3572 *J. Chem. Eng. Data* **2010,** *55,* 3572–3577

Physicochemical Studies on 4-(4′-Phenyl-2′-thiazolylazo) Resorcinol and Its Complexation with Some Metal Ions

F. I. El-Dossoki*,[†] and F. A. El-Seify[‡]

Chemistry Department, Faculty of Science and Faculty of Engineering, Suez-Canal University, Port-Said, Egypt

---

The ligand 4-(4′-phenyl-2′-thiazolylazo)-resorcinol (L) was prepared. The ionization constants of the ligand (pK_a) and the stability constants of the complexes with Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) have been estimated spectrophotometrically and pH-metrically at 298 K. The effect of some organic solvents and pH on the absorption spectra of the ligand and its complexation with the cations above was studied and discussed. The use of this ligand for spectrophotometric determination of the cations under investigation was also studied. Stoichiometric complexes with ratios 1:1 and 1:2 (M:L) were formed for all cations used except Cd(II) which forms only a 1:1 stoichiometric complex. Also, a conductometric study has been carried out, and the results show that the same stoichiometric complexes have formed in the solution.

Introduction

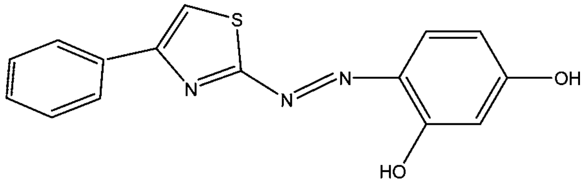
The importance of the azo colorants is shown by the fact that they embrace over 60 % of the total number of dyes.[1,2] Some azodyes have been used for spectrophotometric determinations of some transition metals.[3–5] Thiazolylazo compounds have attracted much attention as analytical reagents owing to their higher sensitivity and selectivity. A large number of analytical applications of thiazole derivatives have been described and resorcinol-based dyes used for determination of many transition metals spectrophotometrically.[6,7] In our previous work, some azo dyes of some heteroamines have been used as analytical reagents for determination of micro amounts of some transition metals.[8,9]

To investigate the analytical applications of a new thiazole derivative of a resorcinol-based dye for determination of many transition metals, the present investigation deals with the spectrophotometric, pH-metric, and conductometric behavior of the ligand 4-(4′-phenyl-2′-thiazolylazo)-resorcinol and its complexation with Co(II), Ni(II), Zn(II), and Cd(II) at 298 K.

Experimental Section

Infrared spectra were measured in KBr discs using a Mattson 5000 FT-IR spectrometer. All chemicals and reagents used in this study were either A.R. grade or purified with recommended methods.[10] Metal ion solutions (0.001 M) in bidistilled water were prepared and standardized with EDTA using the proper indicator. Also, a 0.01 M solution of the ligand was prepared in ethanol. The used solvents have the following refractive index (n)[11] and dielectric constants (D):[11] isopropanol ($n = 1.3752$, $D = 19.92$), ethanol ($n = 1.3594$, $D = 24.55$), acetone ($n = 1.3560$, $D = 20.56$), dioxane ($n = 1.4203$, $D = 2.21$), chloroform ($n = 1.4420$, $D = 4.89$), DMF ($n = 1.4280$, $D = 36.71$), DMSO ($n = 1.4770$, $D = 46.45$), and water ($n = 1.3325$, $D = 78.36$) at 298 K.

Chart 1. 4-(4′-Phenyl-2′-thiazolylazo)-resorcinol ($C_{15}H_{11}O_2N_3S$)



4-Phenyl-2-aminothiazol was prepared from condensation of bromoacetophenone and thiourea.[12] The 2-aminothiazol derivatives are readily diazotized to diazonium salts with sodium nitrite in strong oxyacids such as phosphoric acid, sulfuric acid, or nitric acid. The diazonium salts couple normally with phenols.[10] The obtained azodye was crystallized from ethanol, and its purity was confirmed by elemental analysis and IR spectra. The elemental analysis is: calculated (found), $C = 60.60$ % (60.80 %), $N = 14.14$ % (14.10 %), $H = 3.70$ % (3.60 %), and $S = 10.77$ % (10.58 %) according to the empirical formula ($C_{15}H_{11}O_2N_3S$). The melting point was >350 °C. The purity of the investigated ligand was confirmed by elemental analysis to be more than 99.5 %.

The IR spectra of the prepared azodye displays a weak broad band in the region (3400 to 300) cm^{-1}. This band is due to the stretching frequency of the hydroxyl group.[9] This may be taken as evidence for the existence of an intermolecular hydrogen bond. Two absorption bands were detected: the first one around 1088 cm^{-1} while the second is in the region (1207 to 1244) cm^{-1}. This may be assigned to a γ and δ OH. Also, the studied azodye displays a band due to N═N which appears at 1400 cm^{-1}. The band occurring at 1300 cm^{-1} is considered to be associated with the C−N bond. The confirmed structure of the ligand is shown in Chart 1.

The electronic absorption spectra of the ligand in different organic solvents (isopropanol, ethanol, acetone, dioxane, chloroform, DMF, and DMSO), at different pH values (2, 3, 4, 5, 6, 7, 8, 9, 10, and 11), and after a time interval of 48 h are also reported using a UV−vis spectrophotometer (Jasco 550). The buffers used were the modified Britton and Robinson universal series.

