ANALELE UNIVERSITĂȚII BUCUREȘTI
Department of Physical Chemistry
4-12 Regina Elisabeta Blvd, District 3, Bucharest
phone: +40-21-3143508; fax: +40-21-3159249
*p*ISSN: 1220-871X *e*ISSN: 1844-0401

ARS DOCENDI PUBLISHING HOUSE
Sos. Panduri 90, District 5 Bucharest
phone/fax: +40-21-4102575
e-mail: arsdocendi@yahoo.com

THE ASSOCIATION AND FORMATION CONSTANTS FOR $NiCl_2$ STOICHIOMETRIC COMPLEXES WITH (E)-3-(2-BENZYLIDENE HYDRAZINYL)-3-OXO-N-(THIAZOL-2-YL)PROPANAMIDE

K.M. Ibrahim, E.A. Gomaa *, R.R. Zaky and M.N. El-Hady

abstract: The association constants, formation constants and Gibbs free energies are calculated from the conductometric titration curves of $NiCl_2$ with (*E*)-3-(2-benzylidene hydrazinyl)-3-oxo-N-(thiazol-2-yl)propanamide (H_2L) in absolute ethanol at 294.15 K. On drawing the relation between molar conductance and the ratio of metal to ligand concentrations, different lines are obtained indicating the formation of 1:1 and 2:1 (M:L) stoichiometric complexes. The formation constants and Gibbs free energies of different complexes in absolute ethanol at 294.15 K follow the order: K_f (2:1) › K_f (1:1) for (M:L); and ΔG_f (2:1) › ΔG_f (1:1) for (M:L).

key words: association constants; formation constants; Gibbs free energies.

received: May 7, 2011 *accepted*: July 5, 2011

Introduction

The synthesis of transition metal complexes with Schiff bases of nitrogen and oxygen donor has stimulated interest due to their vast variety of biological activities ranging from pharmacological, antitumour, fungicide, bactericide, anti-inflammatory, and antiviral activities [1, 2]. Nickel is an essential component in at least 4 types of enzymes *viz*. urease, carbon monoxide dehydrogenase (CODH) or acetyl coenzyme A synthase, hydrogenase and methyl-S-coenzyme M reductase [3, 4]. The aim of this work, consists in evaluation of the non-covalent behavior of $NiCl_2$ in presence of (*E*)-3-(2-benzylidene hydrazinyl)-3-oxo-*N*-(thiazol-2-yl)propanamide (H_2L) in absolute ethanol solutions at 294.15 K. These non-covalent interactions can help us for analysis of salts role influence in bodies and environnement.

Experimental

Material and methods

All manipulations were performed under aerobic conditions. The nickel chloride and the used reagents were Merck pure.

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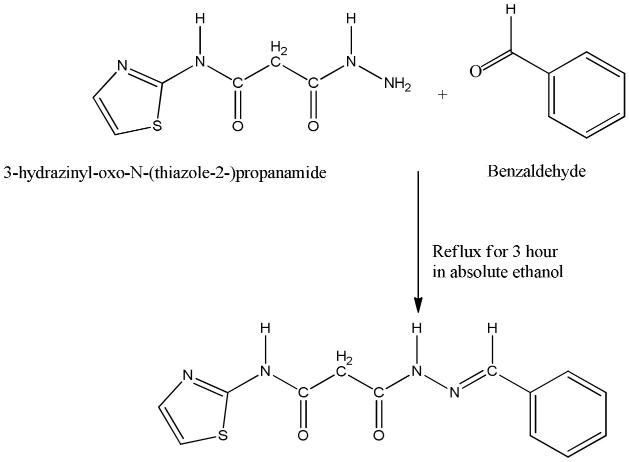
* Department of Chemistry, Faculty of Science, Mansoura University, Mansoura, EGYPT, *corresponding author e-mail*: esam1947@yahoo.com

Preparation of the ligand

(*E*)-3-(2-benzylidenehydrazinyl)-3-oxo-*N*-(thiazol-2-yl)propanamide (H_2L) (Scheme 1) was prepared by heating a mixture of 3-hydrazinyl-oxo-*N*-(thiazole-2-) propanamide (0.01 mol; 2.00 g) and benzaldehyde (0.01 mol; 1.06 g) under reflux in absolute ethanol for 3 h. On cooling, white crystals were formed, filtered off, washed with EtOH and Et_2O and recrystallized from absolute ethanol (M.p.: 230 ^{o}C; yield 80%). The purity of the compound was checked by TLC.



Scheme 1 *The outline of the synthesis of (E)-3-(2-benzylidenehydrazinyl)-3-oxo-N-(thiazol-2-yl)propanamide.*

Conductometric titration

The conductometric titration of the ligand ($1x10^{-4}$) mole/L against $NiCl_2$ ($1x10^{-4}$) mole/L in absolute ethanol was performed with 0.5 ml interval additions from $NiCl_2$ solution. The specific conductance values were recorded using conductivity bridge HANNA, H1 8819N with a cell constant equal to 1 cm^{-1}. The conductometer was connected to the type Kottermann 4130 ultrathermostate. The temperature was adjusted at 294.15 K.

