J. Chem. Eng. Data **2008,** *53,* 2341–2345

Spectrophotometric and Potentiometric Study of (*E*)-*N*′-(2-Hydroxy-3-methoxybenzylidene)benzohydrazide with a Ferric Ion in the Methanol−Water Mixture

Mohammad Ali Kamyabi,* Shirin Shahabi, and Hassan Hosseini-Monfared

Department of Chemistry, Faculty of Sciences, Zanjan University, Zanjan 45195-313, Iran

---

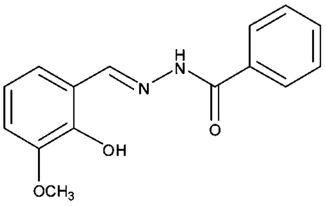
Spectrophotometric and potentiometric equilibrium measurements of hydrogen ion concentration have been employed for the determination of acidity constants of (*E*)-*N*′-(2-hydroxy-3-methoxybenzylidene)benzohydrazide (H_2L) in 0.9 volume fraction of methanol solution at (25.0 ± 0.1) °C and an ionic strength of 0.10 M tetraethylammonium bromide (TEAB). In the spectrophotometric method, only the acidity constant of the hydroxy group that is directly attached to the aromatic ring (phenolic group) was determined, whereas, by the potentiometric method, the acidity constants of both hydroxy groups could be determined. The pK_{a1} values obtained for the first acidity constant by both techniques, potentiometry and spectrophotometry, are 9.03(± 0.05) and 9.07(± 0.04), respectively, which are in good agreement. The pK_{a2} value obtained for the second acidity constant by potentiometry is 10.92(± 0.07). The complexation reaction of the ligand with Fe(III) ions in 0.9 volume fraction of methanol solution was also investigated by both the spectrophotometric and potentiometric methods. Ferric ions form only the ML type complex with this ligand. The stoichiometry of the complex was also determined by Job's method.

Introduction

The acidity constants of a compound influence many of its characteristics such as reactivity and spectral properties (color). In biochemistry, the pK_a values of proteins and amino acid side chains are of major importance for the activity of enzymes and the stability of proteins. The acidity constants also play a very fundamental role in many analytical procedures such as acid−base titrations, solvent extraction, and complex formation.[1,2] Sometimes in determining the acidity constants of a compound, we are faced with several drawbacks, such as low solubility in aqueous solution and the low values of acidity constants. Therefore, to enhance the acidity constants on one hand and to increase the solubility on the other, we should choose mixed solvents.[3] By mixing solvents of different polarity in proper ratios, the dielectric constant of the medium as well as the strength of dissolved acids and bases can be varied.[4−6] The accurate determination of acidity constant values is often needed in various chemical and biochemical areas. These are of vital importance in understanding the distribution, transport behavior, binding to receptors, and the mechanism of action of certain pharmaceutical preparations.

Hydrazones are a kind of Schiff base with the general formula RR′C=N−NR″R‴, which are used as intermediates in synthesis, as functional groups in metal carbonyls,[7] in organic compounds,[8,9] and in particular in hydrazone Schiff base ligands,[10−13] which are among others employed in dinuclear catalysts.[6] Furthermore, hydrazones exhibit physiological activities in the treatment of several diseases such as tuberculosis. This activity is attributed to the formation of stable chelate complexes with transition metals, which catalyze physiological processes.[14] They also act as herbicides, insecticides, nematocides, rodenticides, plant growth regulators, and sterilants for houseflies.[14] In analytical chemistry, hydrazones find applications as multidentate ligands for transition metals in colorimetric or fluorimetric determinations.[15,16]

Scheme 1. Tridentate Hydrazone Schiff Base Ligand



(E)-N'-(2-hydroxy-3-methoxybenzylidene)benzohydrazide

H_2L

In this study, the acidity constants of the hydrazone Schiff base, (*E*)-*N*′-(2-hydroxy-3-methoxybenzylidene)benzohydrazide, H_2L (Scheme 1), were calculated via the potentiometric and spectrophotometric methods in 0.9 volume fraction of methanol. The formation constant of the (*E*)-*N*′-(2-hydroxy-3-methoxybenzylidene) benzohydrazide−ferric ion system was also calculated using the BEST program[17,18] via the potentiometric method in 0.9 volume fraction of methanol. This program is for the refinement of formation constants on complex systems containing any number of interacting components. In the spectrophotometric method, the EQUISPEC program[19,20] was used to calculate the formation constant of the (*E*)-*N*′-(2-hydroxy-3-methoxybenzylidene)benzohydrazide−ferric ion system. This program is a computer program using the matrix-based MATLAB environment for the second-order global analysis of spectrophotometric equilibrium data.

