

2-Thenoyl Ethylpyruvate의 몇 가지 3-Arylhydrazone 유도체에 대한 분광광도법, pH 및 전도도법 연구

F. A. El-Seify[†] and F. I. El-Dossoki^{*}

[†]Chemistry Department, Faculty of Engineering, Port-Said, Suez Canal University, Egypt

^{*}Chemistry Department, Faculty of Education, Port-Said, Suez Canal University, Egypt

(2005. 8. 18 접수)

Spectrophotometric, pH-metric and Conductometric Studies on Some 3-Arylhydrazone Derivatives of (2-Thenoyl) Ethylpyruvate)

F. A. El-Seify[†] and F. I. El-Dossoki^{*}

[†]Chemistry Department, Faculty of Engineering, Port-Said, Suez Canal University, Egypt

^{*}Chemistry Department, Faculty of Education, Port-Said, Suez Canal University, Egypt

(Received August 18, 2005)

요 약. 3-(2-thenoyl) 3-(p-NO₂-phenylhydrazone) ethyl pyruvate(I), p-Br(II) 및 p-CH₃(III)의 에탄올 용액의 전자 흡수 스펙트럼을 조사하여 스펙트럼이 전자 전이에 해당하는 4개의 흡수띠로 구성되어 있음을 알았다. 이들 화합물의 pK 값을 분광광도법 및 pH 측정법으로 조사한 결과, 화합물(I)의 변색 범위는 페놀프탈레인과 유사한 8~10으로, 산-염기 지시약으로 사용될 수 있음을 알았다. 몇 가지 전이원소 (Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), UO₂(II), La(III) 및 Zr(IV))와 이들 화합물과의 연속안정도상수를 pH 법으로 조사하여 본 결과, 모든 금속과 몰 비 1:1 및 1:2 (M: L)의 화학양론적 착물을 형성하며, 세 가지 유도체의 pK 값과 착물의 안정도 상수(log K)의 순서는 III > II > I임을 알았다. 또한 전도도법 적정을 수행하여 이 적정이 금속이온과 리간드를 정량하는데 사용할 수 있음을 알았다.

주제어: Conductometric Titration, Acid-base Indicator, Pyruvate Derivatives

ABSTRACT. The electronic absorption spectra of [3-(2-thenoyl) 3-(p-NO₂-phenylhydrazone) ethyl pyruvate] (I), p-Br (II) and p-CH₃ (III) were studied in ethanol and the spectra comprise four absorption bands which assigned to the corresponding electronic transition. The pK values of these compounds have been determined spectrophotometrically and pH-metrically, the results shown that the interval range for color change of compound (I) is (8-10) similar to that of phenolphthalin indicator, indicating that this compound can be used as acid-base indicator. The successive stability constants of the compounds under study with some transition elements (Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), UO₂(II), La(III) and Zr(IV)) have been determined pH-metrically, Stoichiometric complexes with ratios 1:1 and 1:2 (M: L) were formed for all metals. The pK of the three derivatives and the values of the stability constant (logK) of the complexes have the order; III > II > I. Also conductometric titrations have been carried out and the results show that this titration can be used for determination of both the metal ion and the ligand concentrations by each others.

Keywords: Conductometric Titration, Acid-base Indicator, Pyruvate Derivatives

INTRODUCTION

Arylhydrazone and their metal complexes are characterized by considerable significance and impor-

tance due to their applications as chemotherapeutic agents,¹ insecticides² chromogenic reagents,³ photo-receptors in electrophotography and also in analytical chemistry.⁴ Some binuclear complexes of some

transition metals with some 2-arylhydrazone of 2,3-dioxopentanedioate derivatives were also prepared.^{5,6} The formation of different stoichiometric complexes in solution^{7,8} and the solvation process⁹ have been studied conductometrically not only in aqueous solutions but also in non aqueous or mixed ones. In continuation of our previous work on the acid-base indicators,^{10,11} the present study deals with spectrophotometric, pH-metric and conductometric investigations to evaluate both the proton-ligand ionization constants of some arylhydrazone derivatives of (2-thenoyl) ethyl pyruvate and the stability constants of their stoichiometric complexes with some transition elements.