---

* Corresponding author. E-mail: feldossoki@yahoo.com. Present address: Chemistry Department, Faculty of Arts and Science (Tobruk), Omar Al-Mukhtar University, 919 El-Beida, Libya.

[†] Faculty of Science.

[‡] Faculty of Engineering.

10.1021/je100205u

The stoichiometric complexes which can be formed in solution between the ligand and the cations, Co(II), Ni(II), Zn(II), and Cd(II), at 298 K were also studied spectrophotometrically, potentiometrically (pH-metric), and conductometrically. To determine the optimum pH value for the complexation process, the absorption spectra of all studied complexes were investigated at different pH values (3, 4, 5, 6, 7, 8, and 9) where the molar concentrations of both metal and ligand are $5.0 \cdot 10^{-5}$ M (in the case of the 1:1 (M:L) complex) and $0.5 \cdot 10^{-4}$ M metal, $1.0 \cdot 10^{-4}$ M ligand (in the case of the 1:2 (M:L) complex).

The pH-metric measurements were carried out where the following three mixtures were prepared where HCl, KCl, and the metal ion were prepared in water, while the ligand was prepared in ethanol:

(a) 1 mL of 0.01 M HCl + 1 mL of 1 M KCl + 5 mL of ethanol + 3 mL of bidistilled water.

(b) 1 mL of 0.01 M HCl + 1 mL of 1 M KCl + 0.5 mL of 0.01 M ethanolic solution of ligand + 4.5 mL of ethanol + 3 mL of bidistilled water.

(c) 1 mL of 0.01 M HCl + 1 mL of 1 M KCl + 1 mL of 0.001 M of the metal ion solution + 0.5 mL of 0.01 M ethanolic solution of ligand + 4.5 mL of ethanol + 2 mL of bidistilled water.

The ionic strength and the activity coefficient of these solutions are 0.10125 and 0.4241 M, respectively. The mixtures were then titrated potentiometrically against 0.0064 M KOH solution and prepared in 50 % (v/v) ethanol−water, using a Mettler Toledo MP 220 pH-meter with a new glass electrode at 298 K. The pH-meter was connected with a MLW Prufgerate−Werk ultrathermostat to maintain the temperature at (298 ± 0.15) K. The pH-meter was calibrated using buffers of pH 4, 7, and 10. The pH values were precise to ± 0.01 pH units. The pH-metric readings in 50 % (v/v) ethanol−water mixtures are corrected according to the Uitert et al. relation.[13]

In a typical experiment of the conductometric study, 10 mL of a $1 \cdot 10^{-4}$ M metal salt solution was prepared in 50 % (v/v) ethanol−water by dilution from the stock solution of 0.001 M in bidistilled water and was placed in a double-jacketed cell connected to the ultrathermostat at the desired temperature. Then, a known amount of $1 \cdot 10^{-3}$ M ligand solution, prepared in 50 % (v/v) ethanol−water by dilution from the stock solution of 0.01 M in ethanol, was added by means of a micropipet. The conductance of the mixture was then measured after each addition and after stirring using a Jenway conductivity bridge. The error in conductance measurement was $\pm\ 0.1\ \mu S \cdot cm^{-1}$. Because of the low solubility of the ligand (L) in water, an ethanol−water (50 % v/v) mixed solvent was chosen as the solvent in both the potentiometric and conductometric measurements.

Results and Discussion

(i) Spectrophotometric Study. Effect of Solvents on the Electronic Absorption Spectra of the Ligand. The wavelength maxima λ_{max} and the molar absorptivities ε of electronic absorption bands in the spectra of the investigated ligand in the different organic solvents are listed in Table 1 and shown in Figure 1.

Band Assignment. The spectra of the ligand (with a concentration of $5.0 \cdot 10^{-5}$ M) in ethanol display mainly two bands. The first band at 220 nm may be assigned to the medium energy local $\pi-\pi^*$ electronic transition (1_A-1_{Bb}) within the benzene nucleus.[14] This is characterized by its high ε value (10^4 M^{-1} cm^{-1}), which may be taken as evidence for its assignment. The second band at 475 nm may be assigned to a $\pi-\pi^*$ electronic transition within the azo group, influenced by an intermolecular transfer within the whole molecule.

Table 1. Effect of Solvent on the Spectra of the Ligand[a]

solvent	λ ($\varepsilon \cdot 10^{-4}$)	λ ($\varepsilon \cdot 10^{-4}$)	λ ($\varepsilon \cdot 10^{-4}$)
ethanol	216.0 (4.30)	-	478.0 (1.20)
methanol	211.5 (5.36)	-	462.0 (1.02)
isopropanol	211.0 (5.86)	-	464.0 (1.13)
DMF	269.0 (0.97)	-	493.0 (1.26)
DMSO	260.0 (1.08)	-	497.0 (1.30)
chloroform	245.0 (1.19)	339.5 (0.53)	462.0 (1.03)
dioxan	240.0 (1.32)	340.0 (0.57)	459.0 (1.02)
acetone	211.5 (1.97)	340.5 (0.57)	460.0 (1.11)

[a] λ in nm and ε in $M^{-1} \cdot cm^{-1}$.