Experimental Section

Reagents. All reagents were of analytical grade from Merck or Fluka and used without further purification. The KOH

---

* Corresponding author. E-mail: makamyabi@gmail.com.

10.1021/je800202u CCC: $40.75

solution was standardized by potassium hydrogen phthalate. Triply distilled water was used in the preparation of all solutions. Synthesis of (*E*)-*N*′-(2-hydroxy-3-methoxybenzylidene)benzohydrazide was prepared according to the reported procedure.[21]

Apparatus. The pH measurements were carried out with a 780 Metrohm pH-meter (Metrohm Ltd., CH-9100-Hersau, Switzerland) using a combined glass electrode. Temperature was maintained at (25.0 ± 0.1) °C by circulation of thermostatted water through the jacket. In these pH measurements, nitrogen purge gas was used to remove CO_2. An Eppendorf micropipette (± 0.6 %) was used for the addition of a standard base to the solution. A Thermospectronic model α, UV−vis spectrometer with 1 cm quartz cells was used for recording and storage of UV−vis absorbance spectra.

IR spectra were recorded in KBr disks with a Matson 1000 FT-IR spectrophotometer. An ^{1}H NMR spectrum of the ligand in DMSO-d_6 solution was recorded on a Bruker 250 MHz spectrometer, and chemical shifts are indicated in parts per million relative to tetramethylsilane.

Procedure for Calculation of K_w in Methanol−Water Mixture. Before each experiment, it is necessary to calibrate[22−26] the pH meter and electrode system in terms of pH. For determination of K_w in the methanol−water mixture, at an ionic strength of 0.10 M TEAB and $t = (25.0 \pm 0.1)$ °C, the cell was charged with 5.0 mL of 0.10 M HCl, 5.0 mL of 1.00 M TEAB, and the appropriate volume of methanol and water until the total volume was equal to 50.0 mL. The cell was capped (letting inert gas flow), equilibrated until pH drifts were < 0.001 unit/5 min (usually between 5 min and 0.5 h), and titrated with standard KOH (which is prepared in a 0.9 volume fraction of methanol). The ion product ($K_w = [H^+][OH^-]$) was determined in the mixture by several series of $[OH^-]$ and $p[H^+]$ measurements. The p[H] was measured with a pH-meter, while $[OH^-]$ was calculated from the amount of base added to the solution. K_w and then pK_w were calculated. The pK_w value that was obtained was 14.12 for a 0.9 volume fraction of methanol.

Procedure for Calculation of pK_a via Potentiometry. In a potentiometric study, Martell's computer program[17,22−26] was used to calculate the acidity constants of the (*E*)-*N*′-(2-hydroxy-3-methoxybenzylidene)benzohydrazide. The acidity constants were determined by titrating 50.0 mL of ($4.00 \cdot 10^{-5}$ to $1.00 \cdot 10^{-3}$) M analyte with KOH, and the ionic strength of the solution was adjusted with 0.10 M TEAB. The temperature was maintained at (25.0 ± 0.1) °C by circulation of thermostatted water through the jacket. Before doing each titration, the solution was allowed to equilibrate until pH drifts < 0.001 unit/5 min (usually between 5 min and 0.5 h) were obtained. N_2 gas was pumped through the solution to remove CO_2. During the titration, the pumping of N_2 was continued above the solution. The titroprocessor was calibrated to read hydrogen ion concentration. To obtain each pK_a value, at least five titrations were made, and each titration had almost 30 to 40 points.

Procedure for Stability Constant Calculation. In this study, different M:L solution ratios were examined as shown in Table 1. Typical concentrations of experimental solutions are in the order of $1.00 \cdot 10^{-5}$ M to $1.00 \cdot 10^{-4}$ M metal ion and several times the molar equivalent concentrations of ligand in 50 mL of solution. The ionic strength of each solution was adjusted to 0.10 M by the addition of the appropriate amount of TEAB. The temperature was maintained at (25.0 ± 0.1) °C by circulation of thermostatted water through the jacket. Before doing each titration, the solution was allowed to equilibrate until pH drifts < 0.001 unit/5 min (usually between 5 min and half an hour) were obtained. Carbon dioxide was excluded from the reaction mixture by maintaining a slight positive pressure of purified nitrogen in the reaction cell. During the titration, the pumping of N_2 was continued above the solution. A solution of carbonate-free KOH was used as a titrant. The pH profiles obtained consisted of approximately 35 to 40 pH measurements vs moles of standard base per moles of ligand in the experimental solution. The BEST computer program[17,22−26] has been used to calculate the stability constant of (*E*)-*N*′-(2-hydroxy-3-methoxybenzylidene)benzohydrazide with the ferric ion.

