

Full Paper

Potentiometric Determination of the Stability Constants of 3-Thioacetyl-, and 2-benzoyl-3-amino-1, 4-naphthoquinone Chelates with Co(II), Ni(II) and Cu(II) Ions

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ABSTRACT

The acid dissociation constant of the two ligands 3-thioacetyl-3-amino-1.4-naphthoquinone [**L**₁] and 2-benzoyl-3-amino-1.4-naphthoquinone [**L**₂] in ethanolic solution was determined by pH-metric technique at different temperatures (25, 35°C), and at various ionic strengths (I= 0.02, 0.1, 0.15 M NaCl) The stability constants of the formed chelates between **L**₁ and **L**₂ and Co(II) , Ni(II) and Cu(II) at two temperature degrees (25, 35°C) have been investigated . It has been found that it increase in the order Co (II) < Ni (II) < Cu (II) .The thermodynamic parameters (ΔG° , ΔH° , ΔS°) of the chelates were deduced.

Keywords: 1.4-naphthoquinone, transition metal chelates, thermodynamic parameters

Introduction

Naphthoquinones are largely found in plants, microorganisms, and some animals. These compounds have been widely used in diverse cultures such as colorants for cosmetics, fabrics, foods, and for medical purposes, including antitumor, anti-inflammatory, and antimicrobial agents [1, 2].The biological activity of several well-know and widely used anthracycline

antibiotics such as daunomycin and doxorubicin is thought to be associated to the hydroxyquinone structure [3].

Potentiometric titrations are among the most accurate techniques known, because the potential follows actual change in activity and therefore the end point coincide with the equivalent point [4, 5]. The study of metal-ligand complexes in a solution would be interesting which throw

a light on the mode of storage and transport of metal ion in biological kingdom with a view to understand the bioinorganic chemistry of the metal ions [6,7]. All metal complexes or chelates may be considered as being formed by displacement of one or more usually weakly acidic protons of the complexing or chelating agent by a metal ion in a solution, which result in pH drop [8]. The stability constant of the reaction between metal and ligand has been found to be greater than zero, is perhaps the most convincing evidence for the existence of the complex species [9]. The main aim of the present work is to synthesize, characterize and evaluate the stability constants of 3-thioacetyl-3-amino-1,4-naphthoquinone [L_1] and 2-benzoyl-3-amino-1,4-naphthoquinone [L_2] ligands and their some metal chelates pH-metrically.

EXPERIMENTAL

Materials and Solutions

All chemicals used were of analytical-reagent grade the ligands L_1 and L_2 were synthesized according to the method described in literature [10]. The purity of the organic ligands was confirmed by infrared spectroscopy.

Stock solutions (1×10^{-2} M) of the ligands were prepared by dissolving the required weighed amounts in ethanol and (1×10^{-2} M) of metal salt $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ were prepared by dissolving the required weighed amounts of each in double distilled water.

Standard sodium hydroxide (0.1M) was prepared in the usual way. Pure sodium chloride solution (1M) was used as supporting electrolyte to keep the ionic strength constant. All pH-metric titration were carried out using a WTW Model7110 BNC pH-meter. All the potentiometric measurement were performed in 50% v/v ethanol-water at 25°C, and 35°C. The pH values in 50% v/v ethanol were corrected as described [11]

The following solution (a-c) (total volume 50 ml, ionic strength being adjusted with 1M NaCl (in ethanol medium) were prepared and titrated potentiometrically at different temperatures at 25°C and 35°C against standard (0.1M) NaOH in ethanol-water mixture (50 vol%): -

- (a) 3 ml HCl (0.1M)
 - (b) a + 20 ml (0.01M) ligand solution.
 - (c) b + 5 ml (0.01M) Metal ion solution.
- In all cases, correction was made for change in volume occurring during titration, due to the addition of sodium hydroxide.

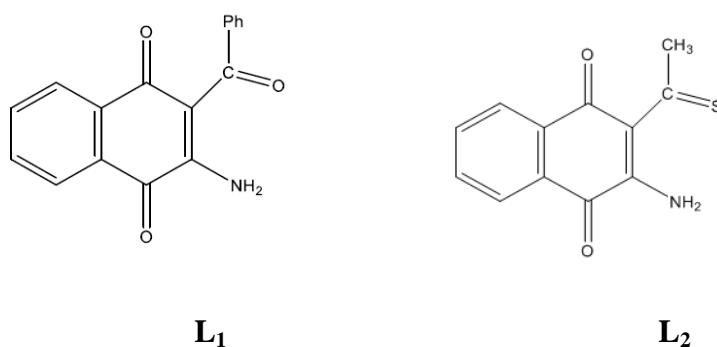


Figure (1): Structure of ligands.