EXPERIMENTAL

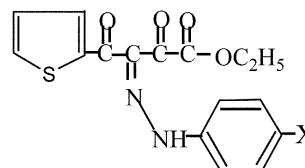
The ligands under investigation (3-(2-thenoyl), 3-(p-nitrophenylhydrazone) - ethylpyruvate), p- Br and p- Cl, were prepared as reported earlier¹² (structures I, II, and III respectively). All other chemicals and reagents used in this study were either of A.R. grade or purified with the recommended methods.¹³ Solutions (0.01) molar of the ligands were prepared in ethanol and the metal ion solutions (0.001) molar in bidistilled water were also prepared and standardized with EDTA using the proper indicator.¹³⁻¹⁵ Also solutions of HCl (0.01 N) and KCl (1 M) were prepared in bidistilled water. A carbonate free KOH solution (0.004 N) in 50% (v/v) ethanol-water mixtures was standardized against Analar oxalic acid and used as titrant. Modified Britton-Robinson universal buffer series¹⁶ and a Jasco recording spectrophotometer model 550 were used for spectrophotometric measurements. The pH- metric titration was carried out as reported in our previous work¹⁷ where the following three mixtures were prepared:

- 1 ml 0.01 N HCl + 1 ml 1 M KCl + 5 ml ethanol.
- 1 ml 0.01 N HCl + 1 ml 1 M KCl + 0.5 ml 0.01 M ethanolic solution of ligand + 4.5 ml ethanol.
- 1 ml 0.01 N HCl + 1 ml 1 M KCl + 0.5 ml 0.01 M ethanolic solution of ligand - 1 ml 0.001 M of the metal ion solution + 4.5 ml ethanol.

the volume in the three mixtures was made up to 10 ml with bidistilled water, then the mixtures were

titrated potentiometrically against 0.004 N KOH solution prepared in 50% (v/v) ethanol-water using a pH-meter of a type (Mettler Toledo MP 220) at 298 K.

The pH- metric reading in 50% (v/v) ethanol-water mixtures are corrected according to Uiter and Hass relation.¹⁸



Structures: (I): (X=NO₂); (II): (X=Br); (III): (CH₃)

The conductometric titration was carried out at 298 K by addition of (0.001 M) solution of the used ligands to 10 ml (0.0001 M) solution of the metal cation (all in 50% (v/v) ethanol-water solvent) and vice-versa. The conductance of the metal ion solution was measured ($\approx 0.1 \mu\text{s cm}^{-1}$) before and after each addition of 0.2 ml of the titrant solution using a conductivity bridge of a type (Jenway). The pH-meter and the conductivity bridge were connected with Ultrathermostat of a type (MLW Prufgerate - werk) to maintain the temperature at 298 K.

RESULTS AND DISCUSSION

Spectrophotometric studies

The electronic spectra of p- NO₂ derivative (I) in ethanol display mainly four absorption bands, the first band at 200 nm may be assigned to the medium energy (π - π^*) transition of phenyl moiety ($1L_s-1_A$)¹⁹ which is supported by the high ϵ values amounting to ($4-5 \times 10^4$). The second band absorbed at 270 nm due to (π - π^*) transition thiophene moiety. The third band observed at 400 nm has been attributed to the methene group (C=N) in the compound. The fourth band observed at 500-550 nm in alkaline medium can be related to quinoidal structure of the nitro benzene ring as a result of charge transfer in the molecular as all.²⁰

Absorption spectra and indicator constant

Absorption spectra of p- NO₂ derivative (I) at vari-

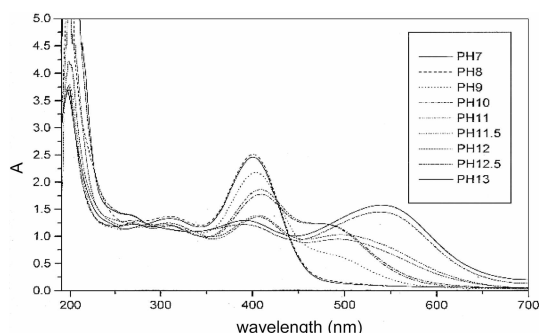
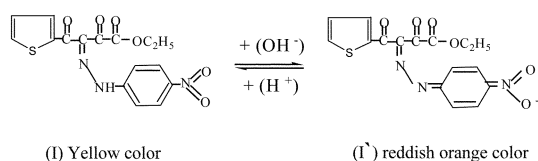