Table 1. Experimental Conditions of the Experiments Performed at $\mu = 0.10$ M TEAB and $t = (25.0 \pm 0.1)$ °C in 0.9 Volume Fraction of Methanol

technique	M:L ratio	C_L	C_M	pH range	no. of spectra
		Potentiometric			
A	0	$1.00 \cdot 10^{-3}$	0.0	5.20 to 11.20	- --
B	0	$4.00 \cdot 10^{-4}$	0.0	5.20 to 11.20	- --
C	0	$4.00 \cdot 10^{-5}$	0.0	5.20 to 11.20	- --
D	2:1	$1.00 \cdot 10^{-4}$	$2.01 \cdot 10^{-4}$	- - -	- --
E	1:1	$1.00 \cdot 10^{-4}$	$1.00 \cdot 10^{-4}$	5.20 to 11.30	- --
F	1:1	$1.00 \cdot 10^{-5}$	$1.00 \cdot 10^{-5}$	5.20 to 11.30	- --
G	1:2	$2.00 \cdot 10^{-4}$	$1.00 \cdot 10^{-4}$	5.20 to 11.02	- --
H	1:4	$4.00 \cdot 10^{-4}$	$1.00 \cdot 10^{-4}$	5.20 to 11.20	- --
I	1:8	$4.00 \cdot 10^{-4}$	$5.00 \cdot 10^{-5}$	5.20 to 11.00	- --
J	1:10	$2.00 \cdot 10^{-4}$	$2.00 \cdot 10^{-5}$	5.20 to 11.40	- --
		Spectrophotometric			
K	- - -	$3.00 \cdot 10^{-5}$	- - -	1.52 to 11.56	17
L	- - -	$1.50 \cdot 10^{-5}$	- - -	1.60 to 11.60	15
M	1:1	$1.00 \cdot 10^{-5}$	$1.00 \cdot 10^{-5}$	1.60 to 6.00	15
N	1:1	$2.00 \cdot 10^{-5}$	$2.00 \cdot 10^{-5}$	1.45 to 6.20	16
O	1:2	$3.00 \cdot 10^{-5}$	$1.50 \cdot 10^{-5}$	1.59 to 11.00	17
P	1:3	$3.00 \cdot 10^{-5}$	$1.00 \cdot 10^{-5}$	1.58 to 11.32	15
Q	1:6	$6.00 \cdot 10^{-5}$	$1.00 \cdot 10^{-5}$	1.35 to 10.66	14
R	- - -	$1.00 \cdot 10^{-5}$	0.0 to $1.60 \cdot 10^{-5}$	10.00	12

Table 2. Acidity Constants and Stability Constant of (*E*)-*N*′-(2-Hydroxy-3-methoxybenzylidene)benzohydrazide with the Ferric Ion at 0.1 M TEAB, $t = (25.0 \pm 0.1)$ °C, in 0.9 Volume Fraction of the Methanol−Water Mixture

K	spectrophotometry	potentiometry
pK_{a1}	9.07 (± 0.04)	9.03 (± 0.05)
pK_{a2}	- - -	10.92 (± 0.07)
log (K_{ML})	6.60 (± 0.07)	6.52 (± 0.09)

In spectrophotometric studies, several series of titrations containing different M:L ratios at a constant ionic strength of 0.10 M TEAB were performed (Table 2). The spectra (baseline corrected) of the samples were recorded from (250 to 650) nm at 1 nm intervals. The EQUISPEC program[19,20,23,26] was used for the determination of the acidity and stability constants.

Results and Discussion

Potentiometric Method. In potentiometry, the refinement of the acidity constant is the process where the computer adjusts parameter(s) with a programmed algorithm to obtain the best possible least-squares fit of the calculated data to the observed data. σ_{fit}, which is a measure of the weighted sum of the squares of $pH_{calcd} - pH_{obsd}$, is a measure of the goodness of fit. The purpose is to minimize σ_{fit} through refinement of the parameter(s). The program BEST has evolved into a very useful and friendly interactive program which, although basically designed to solve for the set of equilibrium constants corresponding to the model selected, has features that make it possible to explore all aspects and variations of the model. The algorithm for computing equilibrium constants in the BEST program[17,22] is the following sequence: (1) start with a set of known and estimated overall stability constants and compute $[H^+]$ at all equilibrium points and (2) compute the weighted sum of squares of the deviations in p[H] as in eq 1