The investigation of the solvent effect on the spectra of the solute molecules is rather important because most spectral investigations of molecules are performed in solutions. It is known that the bands due to local transitions are sensitive to environmental changes. The solvent effect may lead to substantial changes in the optical properties, absorptivites (ε), and the absorption maximum (λ_{max}). However, the absorption spectra in different solvents are influenced by the physical properties of the solvent (dipole moment, dielectric constant, and refractive index), the difference in solvation energy from one solvent to another, and the change in the polarity and dipole moment of the solute through excitation. Accordingly, the solvent effect is the sum of the different factors, which may be additive or cancel out one another. Solvent-induced frequency shifts were interpreted in terms of electric dipole interactions. The well-known red shift in the spectra of nonpolar solutes was related to the solvation energy of the transition dipole[15] or by dispersive interactions.[16] To verify whether the band shift is due to change in solvation energy or pure dielectric effects, the relation given by Gati and Szalay[17] was applied in the form

$$\nu' = \{(a - b)(n^2 - 1/2n^2 + 1)\} + b(D - 1)/(D + 1) \qquad (1)$$

In which n and D are the refractive index and dielectric constants of the media; a and b are constants of the solvent which shows a reasonable degree of correlation with the transition energy that is the static dielectric constant (D) or more precisely a function thereof, $f(D)$[18] or $\theta(D)$.[19] The total solvent effect is composed of three independent contributions: solvent polarity (π^*),[20] acidity (α),[21] and basicity (β)[22] for a hydrogen bond acceptor (HBA). These contributions are gathered in one equation as follows

$$\nu' = \nu'_o + s\pi^* + a\alpha + b\beta \qquad (2)$$

where s, a, and b are factors and their values depend on the extent of contribution of each parameter (π^*, α, β) to the predicted value ν'.

The π^* scale is considered as a general solvent polarity scale. It gives the best correlations with the solvatochromic effect on $p-\pi^*$ and $\pi-\pi^*$ electronic spectral transitions, while α and β donate to the hydrogen bonding strength. Other solvent parameters, which can be taken into consideration, are the molecular energy (E_r) and Z-values.[23] E_r values are sensitive to polar and hydrogen bonding interaction, and also other interactions such as dispersion forces are probably operative. High Z-values correspond to high transition energy.

The stronger the stability effect of the solvent on the ion pair in the ground state as compared with that in the less polar excited state, the lower the wavelength of the intermolecular (CT) band. Therefore, Z-values provide a direct empirical measure of the

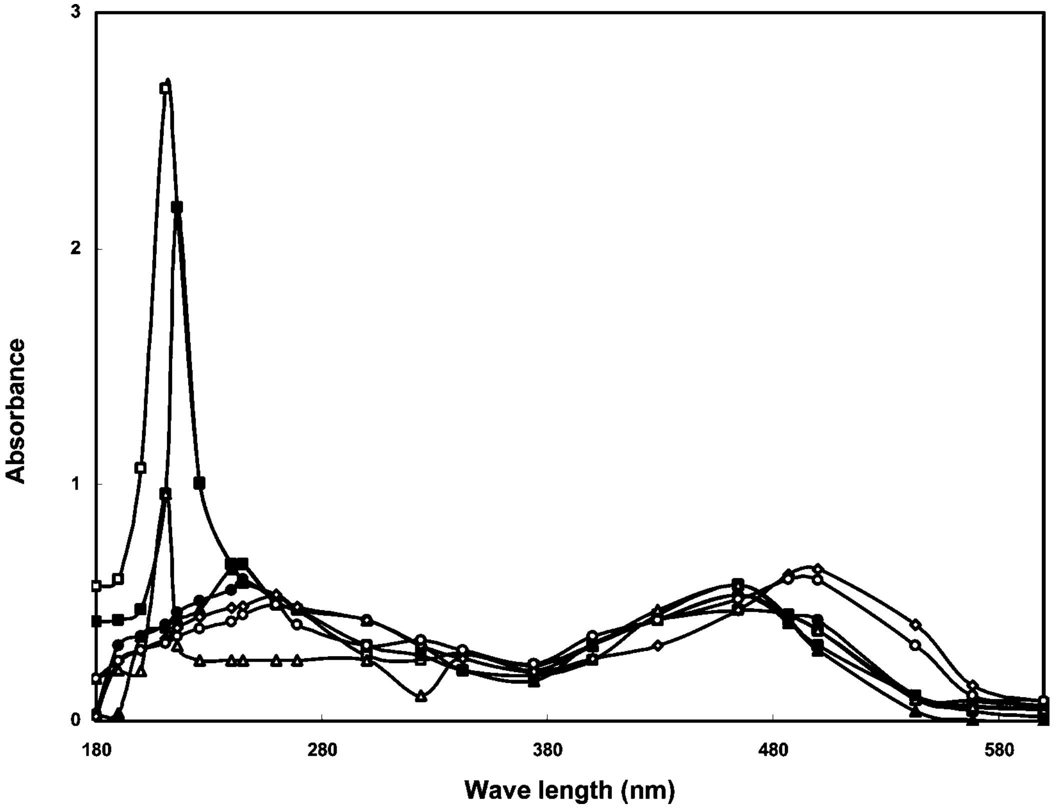


Figure 1. Absorption spectra of the ligand in different solvents: □, isopropanol; ■, ethanol; Δ, acetone; ▲, dioxane; ●, chloroform; ○, DMF; and ◇, DMSO.