Fig. 1. Effect of pH on the spectra of ligand (I) in alkaline medium.

ous pH values are shown in Fig. 1 in alkaline media (7-13 pH). As the pH raised, deprotonation of hydrazone occurs result in the quinolidal chromophore (I') as the following equilibrium suggested;



This structure modification are related to a bathochromic shift (Shift of light absorption towards a low frequencies or higher wavelengths) and a hypochromic effect (decrease in the intensity of an absorption band) from 400 to 420 nm for the first band continued in a bathochromic shift and a hyperchromic effect (increase in the intensity of an absorption band) from 500 to 560 nm for the second band with increasing the pH value (Fig. 1). This effect is conditioned by intensification of the conjugated nature of the molecule. The $pK_a^{H^+}$ of the investigated compound (I) was determined with value equal (9) applying the half height method where the pK is equal to pH when two forms exist in equivalent amounts, then the pH corresponding to half the height of the absorbance- pH curve is equal to pK . hence the interval range for color change is (9 ± 1) i.e (8-10 pH) similar to that of phenolphthalein indicator. The color change of the reagent as a result of pH change indicates that it would be suitable as acid - base indicator (for titration of strong and weak acids with strong base and given very

clear end points).

For other arylhydrazone derivatives (p- Br(II) and p- CH_3 (III)), the absorption spectra curves at different pH values (7-13 pH) were carried out with no sharp change in the color hence, these derivatives are not suitable to be used as acid - base indicators. This may be due to the high donor property of (CH_3) and low withdrawing property of (Br) comparing to (NO_2) group. Also this may be due to the absence of conjugation and so the quinolidal chromophore in ligands II and III.

Application as acid - base indicators:

i) Indicator concentration and reversibility: hydrochloric acid solution were titrated with standard sodium hydroxide solutions in the presence of different concentrations of indicator (I) (1.25×10^{-5} – 10^{-3} M); volumes were about 40 ml at the end point. These indicator concentrations suffice to give sharp changes of color at the end - points. The recommended quantities of the indicators are about 0.5 ml of 10^{-3} M solution in a total volume of about 40 ml.

ii) The reversibility of the indicator was satisfactory: one drop of 0.05 N alkali or acid gave the color change from yellow to reddish orange or vice - versa.

iii) Precision and accuracy: precision and accuracy were calculated^[1] from the results of a large number of titrations with the indicator using acid or base as titrant. The typical results given in Table 1 show that the proposed indicator have nearly the same accuracy and precision in most cases as phenolphthalein. Analogous results were obtained when HCl solutions were titrated with different concentrations of NaOH between (0.1-0.001 N). However, very sharp end-points were obtained only when the NaOH concentration is 0.01. As the indicator change color in basic medium, it is suitable for titrations of many weak acids with NaOH; oxalic, acetic, tartaric, citric, succinic and phosphoric acids were titrated in water and benzoic, phthalic, salicylic acids in aqueous ethanol solvent. The titration of benzoic and phthalic acids with KOH was also carried out in non aqueous (ethanol) media. A clear and sharp end points

Table 1. Comparison of results for titrations of different weak and strong acids with 0.10 N NaOH in the presence of indicator (L.) and phenolphthaline (ph ph).

Acid	Acetic acid 0.1 N		Oxalic acid 0.1 N		Benzoic acid 0.1 N	
Indicator	L.I ph ph		L.I ph ph		L.I ph ph	
$\bar{X} \pm t_{0.95} S/\bar{X}$	19.9±0.014	19.88±0.069	20.15±0.069	20.15±0.014	20.94±0.052	20.50±0.053
S	0.011	0.057	0.011	0.027	0.041	0.041
Average deviation from mean	--	0.211	--	0.12	0.12	0.16
Maximum deviation from mean	--	0.38	--	0.15	0.30	0.30
Acid	o- Phthalic acid 0.1 N		Salicylic acid 0.1 N		Citric acid 0.1 N	
Indicator	L.I ph ph		L.I ph ph		L.I ph ph	
$\bar{X} \pm t_{0.95} S/\bar{X}$	20.25±0.16	20.21±0.053	19.00±0.044	18.92±0.033	19.98±0.058	19.84±0.050
S	0.012	0.042	0.035	0.027	0.045	0.042
Average deviation from mean	--	0.15	0.105	0.127	0.21	0.19
Maximum deviation from mean	--	0.28	0.26	0.16	0.24	0.36
Acid	Tartaric acid 0.1 N		HCl acid 0.1 N		H ₃ PO ₄ acid 0.1 N	
Indicator	L.I ph ph		L.I ph ph		L.I ph ph	
$\bar{X} \pm t_{0.95} S/\bar{X}$	19.68±0.033	19.61±0.053	18.85±0.014	18.87±0.033	13.85±0.019	13.80±0.019
S	0.027	0.032	0.012	0.024	0.011	0.012
Average deviation from mean	0.12	0.16	--	0.15	--	0.15
Maximum deviation from mean	0.15	--	--	0.15	--	0.15

