrystallization. ^{1}H NMR, IR, and elemental analysis confirmed the structures of the prepared hydrazones (Scheme 4).



Scheme 4

Solutions

Solutions (1×10^{-3} *M*) of each of the examined hydrazones were obtained by dissolving the accurate weight of the solid compound in appropriate volumes of ethanol. Solutions of 1×10^{-4} *M* of each of the metal salts ($MnCl_2{\cdot}4H_2O$, $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $ZnCl_2{\cdot}6H_2O$, $CdCl_2{\cdot}1H_2O$, $CrCl_3{\cdot}6H_2O$, $FeCl_3$, $La(NO_3)_3{\cdot}6H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$, $Th(NO_3)_4$, and $UO_2(Ac)_2{\cdot}2H_2O$) were prepared by dissolving the accurate weight of the metal salt in appropriate volumes of deionized water. Solutions of 0.1 *M* HCl, 1 *M* KCl and 0.1 *M* NaOH were also prepared in deionized water.

A series of the *Britton-Robinson* universal buffer [49] of *pH* 2–11 containing 35% (*v*/*v*) ethanol was prepared and used as a supporting electrolyte. A *pH*-meter (Crison, Barcelona, Spain) with combined glass and calomel (KCl_s) electrodes was used for the *pH* measurements.

Nessler's reagent ($K_2(HgI_4)$ in dilute sodium hydroxide) was used for testing the formation of ammonia during the controlled-potential electrolysis of the investigated hydrazones. On mixing the electrolyzed solution with *Nessler*'s reagent while warming to about 40°C the presence of ammonia gives a reddish brown coloration and a yellow or orange-red to brown precipitate of basic mercury(II) amido-iodide ($HgO{\cdot}Hg(NH_2)I$), depending on the amount of ammonia [17].

Instrumentation and Procedures

Dc-polarogramic measurements were recorded using a pen recording Polarography Model 4001 (Sargent–Welch, USA). A polarographic cell described by *Meites* [14] was used. The characteristics of the dropping mercury electrode (DME) were: $m = 1.07$ mg/s, $t = 3.3$ s, at a mercury height = 60 cm in 0.1 *M* KCl at open circuit.

A computer controlled Electrochemical Analyzer Model 273-PAR (Princeton Applied Research PAR, Princeton, NJ, USA) and the electrode assembly Model 303A, incorporated with an electrochemical cell comprising of a hanging mercury drop electrode (HMDE) of area 0.026 cm^2 as a working electrode, an $Ag/AgCl/KCl_s$ as a reference electrode, and a platinum wire as a counter electrode were used for cyclic voltammetric measurements.

A potentiostat/galvanostat Model 173-PAR incorporated with a digital coulometer model 179-PAR was used for controlled-potential electrolysis of the investigated hydrazones at a mercury pool as a working electrode. A saturated calomel electrode as a reference electrode and a platinum gauze immersed in a bridge tube as a counter electrode were used. The potential selected was adjusted to a value equal to the $E_{1/2}$ of the polarographic wave of reactant plus 0.1 V or at the beginning of the limiting current of the polarographic wave. The number of electrons (n) transferred per hydrazone molecule was determined using *Faraday*'s relation: $N = Q/nF$ (where N is the number of moles of substance being electrolyzed) and was found to equal four in case of compounds L1–L7, whereas it was two in case of compound L0. Thin layer chromatographic (TLC) analysis was used for characterization of the extracted electrolysis products of the investigated hydrazones L1–L7.

Electronic absorption spectra of the hydrazones under consideration in the ethanolic-aqueous *B-R* universal buffer of *pH* values 2–11 were recorded at room temperature within the wavelength range 200–600 nm using a Shimadzu UV-visible spectrophotometer Model 160A.

Potentiometric measurements were performed using a *pH*-meter Model HI8014 (Hanna Instruments, Italy) accurate to ±0.01 *pH* units. The electrode was standardized before and checked after each titration with buffer solutions produced by FISHER (New Jersey, USA). All the titration measurements were carried out at different temperatures by circulating water from an Ultra-thermostat (JULABO F10, Seelbach, Germany) through the annular space of a double-walled Pyrex titration cell of 50 ml capacity. A standard solution of 0.02 *M* NaOH (40% v/v ethanol-water) was added from the micro burette (5 cm^3) and the contents of the titration vessel were stirred using a magnetic stirrer (Sargent-Welch, USA). The following mixtures were prepared and titrated potentiometrically at different temperatures (293, 303, and 313 K) against ethanolic-aqueous (40% v/v) 0.02 *M* NaOH solution. For each mixture, the volume was made up to 50 cm^3 using bidistilled water before the titration:

(i) $5\,cm^3$ $0.1\,M$ HCl $+ 5\,cm^3$ $1\,M$ KCl $+ 20\,cm^3$ $H_2O + 20\,cm^3$ *Et*OH
(ii) $5\,cm^3$ $0.1\,M$ HCl $+ 5\,cm^3$ $1\,M$ KCl $+ 5\,cm^3$ $1 \times 10^{-3}\,M$ hydrazone $+ 20\,cm^3$ $H_2O + 15\,cm^3$ *Et*OH
(iii) $5\,cm^3$ $0.1\,M$ HCl $+ 5\,cm^3$ $1\,M$ KCl $+ 5\,cm^3$ $1 \times 10^{-3}\,M$ hydrazone $+ 10\,cm^3$ $1 \times 10^{-4}\,M$ metal ion (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+}, Fe^{3+}, La^{3+}, Ce^{3+}, Th^{4+}, and UO_2^{2+}) $+ 10\,cm^3$ $H_2O + 15\,cm^3$ *Et*OH

The obtained potentiometric titration curves were analyzed using a constructed basic language – PC program.