$$U = \Sigma w(\text{p[H]}_{\text{obsd}} - \text{p[H]}_{\text{calcd}})^2 \qquad (1)$$

where $w = 1/(\text{p[H]}_{i+1} - \text{p[H]}_{i-1})^2$, a weighting factor that serves to lessen the influence of the less accurate p[H] values in the steeply sloped regions of the p[H] profile on the calculation; (3) adjust the unknown stability constants and repeat the calculations with the algorithm, which reproduces pH values according to the physicochemical model fitted and minimizes the sum of the weighted calculations until no further minimization of U (i.e., the Σ fit has been minimized) can be obtained, thus providing the final calculated β values. The standard deviation in pH units is obtained by the use of eq 2.

$$\sigma_{\text{fit}} = \Sigma(U/N)^{1/2} \qquad (2)$$

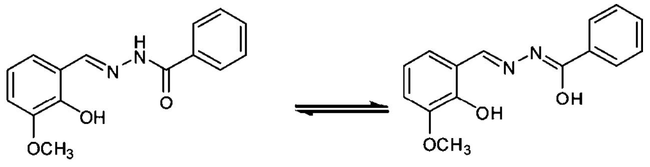
where $N = \Sigma w$.

The hydrazone Schiff base, (*E*)-*N*′-(2-hydroxy-3-methoxybenzylidene)benzohydrazide, shows a keto−enol tautomerism, as illustrated in Figure 1. On the basis of this tautomerism, this ligand has two acidic hydrogens (in enol form), which can be measured by the potentiometric method. The X-ray structural analysis of the Cu(II) complex of this ligand shows coordination of the doubly deprotonated hydrazone Schiff base dianion (L^{2-}) to copper through the 2-hydroxy, hydrazone nitrogen, and benzocarboxide group.[27]

The pK_a values of the hydrazone Schiff base, (*E*)-*N*′-(2-hydroxy-3-methoxybenzylidene)benzohydrazide, were calculated in methanol−water mixture solutions. Experimental conditions of the experiments performed at $\mu = 0.10$ M TEAB were $t = (25.0 \pm 0.1)$ °C in 0.9 volume fraction of methanol (samples A−C in Table 1). The results using the potentiometric method are given in Table 2.

In this potentiometric study, different M:L solutions of the ligand and metal ion were examined (samples D−J in Table 1). As Table 1 shows, solutions with more than $2.00 \cdot 10^{-4}$ M concentration of ferric ion precipitate in pH's higher than 5. For this reason, we lowered the concentration of the metal ion, and then to have significant interaction between the metal ion and the ligand, higher concentrations of the ligand relative to the metal ion were used (i.e., M:L equal to 1:4, 1:8, and 1:10). These data then were used to obtain the stability constants of the system. In this method, it was found that in the pH range 5.0 to 11.5 only the ML species is formed. The result is given in Table 2.

Spectrophotometric Method. In spectrophotometry, hard-modeling approaches solve Beer−Lambert's law assuming the fulfillment of the mass-action law and a particular chemical model, in which a set of chemical species in equilibrium are defined by their composition, stoichiometries, and equilibrium constants. By use of the EQUISPEC program, the formation constants were determined.[19,20,23,26] The EQUISPEC procedure is a second-order global analysis that simultaneously analyzes a number of spectrophotometric titrations with different initial concentrations; therefore, conditions for the significant formation of each species can be obtained.


(E)-N'-(2-hydroxy-3-methoxybenzylidene)benzohydrazide

H_2L

Figure 1. Keto−enol tautomerism of the (*E*)-*N*′-(2-hydroxy-3-methoxybenzylidene)benzohydrazide.