Each titration was done 5 times. The mean result, \bar{X} , is given with a probability of 0.95 ($t_{0.95} S/\bar{X}$; $t_{0.95} = 2.76$ for $n = 5$ and $S/\bar{X} = S/n^{1/2}$, S being the standard deviation).

were observed.

iv) Indicator errors: the indicator solutions were prepared in their acidic form. To convert 2 ml of a 10^{-2} M solution of the indicator to the fully deprotonated form would theoretically require 0.24 ml of 0.1 N NaOH. With the recommended quantities of indicator, the indicator errors should not exceed 0.02 ml of 0.1 M solution. This small indicator error was confirmed experimentally.

v) Stability of stock indicator solutions: freshly prepared ethanolic solutions of the indicator (10^{-3} M) were stored for several weeks in clear glass bottles exposed to diffused daylight and artificial light not to direct sunlight. The visible absorption spectra recorded immediately, after storage for 3, 7, 10, 14, and 21 days, were exactly the same.

Potentiometric studies:

Potentiometric measurements were carried out as explained in the experimental section for the ligands under investigation and its complexes in 50% (V/V) ethanol-water and 0.1 M KCl at 298 K. The plots of pH versus the ml added from KOH (potentiometric

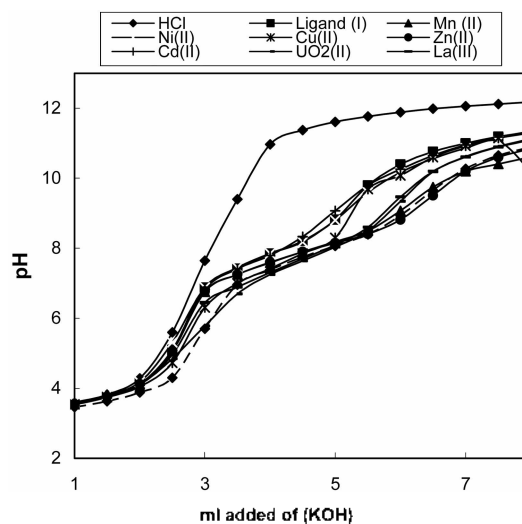


Fig. 2. Potentiometric titration curves of ligand (I) and its metal complexes in 50% (v/v) ethanol-water mixture and 0.1 M KCl at 298 K.

ric titration curves) are shown in Figs 2, 3 and 4. These curves show that the ionization of the ligands and so the complexation process between the metal cations and the ligands under investigation takes

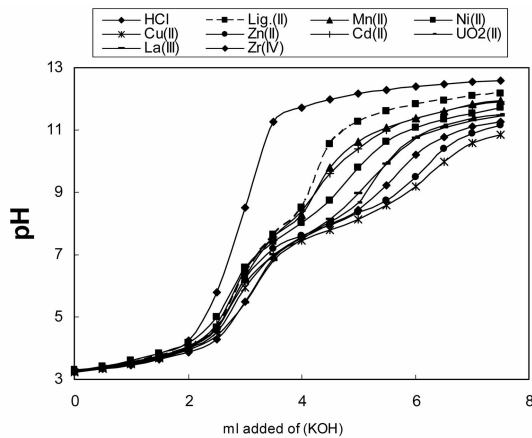


Fig. 3. Potentiometric titration curves of ligand (II) and its metal complexes in 50% (v/v) ethanol-water mixture and 0.1 M KCl at 298 K.