Table 2. Maximum Wavelength (λ_{max}) and the Apparent Stability Constants of the M−L Complexes at the Recommended pH Values[a]

		λ_{max}, nm				color		continuous variation (molar ratio) methods	
metal ion	pH	a	b	c	Δnm	ligand	complex	1:1	1:2
Co(II)	5	460	520	550	60	yellow	red violet	4.36 (4.25)	7.82 (7.79)
Ni(II)	7	480	530	555	50	yellow	red violet	4.41 (4.28)	7.85 (7.88)
Cu(II)	6	470	540	560	70	yellow	purple	5.24 (5.31)	9.59 (9.56)
Zn(II)	8	480	520	555	40	yellow	red violet	4.62 (4.58)	8.18 (8.22)
Cd(II)	8	480	520	560	40	yellow	red violet	4.30 (4.24)	-

[a] a: Ligand against water as a blank. b: Complex against water as a blank. c: Complex against ligand as a blank.

solvation behavior of a solvent. The *Z*-values depend on temperature and electrolyte concentration. Since *Z*-values reflect the dipole−dipole, solute−solvent interaction, they give poor correlations in nonpolar solvents.

In the present article, plots of $D - 1/D + 1$ and $\Phi(D)$ against the wavelength (λ_{max}) in nanometers or the wavenumber (ν') in inverse centimeters are not strictly linear relations which may indicate that the spectral shifts are not governed solely by these parameters. Furthermore, plots of (λ_{max}) or (ν'_{max}) as a function of E_r, *Z*-values, π^*, and β scales display the same deviation from linearity. On the basis of the above results, other factors may influence the spectral shifts such as solvation stabilization of the excited state by polar solvents and hydrogen bonding between solute and solvent molecules leading to an increase in solvolysis of the molecules.[24]

Effect of pH on the Electronic Absorption Spectra of the Ligand. The ligand is a red−orange powder which is soluble in alcohol, and its solution is orange in acidic medium and rose red in alkaline solution. The optimum pH for the studied complexes is listed in Table 2, and the absorption spectra of the ligand (L) at different pH are shown in Figure 2.

The dissociation constants pK_1^H and pK_2^H were evaluated spectrophotometrically by the half height method which depends on the fact that the limiting absorbance Λ_1 represents complete conversion of one form of the compound to the other. To determine the values of the dissociation constants pK_1^H and pK_2^H spectrophotometrically by the half height method, the limiting absorbance−pH curve was obtained. Since pK is equal to pH when the two forms of the compound exist in equivalent amounts, then the pH corresponding to half (0.5) of the limiting absorbance in the limiting absorbance−pH curve is equal to pK_1^H and the pH corresponding to one and a half (1.5) of the limiting absorbance is equal to pK^{H}_2. The values of pK_1^H and pK^{H}_2 were found to be 10.90 and 6.10, respectively. These values are comparable with that obtained for similar compounds (10.30, 10.50, 10.54 and 6.4, 6.55, 5.9).[25] The value of pK_2^H is related to the ionization of the *para*-OH group, while pK_1^H is related to the ionization of the *ortho*-OH group.[25] This can be explained where the *ortho*-OH group can form intermolecular hydrogen bonds with the azo group.[25] Increasing the pH values leads to the bathochromic effect of the main band from about (460 to 500) nm, and this is accompanied by a hypochromic effect as shown in Figure 2.

Chromomeric Reaction with Metal Ions. (a) Optimum pH and Wavelength. The absorption spectra of all studied complexes were investigated at different pH values. The optimum pH for developing the red violet color of the complexes of the ligand L with Co(II), Ni(II), Cu(II), Zn(II), and Cd(II)

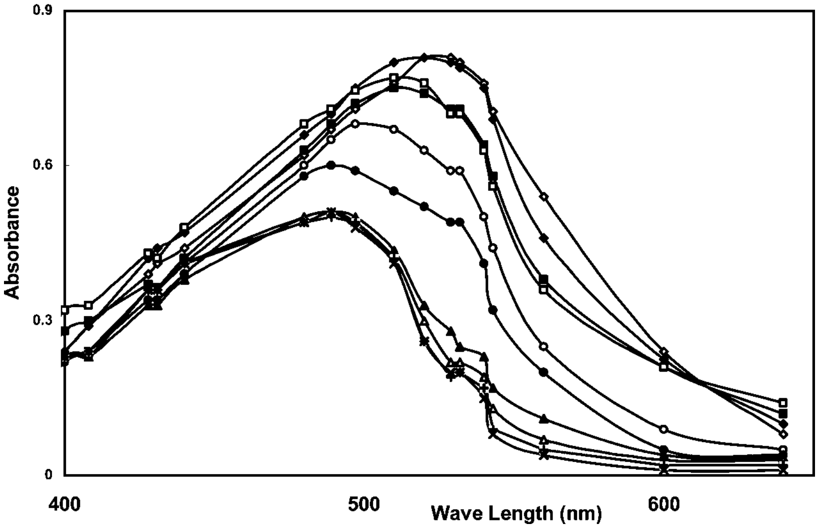


Figure 2. Absorption spectra of the ligand at different pH values: ◇, pH 11; ◆, pH 10; ■, pH 9; □, pH 8; ○, pH 7; ●, pH 6; ▲, pH 5; △, pH 4; +, pH 3; and ×, pH 2.