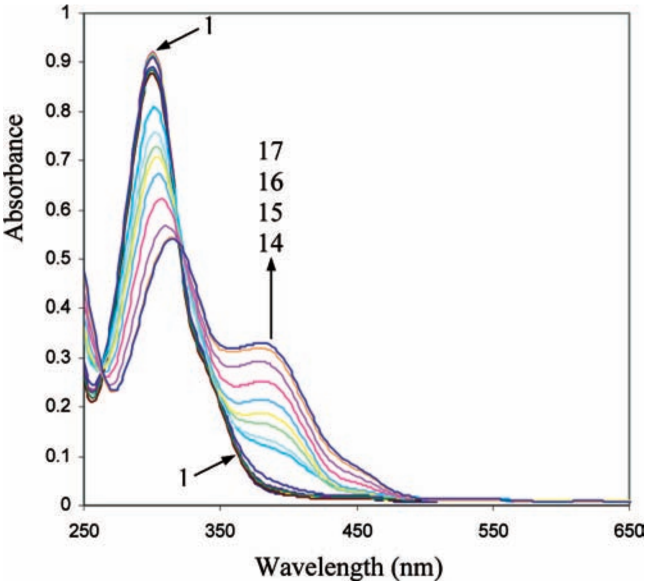


Figure 2. UV−vis spectra of (*E*)-*N*′-(2-hydroxy-3-methoxybenzylidene)benzohydrazide at 0.1 M TEAB. pH values are as follows: 1, 1.520; 2, 1.652; 3, 1.777; 4, 2.450; 5, 2.795; 6, 2.938; 7, 3.458; 8, 4.405; 9, 6.998; 10, 7.373; 11, 8.350; 12, 9.051; 13, 9.591; 14, 10.141; 15, 10.671; 16, 11.211; 17, 11.560.

Figure 2 shows the UV−vis spectra of the (*E*)-*N*′-(2-hydroxy-3-methoxybenzylidene)benzohydrazide (sample K in Table 1). The electronic absorption spectra of this hydrazone Schiff base show mainly two bands. The shorter wavelength band, appearing at low pH values (pH < 6), represents absorption of the nonionized species, while the longer wavelength band, observed at higher pHs (> 8.5), is due to the absorption by ionized species. On increasing the pH of the medium, the absorbance of the former band decreases while that of the latter band increases, so that a fine isosbestic point is achieved, and denoting existence of equilibrium of the type

$$H_2L \rightleftharpoons HL^- + H^+ \qquad (3)$$

In other words, since a phenolic group possesses an absorbance in the vicinity of 305 nm, while the conjugate phenolate group absorbs at around 385 nm (i.e., ~80 nm longer in wavelength), the UV−vis probe is responsive only to the phenol to phenolate conversion.[26] The first acidity constant of the (*E*)-*N*′-(2-hydroxy-3-methoxybenzylidene)benzohydrazide was determined spectrophotometrically, and the result is given in Table 2. The values obtained for the first acidity constant by both techniques (potentiometry and spectrophotometry) are in good agreement.

The titration spectra of the (*E*)-*N*′-(2-hydroxy-3-methoxybenzylidene)benzohydrazide with ferric ion (experiment sample R in Table 1) at a pH of 10.00 are given in Figure 3. As these electronic spectra show, the hydrazone Schiff base−ferric ion system shows two bands. The shorter wavelength band (the shoulder near 350 nm) is due to the absorption by complex ML, whereas the longer wavelength band (i.e., 390 nm) was observed at an M/L ratio near zero (i.e., ligand alone). On increasing the metal concentration of the medium, the absorbance of the former band increases while that of the latter band decreases, where a fine isosbestic point is achieved. The peak near 300 nm is due to ferric salt and increases as the metal ion concentration increases.

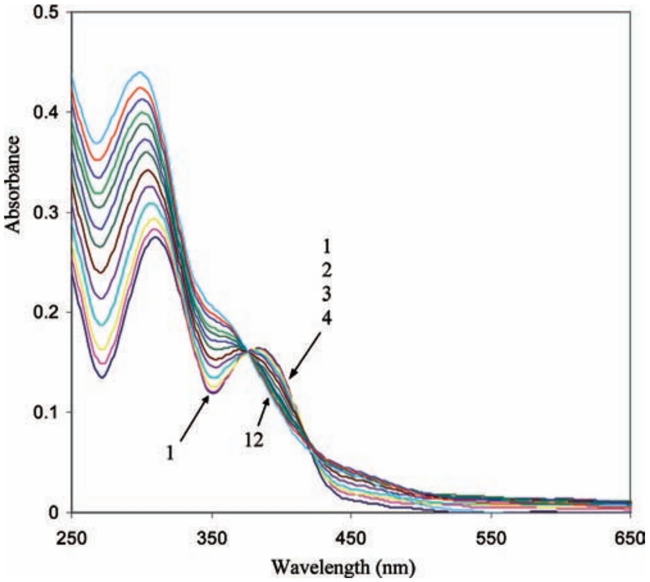


Figure 3. Spectrophotometric titration of the ligand with the ferric ion at pH = 10.00 and M/L ratio equal to 1, 0.0; 2, 0.06; 3, 0.13; 4, 0.26; 5, 0.40; 6, 0.53; 7, 0.80; 8, 0.93; 9, 1.06; 10, 1.20; 11, 1.33; 12, 1.60 (sample R in Table 1).