Result and discussion

The specific conductance values (K_s) of different concentrations of $NiCl_2$ in absolute ethanol were measured experimentally in absence and in the presence of ligand at 294.15 K.

The molar conductance ($/\backslash_m$) values were calculated [5] using equation:

$$\Lambda_m = \frac{(K_s - K_{solv})K_{cell} \times 1000}{C} \quad (1)$$

Where K_s and K_{solv} are the specific conductance of the solution and the solvent, respectively; K_{cell} is the cell constant and C is the molar concentration of the $NiCl_2$ solutions..

The limiting molar conductances (/\$_o$) at infinite dilutions were estimated for $NiCl_2$ in absolute ethanol alone and in the presence of the ligand (H_2L) by extrapolating the relation between /\$_m$ and $C_m^{½}$ to zero concentration (Figs. 1,2). By drawing the relation between molar conductance (/\$_m$) and the molar ratio of metal to ligand (M/L) concentrations (Fig. 3), different lines are obtained with sharp breaks indicating the formation of 1:1 and 2:1 (M:L) stoichiometric complexes. The experimental data of (/\$_m$) and (/\$_o$) were analyzed for the determination of association and formation constants for each type of the stoichiometric complexes.

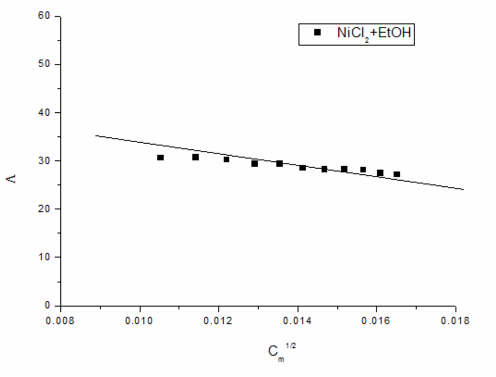


Fig. 1 *The relation between molar conductance (/\$_M$) and ($\sqrt{C}$) of $NiCl_2$ alone in absolute ethanol at 294.15 K.*

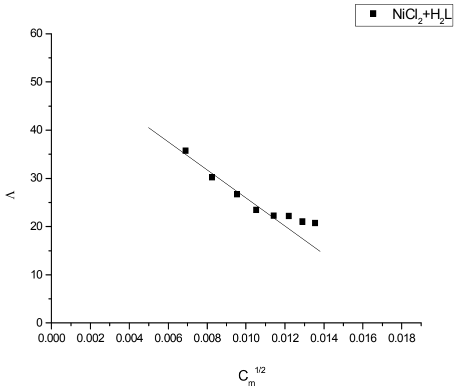


Fig. 2 *The relation between molar conductance (/\$_M$) and ($\sqrt{C}$) of $NiCl_2$ in the presence of H_2L in absolute ethanol at 294.15 K.*

The association constants of $NiCl_2$ in the presence of ligand (H_2L) in absolute ethanol at 294.15 K for 1:2 asymmetric electrolytes were calculated [6, 7] by using equation:

$$K_A=\frac{\Lambda_0^2(\Lambda_0-\Lambda_m)}{4C_m^2+\Lambda^3S(z)} \tag{2}$$

where (/\$_m$, /\$_0$) are the molar and limiting molar conductance, respectively of $NiCl_2$; C_m is molar concentration of $NiCl_2$, S(Z) is Fuoss-shedlovsky factor , equal with unity for strong electrolytes [8]. The calculated association constants are shown in Table 1.

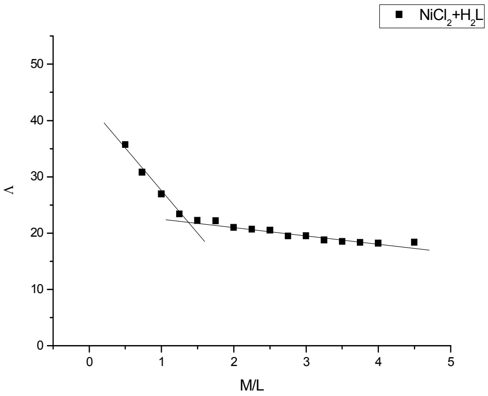


Fig. 3 *The relation between molar conductance (Λ_M) and the molar ratio(M/L) of $NiCl_2$ in the presence of H_2L in absolute ethanol at 294.15 K.*

The Gibbs free energies of association (ΔG_A) were calculated from the association constant [9,10] by applying equation:

$$\Delta G_A = -RT \ln K_A \tag{3}$$

where R is the gas constant (8.341 J) and T is the absolute temperature (294.15 K). The calculated Gibbs free energies were presented in Table 1.