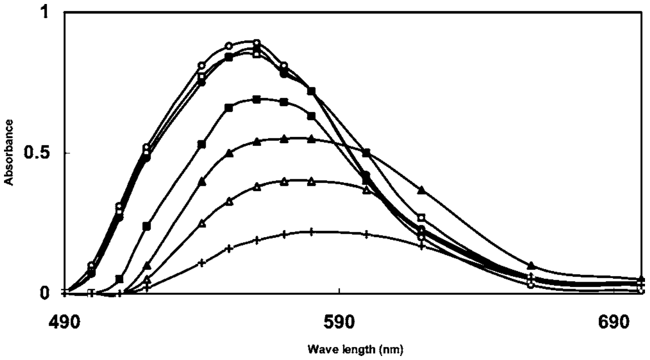
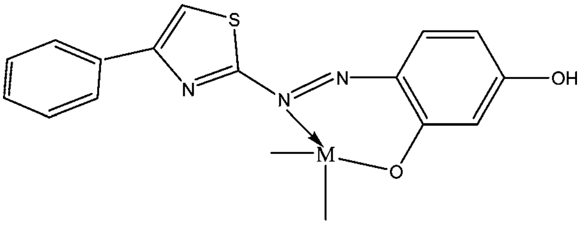


Figure 3. Absorption spectra of the Ni/L complex at different pH values: ■, pH 9; □, pH 8; ○, pH 7; ●, pH 6; ▲, pH 5; △, pH 4; and +, pH 3.

Chart 2. Suggested Structure for 1:1 (L:M) Stoichiometric Complexes in Solution



and the maximum wavelengths are given in Table 2 and shown in Figure 3 for the L−Ni complex as an example where this spectrum is for the complex against the ligand as a blank (case c in Table 2). The suggested reaction between the metal and the ligand is

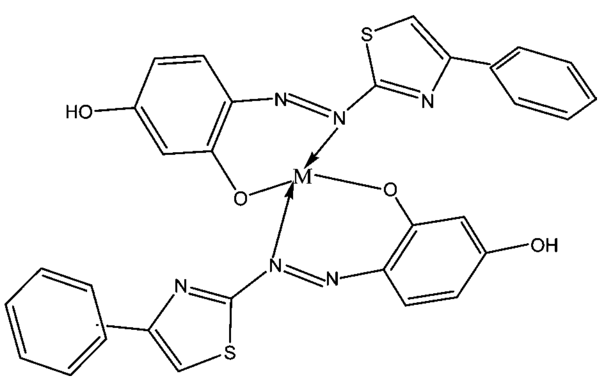
$$H_2L + M^{2+} = MHL^+ \quad \text{for the 1:1 (M:L) complex} \tag{3}$$

$$HLM^+ + H_2L = M(HL)_2 \quad \text{for the 1:2 (M:L) complex} \tag{4}$$

The suggested structures of the formed stoichiometric complexes in solution are shown in Charts 2 and 3.

The presence of the metal ion in the complexation process with the ligand enhances the dissociation of the OH groups so that they dissociate at lower pH values (see Table 2).

Chart 3. Suggested Structure for 1:2 (M:L) Stoichiometric Complexes in Solution



(b) Effect of Time. The effect of time on the stability of the complexes was also studied. The color intensity of the complexes was found to be stable, and no variations were observed after 48 h. All the complexes are formed instantaneously.

(c) Beer's Law Verification. Beer's law was verified and found to be satisfactorily obeyed with a concentration up to (2.96, 2.95, 2.92, 2.94, and 2.24) $mg \cdot L^{-1}$ or $(4.658 \cdot 10^{-5}$, $5.000 \cdot 10^{-5}$, $4.974 \cdot 10^{-5}$, $4.497 \cdot 10^{-5}$, and $1.993 \cdot 10^{-5})$ M for Cu(II), Co(II), Ni(II), Zn(II), and Cd(II), respectively, in methanol or isopropanol.

(d) Composition of the Complexes. The composition and apparent stability constants of the complexes were evaluated by the continuous variation and molar ratio methods (Table 2). Both methods indicate the formation of the 1:1 and 1:2 (M:L) complexes for all metals under investigation except for Cd(II) where only the 1:1 complex is formed. The molar ratios for the L−Ni complex as an example are shown in Figure 4.

Recommended Procedures for the Determination of Metals. The recommended procedures for the spectrophotometric determination of the metals under investigation can take place as follows: Into a 25 mL volumetric flask is prepared a complex solution containing $4 \cdot 10^{-5}$ M ligand, nearly $(1 \text{ to } 2.0) \cdot 10^{-5}$ M of the metal ion, and 5 mL of the universal buffer of the recommended pH for each metal ion. The absorbance of the complex is measured at λ_{max} for each metal against the ligand blank. The concentration of the metal is determined from the standard calibration curve obtained under the same conditions.

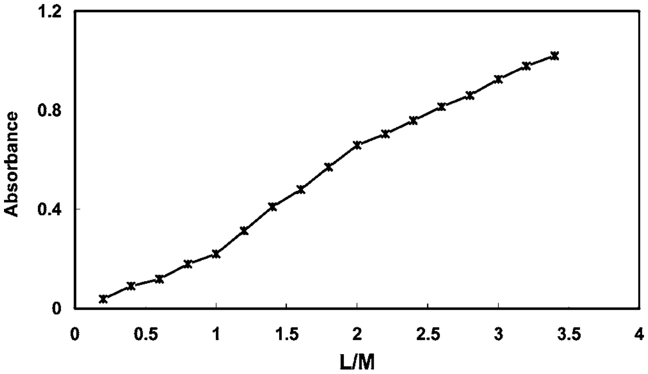


Figure 4. Molar ratio for the ligand/Ni(II) complex at 555 nm and pH 7.