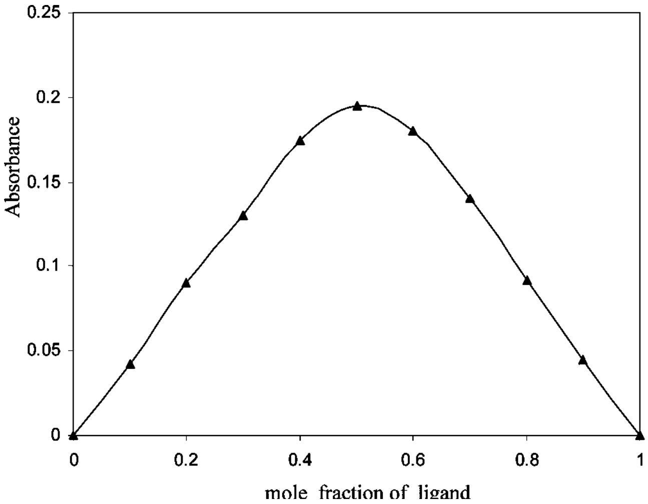


Figure 4. Continuous variation method plot (Job's plot) of the ferric ion with (*E*)-*N*′-(2-hydroxy-3-methoxybenzylidene)benzohydrazide at 460 nm and 0.10 M TEAB (each $4.00 \cdot 10^{-4}$ M).

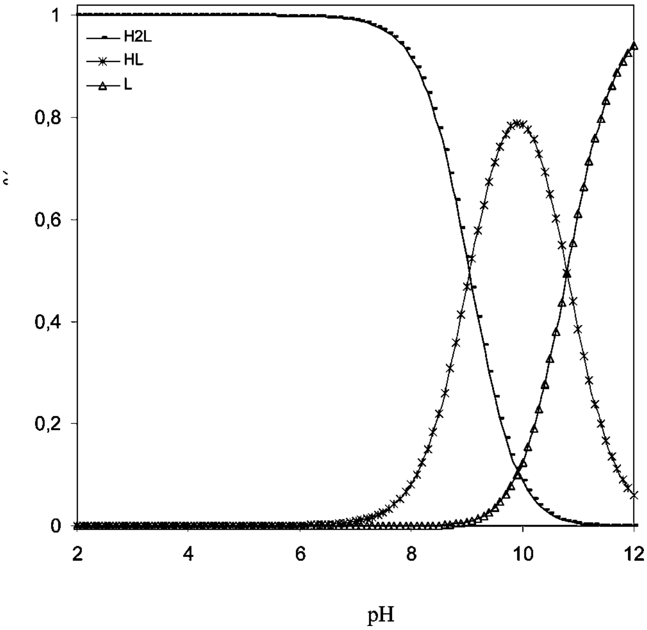


Figure 5. Distribution diagram of (*E*)-*N*′-(2-hydroxy-3-methoxybenzylidene)benzohydrazide at 0.10 M TEAB in 0.9 volume fraction of the methanol−water mixture.

In the spectrophotometric method by using the EQUISPEC program and spectra in different mole ratios of M:L (samples K to R in Table 1), the stability constants of species in this system were calculated. Since in this system the ferric ion precipitates at a hydroxide above pH 5.0, to have no precipitate and receive detectable absorbance, we had to use a very low concentration of ferric ion and a higher concentration of ligand during the titration of the mixture with KOH solution. By using the EQUISPEC program, the results show that only the ML species is present (i.e., mole ratio M:L is equal to 1:1) in this system (Table 2). The continuous variation method, which is illustrated in Figure 4, confirmed this mole ratio of 1:1. The results in Table 2 show that the two methods of potentiometric and spectrophotometric are comparable and are in good agreement with each other.

A distribution diagram of (*E*)-*N*′-(2-hydroxy-3-methoxybenzylidene)benzohydrazide in 0.9 volume fraction of methanol is shown in Figure 5. Because of low acidic constants of this compound, the HL^- and L^{2-} species are present at high pH values. As this figure shows, H_2L and HL^- are the main species in the pH range 2.0 to 10.0, and the other species exist only at higher pH's.

Conclusions

In this work, we characterized that the M:L ratio of this complex is 1:1 and the stability constant of the complex was determined by the spectrophotometric and potentiometric methods at 25.0 °C and at an ionic strength of 0.10 M TEAB in 0.9 volume fraction of methanol. The results of the two methods are comparable with each other.