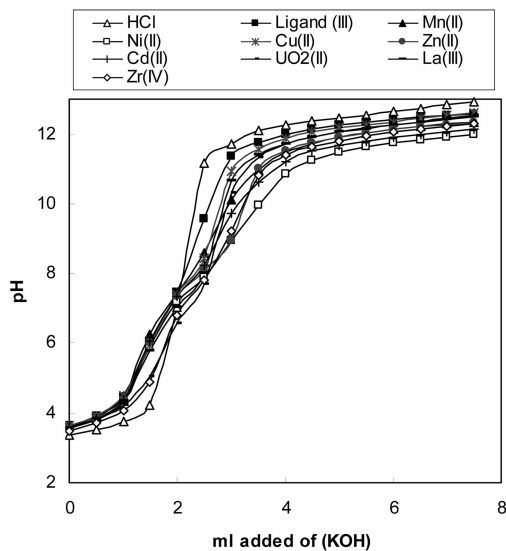


Fig. 4. Potentiometric titration curves of ligand (III) and its metal complexes in 50% (v/v) ethanol-water mixture and 0.1 M KCl at 298 K.

place in the alkaline medium starting with pH ~8. The number of the protons associated with the ligand molecule \bar{n}_L were determined according to Irving and Rossotti²² applying Eq. (1):

$$\bar{n}_L = V \pm ((V_1 - V_2)/(V_1 + V_2))((N^0 + E^0)/(TC_L^0)) \quad (1)$$

Where V^0 is the initial volume (10 ml) of the mixtures, V_1 and V_2 are the volumes of alkali required to

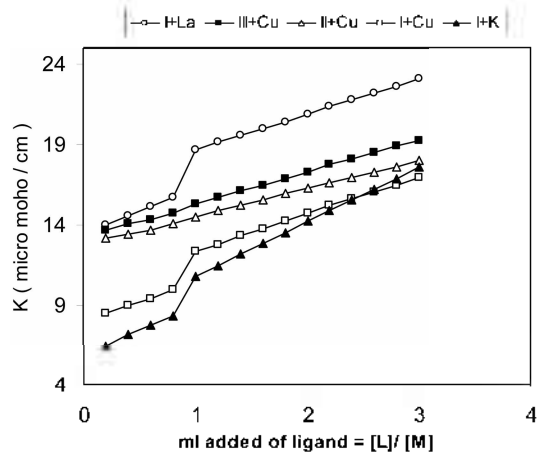


Fig. 5. Conductometric titration curves for ligand (I) with K, Cu and La; ligand (II) with Cu and ligand (III) with Cu, all in 50% (v/v) ethanol-water mixture at 298 K.

reach the same pH in the titration curves of hydrochloric acid and ligand, respectively. TC_L^0 is the total concentration of the ligand, N^0 is the normality of potassium hydroxide solution, and E^0 is the initial concentration of the free acid (HCl). Maximum \bar{n}_L values, in case of all used ligands are ~1, reveal that the ligands under investigation have one dissociable proton (hydrogen ion of the -NH group). A plot of \bar{n}_L values against pH was made and interpolation at half \bar{n}_L values gives the pK_1 ¹¹ value. The values of the ionization constants exponent (pK_1^{11}) (Tables 2) are the average values obtained from two computational methods (interpolation at half \bar{n}_L values method and the least square method).²³

The average number of ligand attached per metal ion (\bar{n}) and the free ligand exponent (pL) were calculated according to Irving and Rossotti²² applying the following equations:

$$\bar{n} = [(V_3 - V_2)/(V^0 + V_2)][1/\bar{n}_L][(N^0 - E^0)/T_M^0] \quad (2)$$

$$pL = \log\left[\frac{(1 + K_1^H[H])}{(TC_L^0 - \bar{n}T_M^0)}\right] \frac{(V_3 + V^0)/V^0}{(V_3 + V^0)/V^0} \quad (3)$$

where V_3 is the volume of alkali required to reach the same pH in the titration curves of the metal solution mixture and T_M^0 is the initial metal cation concentration.

Table 2. The Hammett constant (δ_x), the ionization constants exponent (pK_i^{11}) and the free energy change ΔG (KJmol^{-1}) of the three ligands in 50% (v/v) ethanol – water solvent and in 0.1 M KCl at 298 K.