Table 1 Association constants and Gibbs free energies of association for $NiCl_2$ with (H_2L) in absolute ethanol at 294.15 K.

ΔG_A (k J/mol)	K_A	$4C^2+\Lambda^3_m$	$\Lambda_o^2(\Lambda_o-\Lambda_m)$	$\Lambda_o-\Lambda_m$	C	Λ_m ($cm^2.Ohm^{-1}$)
–3.054	3.488	2.366×10^4	8.252×10^4	26.792	2.439×10^{-5}	28.707
–0.716	1.340	4.549×10^4	6.098×10^4	19.800	4.762×10^{-5}	35.700
–3.571	4.309	2.020×10^4	8.706×10^4	28.265	6.977×10^{-5}	27.235
–4.671	6.759	1.417×10^4	9.579×10^4	31.100	9.091×10^{-5}	24.200
–4.996	7.717	1.281×10^4	9.887×10^4	32.100	1.111×10^{-5}	23.400

$\Lambda_o = 55.5\ cm^2.Ohm^{-1}$

The association free energies evaluated for $NiCl_2$-ligand complexes are small and spontaneous indicating electrostatic attraction.

The formation constants (K_f) for $NiCl_2$ complexes were calculated for each type of complexes (1:1) and (2:1) (M:L) by using equation [11,12]:

$$K_f = \frac{\Lambda_M - \Lambda_{obs}}{(\Lambda_{obs} - \Lambda_{ML})[L]} \tag{4}$$

where Λ_m is the molar conductance of the $NiCl_2$ alone, Λ_{obs} is the molar conductance of solution during titration and Λ_{ML} is the molar conductance of the complex.

The obtained values (K_f) for $NiCl_2$-ligand stoichiometric complexes are presented in Tables 2,3. The Gibbs free energies of formation for each stoichiometric complexes were calculated by using the equation:

$$\Delta G_f = -RT \ln K_f \qquad (5)$$

The calculated ΔG_f values are presented in Tables 2,3.

Table 2 Formation constants and Gibbs free energies of formation for 1:1 (M/L) NiCl$_2$-H$_2$L complexes in absolute ethanol at 294.15 K.

Δ G$_f$ (k J/mol)	K$_f$	(Λ_M-Λ_{obs})	(Λ_{obs}-Λ_{ML}) [L]	[L]	Λ_{obs} (cm^2.Ohm^{-1})
–24.963	2.720×10^4	17.792	6.540×10^{-4}	9.750×10^{-5}	28.708
–27.684	8.276×10^4	10.800	1.305×10^{-4}	9.525×10^{-5}	35.700
–25.878	3.956×10^4	19.265	4.869×10^{-4}	9.302×10^{-5}	27.235
–28.413	1.115×10^5	22.30	1.999×10^{-4}	9.091×10^{-5}	24.200
–29.658	1.856×10^5	23.10	1.244×10^{-4}	8.888×10^{-5}	23.400

Λ_M = 46.5 cm^2.Ohm^{-1}, Λ_{ML} = 22 cm^2.Ohm^{-1}

Table 3 Formation constants and Gibbs free energies of formation for 2:1 (M/L) NiCl$_2$-H$_2$L complexes in absolute ethanol at 294.15 K.

Δ G$_f$ (k J/mol)	K$_f$	(Λ_M-Λ_{obs})	(Λ_{obs}-Λ_{ML}) [L]	[L]	Λ_{obs} (cm^2.Ohm^{-1})
-26.660	5.448×10^4	24.266	4.454×10^{-4}	8.510×10^{-5}	22.234
-26.783	5.727×10^4	24.338	4.249×10^{-4}	8.233×10^{-5}	22.162
-27.535	7.791×10^4	25.492	3.272×10^{-4}	8.163×10^{-5}	21.008
-27.818	8.745×10^4	25.811	2.951×10^{-4}	8.000×10^{-5}	20.689
28.022	9.508×10^4	26.000	2.734×10^{-4}	7.813×10^{-5}	20.500
-29.004	1.421×10^5	27.027	1.902×10^{-4}	7.692×10^{-5}	19.473
-29.021	1.431×10^5	26.939	1.887×10^{-4}	7.547×10^{-5}	19.561

Λ_M = 46.5 cm^2.Ohm^{-1}, Λ_{ML} = 17 cm^2.Ohm^{-1}

The association free energies evaluated for NiC1$_2$-1igand complexes indicating a spontaneous electrostatic attraction.

The formation constants and Gibbs free energies of different complexes in absolute ethanol at 294.15 K follow the order: K_f (2:1) > K_f (1:1) for (M:L), and ΔG_f (2:1) > ΔG_f (1:1) for (M:L).

The formation of 2:1 and 1:1(M: L) complexes indicate that (H$_2$L) may act as flexidentate ligand.

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