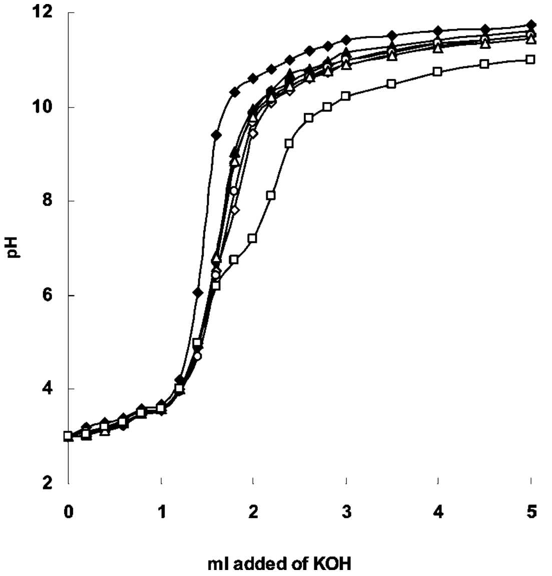


Figure 5. Potentiometric titration curves of: ♦, acid; ▲, ligand; □, Cd(II); Δ, Zn(II); ◇, Ni(II); ○, Cu(II); and ●, Co(II).

As an example, for Cu(II), into a 25 mL volumetric flask was prepared a Cu−L complex solution which contains 1 mL of 0.001 M ligand, 0.3 mL of 0.001 M of Cu(II), and 5 mL of the universal buffer of the recommended pH = 6, and the measuring flask was completed with bidistilled water. The absorbance of the complex at $\lambda_{max} = 560$ nm was measured against the ligand blank, and the concentration of Cu(II) was determined from the standard calibration curve obtained under the same conditions.

(ii) Potentiometric Study. pH-metric measurements were carried out as reported in the Experimental Section. For the ligands and their complexes with Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) in a 50 % (v/v) ethanol−water mixture at 298 K, the plots of pH versus the milliliters of added KOH are shown in Figure 5. These curves show that the ionization of the ligand and so the complexation process with the cations under study take place starting from pH ~4. As can be noted from Figure 5, there is an overlap of the curves at some points which can be related to the small difference in the pH values and so a small difference in the volume consumed of the KOH solution in addition of the metal ions to the ligand compared to that in the case of the ligand itself. It must be noted that the analysis of the curves was made for each curve separately to prevent any confusion. Also, it must be noted that the pH of the ligand is higher than that of (L + metal ion), which indicates a complexation process.

The Irving and Rossotti equation was used to determine the number of protons associated with the ligand molecule ($\bar{n}_A$)

$$\bar{n}_A = y + \{(v_1 - v_2)(N^o + E^o)/(v^o + v_1)TC_L^o\} \quad (5)$$

where v_1 and v_2 are the volume of KOH required to reach the same pH in the titration curve of the free acid and the ligand, respectively; v^o is the initial volume of the mixture; TC_L^o is the total concentration of the ligand; N^o is the normality of KOH solution; and E^o is the initial concentration of the free acid. A plot of $\bar{n}_A$ versus pH gives the proton−ligand formation curves. Then the values of pK_1^H and pK_2^H are the values of pH at $\bar{n}_A$ equal to values of 0.5 and 1.5, respectively. The obtained pK_1^H and pK_2 of the ligand were also refined (recalculated) with the ESAB2M computer program[26] with a deviation of less than ± 0.12 between the two methods. The maximum $\bar{n}_A$ value is ~2, revealing that the ligand has two dissociable protons (the hydrogen ions of the two −OH groups in the resorcinol moiety). The value of pK_2^H of the ligand equals 4.8 related to the ionization of the *para*-OH group,[27] while the pK_1^H value is 10.8 and related to the ionization of the *ortho*-OH group.[9] This can be explained where the ionization of the two −OH groups proceeds in different steps with increasing pH; i.e., the ionization of the *para*-OH group occurs first in acidic media, after the ionization of the *ortho*-OH group which can form an intermolecular hydrogen bond with the azo group that takes place in the basic media.[27]

The stability constants of the stoichiometric 1:1 and 1:2 (M:L) complexes formed in solution between the ligand and the studied cations have been determined using the Rossotti and Iriving formula and then refined with the Superquad computer program[28] with a deviation of ± 0.15 between the two methods.

The standard Gibbs energy changes ($\Delta G°$) of the ionization and complexation processes were calculated using eq 6

$$\Delta G° = 2.303RT \quad pK = -2.303RT \log K \quad (6)$$

The values of the ionization constants of the ligand, the stability constant of the formed complexes, and the standard Gibbs energy change are listed in Table 3. By inspection of the stability constants of the formed complexes in Table 3, we can note that according to the well-known Irving−Williams rule the Cd(II)−organic ligand complexes have lower stability constants than those obtained by the same ligand, in reaction with for example Cu(II) or Ni(II) ions. On the other hand, Figure 5 shows that the Cd(II) curve is below that of other metal ions used. This is considered as an unexpected behavior of the Cd(II) ion where it has a lower stability constant as the results in Tables 2 and 3 indicate. This indicates that Cd(II) consumes a large volume of KOH in the potentiometric titration process compared to the other metal ions studied. This unexpected behavior of Cd(II) can be explained by the suggestion of the formation of $Cd(OH)_2$ instead of Cd−L complexes.