Ligand (X)	δ_x , Ref. [31]	pK_i^{11}	ΔG
I (p-NO ₂)	0.78	8.30 (0.06)	47.3110
II (p-Br)	0.23	11.1 (0.07)	63.2713
III (p-CH ₃)	-0.17	12.2 (0.06)	69.5415

standard deviations are given between parenthesis

Table 3. The logarithm of the stability constants and the free energy changes (ΔG) of ML and ML₂ complexes of the three ligands I, II and III in (50% (v/v) ethanol-water solvent and 0.1M KCl at 298 K.

M ⁿ⁺	Log K						- ΔG (KJmol^{-1})					
	L(I)		L(II)		L(III)		L(I)		L(II)		L(III)	
	log K ₁	Log K ₂	log K ₁	Log K ₂	log K ₁	Log K ₂	ΔG_1	ΔG_2	ΔG_1	ΔG_2	ΔG_1	ΔG_2
Mn ²⁺	5.91(0.08)	5.30(0.06)	7.75(0.07)	7.25(0.06)	7.90(0.09)	5.70(0.08)	33.68	30.21	44.17	41.32	45.03	32.49
Co ²⁺	6.12(0.05)	5.40(0.06)	7.81(0.06)	7.35(0.07)	8.60(0.08)	8.10(0.09)	34.88	30.78	44.51	41.89	49.02	46.17
Ni ²⁺	6.20(0.06)	5.61(0.09)	7.88(0.07)	7.42(0.07)	8.66(0.06)	7.80(0.08)	35.34	31.97	44.91	42.29	49.36	44.46
Cu ²⁺	8.10(0.08)	5.80(0.06)	8.60(0.07)	8.20(0.08)	8.85(0.09)	4.50(0.09)	46.17	33.06	49.02	46.74	50.44	25.65
Zn ²⁺	5.40(0.07)	5.20(0.08)	6.60(0.09)	7.80(0.06)	8.60(0.07)	7.91(0.07)	30.78	29.64	49.02	44.46	49.02	45.08
Cd ²⁺	5.50(0.08)	4.80(0.07)	7.95(0.08)	7.25(0.09)	8.61(0.06)	6.53(0.08)	31.35	27.36	45.31	41.32	49.07	37.22
UO ₂ ²⁺	8.80(0.10)	7.30(0.11)	10.80(0.07)	10.6(0.09)	11.30(0.10)	5.15(0.11)	50.16	41.61	61.56	60.42	64.41	29.35
La ³⁺	6.10(0.07)	5.70(0.09)	8.60(0.08)	8.20(0.10)	9.10(0.11)	4.75(0.09)	34.77	32.49	49.02	46.74	51.87	27.07
Zr ⁴⁺	9.05(0.06)	8.55(0.07)	9.60(0.09)	9.00(0.09)	9.80(0.08)	7.35(0.07)	51.58	48.73	54.72	51.30	55.86	41.89

standard deviations are given between parenthesis

The maximum \bar{n} values in all cases were found to be ~2, indicating that both ML and ML₂ types of complexes were formed in solution.²⁴ Plotting the average number of ligand attached per metal ion (\bar{n}) versus the free ligand exponent (pL) and interpolation at 0.5 and 1.5 \bar{n} values gives the logarithm of the stability constants of the metal-ligand complexes (log K₁ and log K₂ respectively). The values of log K₁ and log K₂ of ML and ML₂ complexes Table 3 are the average values obtained from two computational methods.^{25,26}

The values of the free energy change (ΔG) for the ionization Table 2 and the complexation Table 3 processes were calculated applying Eq. (4):

$$\Delta G = 2.303 RT pK = -2.303 RT \log K \quad (4)$$

The positive values of the free energy change of the ionization process indicate that the dissociation process of the investigated ligands is not spontaneous while the negative values of the free energy change of the complexation process indicate that this process is spontaneous one. The results of the

ionization and the stability constants, Tables 2 and 3, indicate that these values depend on both the nature of the ligand as well as the metal ion. The ionization and the stability constants (for the same metal ion) were found to increase as the donor property of the substitute (x) increases²⁷ i.e ligand I (x = p-NO₂) < ligand II (x = p-Br) < ligand III (x = p-CH₃).