References

[1] Armstrong CM, Bernhardt PV, Chin P, Richardson DR (2003) Eur J Inorg Chem 1145
[2] Schmitt JL, Stadler AM, Kyritsakas N, Lehn JM (2003) Helvetica Chim Acta **86**: 1598
[3] Mezzina E, Spinelli D, Lamaritina L, Buscemi S, Frenna V, Macaluso G (2002) Eur J Org Chem 203
[4] Hegab MI, Hassan NA, El-Telbani EM, Farag ISA, Abdel-Megeid FME (2003) Heteroatom Chem **14**: 223
[5] Hayden LM, Kim WK, Chafin AP, Lindsay GA (2001) J Polym Sci; Part B: Polym Phys **39**: 895
[6] Pelagatti P, Bacchi A, Carcelli M, Costa M, Fruhauf HW, Goubitz K, Pelizzi M, Triclistri M, Vrieze K (2002) Eur J Inorg Chem 439
[7] Bakir M, Hassan I, Johnson T, Brown O, Green O, Gyles C, Coley MD (2004) J Molecular Structure **688**: 213
[8] Ghoneim MM (1978) J Electroanal Chem **94**: 147
[9] Lund H (1959) Acta Chem Scand **13**: 249
[10] Souchay P, Ser S (1952) J Chem Phys **49**: C172
[11] Gardner J, Georgans WJ (1956) J Chem Soc 4180
[12] Zuman P, Exner O (1965) Collection **30**: 1832
[13] Bayma MS, Celik H, Ludvik J, Lund H, Zuman P (2004) Tetrahedron Lett **45**: 5113
[14] Meites L (1965) ‘‘Polarographic Techniques’’, 2nd edn, Interscience Publisher, New York, p 232

[15] Zuman P (1969) "The Elucidation of Organic Electrode Processes", Academic Press, NY, London, p 28

[16] Ghoneim MM, Ashy MA (1979) Can J Chem **57**: 1294

[17] Svehla G (2001) "Vogel's quantitative inorganic analysis", 7th edn, Addison Wesley Longman, Singapore, p 160

[18] Nichlson RS, Shain I (1964) Anal Chem **36**: 706

[19] Galus Z (1976) "Fundamental of electrochemical analysis. In: Reynolds GF (ed) Jon Wiely, New York, p 238

[20] Bard AJ, Faulkner LR (1980) "Electrochemical Methods Fundamentals and Applications", JhonWiley, New York, p 218

[21] Issa RM, Zewail AH (1979) Egypt J Chem **19**: 53

[22] Issa RM, Issa IM, El-Ezabey MS, Ahmed YZ (1969) Z Phys Chem (Leipzig) **242**: 169

[23] Abdelhal FM, Issa RM, El-Ezabey MS, Hasanein AA (1970) Z Phys Chem (Frankfurt) **59**: 73

[24] Issa RM, Zewail AH (1971) Egypt J Chem **14**: 461

[25] Yoe JH, Jones AL (1944) Indust Eng Chem Analyst **16**: 14

[26] Job P (1928) Ann Chem **9**: 123

[27] Vosburgh WC, Cooper GR (1941) J Am Chem Soc **63**: 437

[28] Sherif FG, Awad AM (1962) Inorg Nucl Chem **24**: 179

[29] Zayan SE, Issa RM, Maghrabi Y, Dessoukey MA (1973) Egypt J Chem **6**: 459

[30] Irving HM, Rossotti HS (1954) J Chem Soc **76**: 2904

[31] Lewis J, Wilkins RG (1960) "Modern Coordination Chemistry, Principles and Methods", Interscience, New York

[32] Inczedy J (1976) "Analytical Applications of Complex Equilibria", John-Wiley and Sons Inc., New York

[33] Hughes VL, Martell AE (1956) J Am Chem Soc **78**: 1319

[34] Shehatta I, Kenawy I, Askalany AH, Hassan AA (2001) Can J Chem **79**: 42

[35] El-Bindary AA, Ghoneim MM, El-Sonbati AZ, Barakat SA (1998) Monatsh Chem **129**: 1259

[36] Rossotti FIC, Rossotti HS (1955) Acta Chem Scand **9**: 1166

[37] Beck MT, Nagybal I (1990) "Chemistry of Complex Equilibria", Wiley, New York

[38] Ghoneim MM, El-Bindary AA, El-Sonbati AZ, Barakat SA (1999) Spectrosc Lett **32**: 139

[39] El-Bindary AA, El-Sonbati AZ, Kera HM (1999) Can J Chem **77**: 1305

[40] Irving HM, Williams RJP (1948) Nature **162**: 746

[41] Irving HM, Williams RJP (1952) Analyst **77**: 813

[42] Chppin GR, Brock JL (1985) Inorg Chim Acta **109**: 99

[43] Hammam AM, Ibrahim SA (1980) J Electrochem Soc India **29**: 273

[44] El-Haty MT, Adam FA, Abdel-Hamid R, Abaul-Kasim E (1987) Bull Soc Chem Franc **1**: 53

[45] Temerk YM, Abu Zuhri AZ, Issa IM, Kamal MM (1978) Indian J Chem A **16**: 706

[46] Abdel-Moez M, Sleem H, El-Shetary B (1989) Thermochim Acta **149**: 317

[47] Issa YM, Sherif OE, Abbas SM (1998) Monatsh Chem **19**: 985

[48] Ramadan AEMM, EL-Mehasseb IM (1998) Trans Met Chem **23**: 183

[49] Britton HTS (1952) "Hydrogen Ions", 4th edn, Chapman and Hall, p 113