Literature Cited

(1) Armbruster, F.; Klingebiel, U.; Noltemeyer, M. From Ketazines to 1,2-Diaza-3-phospha-cyclopent-5-enes, -penta-3,5-dienes, 1,5-Diaza-2,6-diphospha-bicyclo[3.3.0]octa-3,7-dien, and Cyclohexaphosphane. *Z. Naturforsch.* **2006**, *61b*, 225–236.

(2) Senturk, O. S.; Sert, S.; Özdemir, Ü. Synthesis and Characterization of Metal Carbonyls [$M(CO)_6$(M = Cr, Mo, W), $Re(CO)_5Br$, $Mn(CO)_3Cp$] with 2-Hydroxy-1-napthaldehyde Ethanesulfonylhydrazone. *Z. Naturforsch.* **2003**, *58b*, 1124–1127.

(3) Chakraborty, J. B.; Singh, R. K.; Samanta, B.; Choudhury, C. R.; Dey, S. K.; Talukder, P.; Borah, M. J.; Mitra, S. Two New Quadridentate Schiff Base Complexes of Nickel(II) and Cobalt(III): Synthesis, Structure and Spectral Characterisation. *Z. Naturforsch.* **2006**, *61b*, 1209–1216.

(4) Zeyrek, C. T.; Elmali, A.; Elerman, Y. Super-Exchange Interaction in a Chair-Piperazine Bridged Dicopper(II/II) Complex: Synthesis, Crystal Structure, Magnetic Properties and Molecular Orbital Calculations. *Z. Naturforsch.* **2006**, *61b*, 237–242.

(5) Dey, D. K.; Samanta, B.; Lycka, A.; Dahlenburg, L. Simple Synthesis, Characterization and Structure of Diorganotin(IV) Complexes Containing the N-(2-Salicylidene)-N′-benzoylhydrazone Ligand. *Z. Naturforsch.* **2003**, *58b*, 336–344.

(6) Janiak, C.; Lassahn, P.-G.; Lozan, V. Metal Complexes for the Vinyl Addition Polymerization of Norbornene: New Compound Classes and Activation Mechanism with $B(C_6F_5)_3/AlEt_3$. *Macromol. Symp.* **2006**, *236*, 88.

(7) Senturk, O. S.; Sert, S.; Ozdemir, U. Synthesis and Characterization of Metal Carbonyls [M(CO)6(M =Cr, Mo, W), Re(CO)5Br, Mn(CO)3Cp] with 2-Hydroxy-1-napthaldehyde Ethanesulfonylhydrazone. *Z. Naturforsch.* **2003**, *58b*, 1124–1127.

(8) Amr, A. E. G. E.; Mohamed, A. M.; Ibrahim, A. A. Synthesis of Some New Chiral Tricyclic and Macrocyclic Pyridine Derivatives as Antimicrobial Agents. *Z. Naturforsch.* **2003**, *58b*, 861–868.

(9) Mohrle, H.; Keller, G. α-Dicarbonylmonohydrazone und ihre Acylderivate als Nucleophile und Nachbargruppen. *Z. Naturforsch.* **2003**, *58b*, 885–902.

(10) Chakraborty, J.; Singh, R. K. B.; Samanta, B.; Choudhury, C. R.; Dey, S. K.; Talukder, P.; Borah, M. J.; Mitra, S. Two New Quadridentate Schiff Base Complexes of Nickel(II) and Cobalt(III): Synthesis, Structure and Spectral Characterisation. *Z. Naturforsch.* **2006**, *61b*, 1209–1216.

(11) Lozan, V.; Lassahn, P.-G.; Zhang, C.; Wu, B.; Janiak, C.; Rheinwald, G.; Lang, H. Dinuclear Nickel(II) and Palladium(II) Complexes in Combination with Different Co-Catalysts as Highly Active Catalysts for the Vinyl/Addition Polymerization of Norbornene. *Z. Naturforsch.* **2003**, *58b*, 1152–1164.

(12) Zeyrek, C. T.; Elmali, A.; Elerman, Y. Super-Exchange Interaction in a Chair-Piperazine Bridged Dicopper(II/II) Complex: Synthesis, Crystal Structure, Magnetic Properties and Molecular Orbital Calculations. *Z. Naturforsch.* **2006**, *61b*, 237–242.

(13) Dey, D. K.; Samanta, B.; Lycka, A.; Dahlenburg, L. Simple Synthesis, Characterization and Structure of Diorganotin(IV) Complexes Containing the N-(2-Salicylidene)-N′-benzoylhydrazone Ligand. *Z. Naturforsch.* **2003**, *58b*, 336–344.