Plotting log K₁ (for the complexes) versus Hammett constant (δ_x) gives a linear correlation with statistically calculated slope (ρ) in the range [(-0.76)-(-2.8)]. This linear correlation indicates that both the ionization and the complexation processes of the ligands under investigation are susceptible to the influence of substituents on the aryl moiety. The negative values of (ρ) indicate that complexation is favored by high electron densities at the coordination sites.²⁸

In comparing the results with that of the same arylhydrazone derivatives of diethyl 2,3-dioxopentanedioate,²⁹ it was found that the ionization constant exponent (pK_{NH}) of ligand (III, II and I) under

study are higher than that of diethyl 2,3-dioxopentanedioate ones. This may be due to the higher donor property of thenoyl moiety and the hydrogen bond between (-NH) and (-S). For ions of similar electronic configuration, the stability constants of complexes metal ions of the same charge should be inversely proportional to the metal ions radii. The order of the stability constants of the complexes under study was; Cu(II) > Ni(II) > Mn(II). This order is quite in accordance with Cotton and Wilkinson.³⁰

Conductometric studies:

The conductometric titration was carried out as explained in the experimental section and the molar conductance (Λ) was calculated. The specific conductance values were found to be generally increased as the ligand added to the metal ion solution. This is due to the relative conductance of the ligand solution. Sudden increase in the conductance at 1:1 (L:M) ratio indicating the complete displacement of H^+ (high conductor ion) in the ligand molecule by M^n (low conductor ion) through the complexation process. The plots of either the measured specific conductance K_s ($\mu S\ cm^{-1}$) or the molar conductance (Λ) ($S\ cm^2\ mol^{-1}$) versus either the ml added from titrant (metal ion or ligand solution) or the ratio of ligand to metal ion concentrations $[L]/[M]$ (Figure V for ligand (I) with K^+ , Cu^{2+} and La^{3+} as examples) gives a straight lines with a sharp break at $[L]/[M]$ ratio (1:1) indicating the formation of (1:1) stoichiometric complex between the metal ion and the ligands under investigation.^{7,8} Sharp increase in the specific conductance at 1:2 (M:L) stoichiometric complexes has not appears in the conductometric titration curves. This may be due to the different titration conditions (such as buffer, alkaline titrant, and ionic strength) than that in pH-metric one. It will be known that the conductometric titration was used to evaluate the end point (neutralization point) in many acid-base neutralization reaction and precipitation ones. On the bases of the obtained results of the conductometric titration, we can conclude that the conductometric titration can be considered a one of the important methods for standardization of many monovalent, divalent and polyvalent cat-

ions using the investigated ligand (I) and vice-versa (i.e use the conductometric titration to standardize the investigated ligand (I) by any one of the investigated metal cations (K(I), Na(I), Mg(II), Ca(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), $UO_2(II)$, La(III) and Zr(IV)). The conductometric standardization method was preferred than others because it need not special conditions such as (buffer solution, ionic strength and suitable indicator). It should be noticed that the concentration of the titrant solution (0.001) molar and the concentration of the titrated solution (0.0001) molar are the suitable concentrations which results in the proper values of specific conductance (not low value), hence decrease the error in the conductance measurements.

Ligands II and III have not show a sharp break (sharp change) at 1:1 (L:M) in the conductance values through its conductometric titration with many metal cations as in the case of ligand I hence, these ligands can not be used for conductometric standardization of the investigated metal cations.

CONCLUSION

As a result of the spectrophotometric and the pH-metric studies, Ligand (I) can be used as acid – base indicator similar to phenolphthaleine one. A volume 0.5 ml (0.001 M) of this ligand in a total volume 40 ml solution is sufficient to change the color from yellow to reddish orange and vice-versa. Also alkaline concentration $\geq 0.01\ N$ is sufficient to give sharp end point in standardization of many strong and weak acids. Clear and sharp end point can be obtained either in aqueous or in ethanolic solutions.

Conductometric studies also indicates that many monovalent, bivalent, and polyvalent metal cations till concentration 0.0001 M solution can be standardized using 0.001 M solution of ligand (I) and vice-versa 0.0001 M of ligand (I) can be standardized using 0.001 M solution of monovalent, bivalent and polyvalent metal cations.

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