The positive values of the standard Gibbs energy change ($\Delta G°$) of the ionization process indicate that the dissociation process of the ligand is not spontaneous which may be related

Table 3. Formation Constants, Ionization Constants, and the Gibbs Energy Change ($\Delta G°$, kJ·mol^{-1}) of the Ligand and the Formed Complexes from the Potentiometric Study[a]

	1:1		1:2	
complex	log K_1	$-\Delta G°_1$	log K_2	$-\Delta G°_2$
ligand	−10.8 (0.04)	−61.6	−4.8 (0.05)	−27.4
Co(II)	4.44 (0.03)	25.3	7.2 (0.03)	41.0
Ni(II)	4.52 (0.03)	25.8	7.3 (0.04)	41.6
Cu(II)	5.18 (0.04)	29.5	9.7 (0.03)	55.3
Zn(II)	4.68 (0.04)	26.7	8.3 (0.05)	47.3
Cd(II)	4.41 (0.04)	25.1	--	--

[a] Standard deviations are given in parentheses.

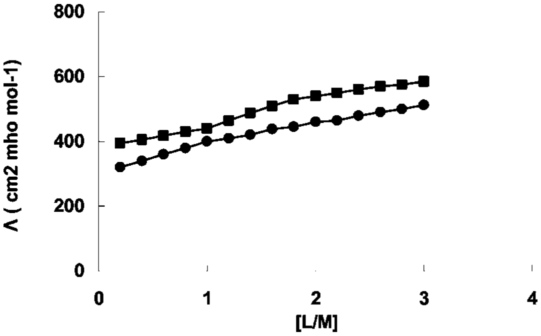


Figure 6. Conductometric titration curves for the ligand with: ●, Cd(II); and ■, Cu(II).

to the presence of intermolecular hydrogen bonds. On the other hand, the negative values ($\Delta G°$) of the complexation process indicate that this process is spontaneous.

(iii) Conductometric Study. The formation of different stoichiometric complexes in aqueous and nonaqueous solution has been studied conductometrically.[29–32] The conductometric titration of the ligand with the metal was carried out as reported in the Experimental Section. A plot of the molar conductance (Λ) $(\mathrm{S\cdot cm^2\cdot mol^{-1}})$ versus the ratio of the ligand to metal ion concentration (L/M) is shown. Figure 6 gives a straight line with two breaks at [L/M] ratios of 1 and 2 for all used cations except Cd(II) which gives one break at an [L/M] ratio of 1.

As shown from Figure 6, the increase of the molar conductance of the metal ion solution in addition of the ligand solution is related to the substitution of a small conducting species {M(II), limiting ionic conductance, $\lambda_o = (100 \text{ to } 110)$ $\mathrm{S\cdot cm^2\cdot mol^{-1}}$} with a high conducting one (H^+, $\lambda_o = 349.8$ $\mathrm{S\cdot cm^2\cdot mol^{-1}}$). This leads to the complexation process and the gradual formation of the MHL^+ and $M(HL)_2$ species. At the equivalent points and complete formation of (MHL^+, 1:1) or {$M(HL)_2$, 1:2} (M:L) species, which have different conductivity than the previous species, a change in the direction of the conductometric titration curve results, leading to a break in this curve. This result indicates the formation of 1:1 and 1:2 (M:L) stoichiometric complexes between the metal ion and the ligand under investigation.[29–32] This result agrees with that obtained from both spectrophotometric and pH-metric studies.