(14) Mohan, M.; Gupta, M. P.; Chandra, L.; Jha, N. K. Synthesis, characterization and antitumor properties of some metal (II) complexes of 2-pyridinecaborxaldehyde 2′- pyridylhydrazone and related compounds. *Inorg. Chim. Acta* **1988**, *151*, 61–68.

(15) Terra, L. H.; Areias, A. M. C.; Gaubeur, I.; Suez-Iha, M. E.V. Solvent extraction-spectrophotometric determination of nickel(II) in natural waters using di-2-pyridyl ketone benzoylhydrazone. *Spectrosc. Lett.* **1999**, *32*, 257–271.

(16) Hu, Q.; Yang, G.; Huang, Z.; Yin, J. Study on Solid Phase Extraction and Spectrophotometric Determination of Nickel in Waters and Biological Samples Spectrophotometric Determination of Nickel. *Bull. Korean Chem. Soc.* **2004**, *25*, 545–547.

(17) Motekaitis, R. J.; Martell, A. E. BEST-A New Program for Rigorous Calculation of Equilibrium Parameters of Complex Multicomponent Systems. *Can. J. Chem.* **1982**, *60*, 2403–2409.

(18) Wang, J.; Martell, A. E.; Reibenspies, J. H. Homo and Hetero Dioxygen Complexes of Co(II), Cu(II), Ni(II) and Pb(II) with the Ligand 3,7,11,19,23,27-Hexaaza-33,34-dihydroxy-15,31-dimethyltricyclotetratriaconta-1(32),13,15,17(34),29 (33),30-hexaene. *Inorg. Chim. Acta* **2002**, *328*, 53–60.

(19) Dyson, R. M.; Kaderli, S.; Lawrence, G. A.; Maeder, M.; Zuberbühler, A. D. Second-Order Global Analysis: The Evaluation of Series of Spectrophotometric Titrations for Improved Determination of Equilibrium Constants. *Anal. Chim. Acta* **1997**, *353*, 381–393.

(20) Abbaspour, A.; Kamyabi, M. A. Characterization and Determination of Stability Constants of Copper (II) L-Histidine Complexation System by Using Multivariate Curve Resolution Method of Visible Spectra and Two Hard Modeling Methods in Aqueous Solutions. *Anal. Chim. Acta* **2004**, *512*, 257–269.

(21) Pouralimardan, O.; Chamayou, A.-C.; Janiak, C.; Hosseini-Monfared, H. Hydrazone Schiff base-manganese(II) complexes: synthesis, crystal structure and catalytic reactivity. *Inorg. Chim. Acta,* **2007**, *360*, 1599–1608.

(22) Martell, A. E.; Motekaitis, R. J. *Determination and Use of Stability Constants*, 2nd ed.; VCH Publishers: New York, 1992.

(23) Abbaspour, A.; Kamyabi, M. A.; Khalafi-Nezhad, A.; Soltani Rad, M. N. Acidity Constants and Thermodynamic Parameters of Some Phenol Derivatives in Methanol + Water Systems Using Potentiometry and Spectrophotometry Methods. *J. Chem. Eng. Data* **2003**, *48*, 911–915.

(24) Durust, N.; Abdulkadir Akay, M.; Durust, Y.; Kilic, E. Protonation Constants of Some N-Substituted Amidoximes in a 50% Ethanol-Water Mixture (v/v). *Anal. Sci.* **2000**, *16*, 825–827.

(25) Abbaspour, A.; Kamyabi, M. A. Acidity Constants and Thermodynamic Parameters of Barbituric and Diethylbarbituric Acids in Water, (Water + Tetrahydrofuran) and (Water + Triton X-100) System. *J. Chem. Eng. Data* **2001**, *46*, 623–625.

(26) Abbaspour, A.; Kamyabi, M. A.; Khalafi-Nezhad, A.; Soltani Rad, M. N. Charge-Transfer Complexometric Study of Ferric Ion with 4-Chloro-2,6-bis(hydroxymethyl)phenol in a Methanol-Water System Using Spectrophotometric and Potentiometric Methods. *J. Chem. Eng. Data* **2004**, *49*, 907–911.

(27) Hosseini-Monfared, H.; Kalantari, Z.; Kamyabi, M. A.; Janiak, C. Synthesis, Structural Characterization and Electrochemical Studies of a Nicotinamide-bridged Dinuclear Copper Complex derived from a Tridentate Hydrazone Schiff Base Ligand. *Z. Anorg. Allg. Chem.* **2007**, *633*, 1945–1948.

Received for review March 24, 2008. Accepted July 17, 2008. The authors wish to express their gratitude to the Zanjan University Research Council for financial support of this work.

JE800202U