Literature Cited

(1) Fabian, J.; Hartman, J. *Light absorption of organic colorants*; Springer-Verlag: New York, 1980.
(2) Allen, R. L. M. *Colour Chemistry*; Nelson: London, 1971.
(3) Marczenco, Z. *Spectrophotometric Determination of Elements*; Wiley: New York, 1976.
(4) Martin, E. M.; Bereman, R. D. Synthesis and characterization of neutral Ni(II) and Cu(II) complexes with bidentate [NS]$^{1-}$ ligands. *Inorg. Chimica Acta* **1991**, *188* (2), 233–242.
(5) Chaisuksant, R.; Palkawong-na-ayuthaya, W.; Grudpan, K. Spectrophotometric determination of copper in alloys using naphthazarin. *Talanta* **2000**, *53* (3), 579–585.
(6) Visser, A. E.; Griffin, S. T.; Hartman, D. H.; Rogers, R. D. Naphthol- and resorcinol-based azo dyes as metal ion complexants in aqueous biphasic systems. *J. Chromatogr. B: Biomed. Sci. Appl.* **2000**, *743* (1−2), 107–114.
(7) Wen-Bin, Q.; Li-Zhong, Z. Spectrophotometric determination of trace amounts of cadmium and zinc in waste water with 4-(2-pyridylazo)-resorcinol and mixed ionic and non-ionic surfactants. *Talanta* **1985**, *32* (10), 1013–1015.
(8) El-Ansary, A. L.; Issa, Y. M.; Ali, A. A. Stability Constants of Dioxouranium (VI) Complexes with Some 5-(Arylazo)-8-hydroxyquinolines. *Indian J. Chem.* **1984**, *22A*, 933–936.
(9) El-Seify, F. A.; El-Dossoki, F. I. Spectrophotometric, Ph-metric and conductometric Studies on Some 3-Arylhydrazone Derivatives of (2-thenoyl) ethylpyruvate. *J. Korean Chem. Soc.* **2006**, *50*, 299.
(10) Vogel, H. I. *Practical Organic Chemistry Including Quantitative Organic Analysis*, 5th ed.; Longmans: London, 1991.
(11) Marcus, Y. *The properties of solvents*, 3rd ed.; John Wiley & Sons: New York, 1999.
(12) Elnagadi, M. H.; El-Moghager, M. R. H.; Fieita, D. H.; Nafez, E. A. A.; Fahmy, S. M. Pyrimidine derivatives and related compounds. 4. A route for the synthesis of pyrazolo [3,4-e]-as-triazines, pyrazolo[3,4-d]pyrimidines, and pyrazolo[1,5-c]-as-triazines. *J. Org. Chem.* **1976**, *41* (24), 3781–3784.
(13) Van Uitert, L. G.; Fernelius, W. C. Determination of thermodynamic equilibrium constants in mixed solvents. *J. Am. Chem. Soc.* **1954**, *76* (22), 5887–5888.
(14) Suppan, P. Charge-transfer states in aromatic molecules: π-π^* States. *J. Mol. Spectrosc.* **1969**, *30* (1−3), 17–28.
(15) Midwinter, J.; Suppan, P. Spectral shifts in solvent mixtures. *Spectrochim. Acta, Part A: Mol. Spectrosc.* **1969**, *25* (5), 953–958.
(16) Suppan, P. Spectral shifts in non-polar solvents. *Spectrochim. Acta, Part A: Mol. Spectrosc.* **1972**, *28* (3), 599–600.
(17) Das, M.; Rabinowitch, E.; Szalay, L.; Papageorgiou, G. Sieve-effect, in Chlorella suspensions. *J. Phys. Chem.* **1967**, *71* (11), 3543–3549.
(18) Suppan, P. Polarizability of excited molecules from spectroscopic studies. *Spectrochim. Acta, Part A: Mol. Spectrosc.* **1968**, *24* (8), 1161.
(19) Kamlet, M. J.; Taft, R. W. The solvatochromic comparison method. I. The beta.-scale of solvent hydrogen-bond acceptor (HBA) basicities. *J. Am. Chem. Soc.* **1976**, *98* (2), 377–383.
(20) Taft, R. W.; Kamlet, M. J. The solvatochromic comparison method. 2. The alpha.-scale of solvent hydrogen-bond donor (HBD) acidities. *J. Am. Chem. Soc.* **1976**, *98* (10), 2886–2894.
(21) Reichard, C. *Solvent and Solvent Effect In Organic Chemistry*, 2nd ed.; VEH: Weinheim, 1988.
(22) Kamlet, M. J.; Dickinson, C.; Taft, R. W. Linear solvation energy relationships Solvent effects on some fluorescence probes. *Chem. Phys. Lett.* **1981**, *77* (1), 69–72.
(23) Yokoyama, T.; Komaki, T.; Sato, H.; Taft, R. W.; Anvia, F. Resonance and solvent effects on absorption spectra. 7. Substituent solvation effects on nitrogen-15 chemical shifts of para-substituted anilines and meta-substituted 2-nitroanilines. *J. Org. Chem.* **1989**, *54* (16), 3983–3984.
(24) Ghoneim, N.; Suppan, P. Solvatochromic shifts of non-dipolar molecules in polar solvents. *Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc.* **1995**, *51* (6), 1043–1050.
(25) Abdel-Mageed, K. A. Physico Analytical Studies on Some Heterocyclic Azo Dyes and their Metal complexes with Some transition Metals. Ms Thesis. Fac. Of Science, Suez- Canal Univ., Egypt, 1996.
(26) De Stefano, C.; Princi, P.; Rigano, C.; Sammartano, S. Computer Analysis of Equilibrium Data in Solution. ESAB2M: An Improved Version of the ESAB Program. *Ann. Chim. (Rome)* **1987**, *77*, 643–675.
(27) Omar, M. Spectroscopic, Spectrophotometric and Potentiometric Studies on 3-(naphthyazo)-5-Phenylpyrazolen Dye and Its Metal Chelates. *Ann. Chim.* **2002**, *92*, 601–614.
(28) Sabatini, A.; Vacca, A.; Gans, P. Mathematical algorithms and computer programs for the determination of equilibrium constants from potentiometric and spectrophotometric measurements. *Coord. Chem. Rev.* **1992**, *120* (1), 389.
(29) El-Dossoki, F. I.; Refat, M. S.; Grabchev, I. Potentiometric and Conductometric Studies on 3-Azomethine Substituted of Benzanthrone dyes. *Orient. J. Chem.* **2007**, *23* (1), 119–128.
(30) El-Dossoki, F. I.; Shoair, A. F.; Hosny, N. M. Hydroxycoumarine azodye, Thermal Stability, Harmonic Vibrational Spectra, Conductance and pH Measurements. *J. Chem. Eng. Data* **2010**, *55* (1), 267–272.
(31) Rounaghi, G. H.; Zavvar, M. H. A.; Saremi, A. Study of Complexation Reactions Between Alkali and Alkaline- Earth Metal Cations With Dibenzo-18-Crown-6(DB18C6) in Mixed Non aqueous Solvents Using the Conductometric Method. *Russ. J. Inorg. Chem.* **2007**, *52* (1), 134–140.
(32) El-Dossoki, F. I. Electric conductance and semi-empirical studies on two thiophene derivatives/metal cation complexation. *J. Mol. Liq.* **2008**, *142*, 53–56.

Received for review March 5, 2010. Accepted May 28, 2010.

JE100205U