RESULTS AND DISCUSSION

The formation functions n_H , \bar{n}_A , and pL were calculated using standard expressions [12] from the titration curves for (a), (b) and (c).

$$\bar{n}_A = Y \pm \frac{(V_2 - V_1)(N^\circ + E^\circ)}{(V^\circ + V_1) T_{CL}^\circ}$$

Where \bar{n}_A is the average number of protons attached per ligand,

Y is the number of available protons

V_1 and V_2 are the volumes of alkali required to reach the same

pH on the titration curve of hydrochloric acid and organic ligand respectively.

V° is the initial volume (50ml) of the mixture

N° is the initial concentration of sodium hydroxide solution

T_{CL}° is the total concentration of the ligand

The titration curves (\bar{n}_A vs. pH) for the proton- ligand systems were constructed and found to extend between 0 and 1 on the \bar{n}_A scale. This means that L_1 and L_2 have one ionisable proton (Figure 2). The proton-ligand stability constants were calculated [13]. The data obtained are listed in Table (1).

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ions (\bar{n}) vs. the free ligand exponent (pL) in a similar fashion to \bar{n}_A [13] (Figure3). The average number of the reagent molecules attached per metal ion \bar{n} and free ligand exponent, pL , can be calculated using the equations (2, 3).

$$\bar{n} = \frac{(V_3 - V_2)(N^\circ + E^\circ)}{(V^\circ + V_1) \bar{n}_A T_{CM}^\circ}$$

$$pL = \log \left[\frac{\sum_{n=0}^{n=i} \beta_n^H [1/\text{anti log } B]^n}{(1)T_{CL}^\circ - \bar{n} T_{CM}^\circ} \cdot \frac{V^\circ + V_3}{V^\circ} \right] \quad (3)$$

Where \bar{n} is the average number of ligands attached per metal ion

T_{CM}° is the total concentration of the metal ions present in the solution,

β_n^H is the overall proton reagent stability constant.

V_1 , V_2 , V_3 are the volumes of alkali required to reach the same pH on the titration curves of hydrochloric acid, organic ligand and complex, respectively.

v° is the total volume of the solution.

N° is the normality of NaOH

E° is the initial concentration of HCl

The formation constant for the metal complexes obtained from the interpolation at $\bar{n} = 0.5$ according to Irving and Rosotti [13].

From the above stability and change in ionic strengths (0.02, 0.1 and 0.15M), the thermodynamic dissociation and formation constants were obtained. Also, the free energy (ΔG°), the enthalpy (ΔH°) and the entropy (ΔS°) were evaluated. All results are listed in Table (1).

Table (1): Stability Constant, Free Energies[†], Enthalpies[†], and Entropies[†], of (L₁) and (L₂) Ligands and their metal Chelates.

System	Stability Constant	Ionic strength (25°C)			Ionic strength (35°C)(0.1)	log k° (25°C)	ΔG KJ/mol	ΔH KJ/mol	ΔS J/deg/mol	ΔG (35°C) KJ/mol
		0.02	0.1	0.15						
Ligand (L ₁)	LogK ₁ ^H	9.4	9.0	8.85	8.9	9.7				- 56
Co (11)	LogK ₁	5.4	4.8	4.55	4.45	5.8	- 33.09	22.34	- 186	- 30.66
Ni (11)	LogK ₁	5.6	5.0	4.75	4.6	6	- 34.23	22.4	- 190.03	- 32.23
Cu (11)	LogK ₁	6.2	5.4	5.1	5.2	6.75	- 38.51	22.51	- 204.76	- 38.33
Ligand (L ₂)	LogK ₁ ^H	9.5	9.1	8.95	8.95	9.8				- 56.6
Co (11)	LogK ₁	5.98	5.1	4.8	5.0	6.5	- 37.08	22.45	- 199.76	- 36.85
Ni (11)	LogK ₁	6.01	5.21	5.01	5.11	6.75	- 38.51	22.51	- 204.76	- 38.33
Cu (11)	LogK ₁	6.7	5.6	5.15	5.4	7.5	- 42.8	22.54	- 219.26	- 42.46

† Calculate at $I = 0.1M$ NaCl

‡ Log K° denotes to the thermodynamic formation constant and was obtained by the extrapolation of the overall stability constant to zero ionic strength (I) in the plot of log K against \sqrt{I} .

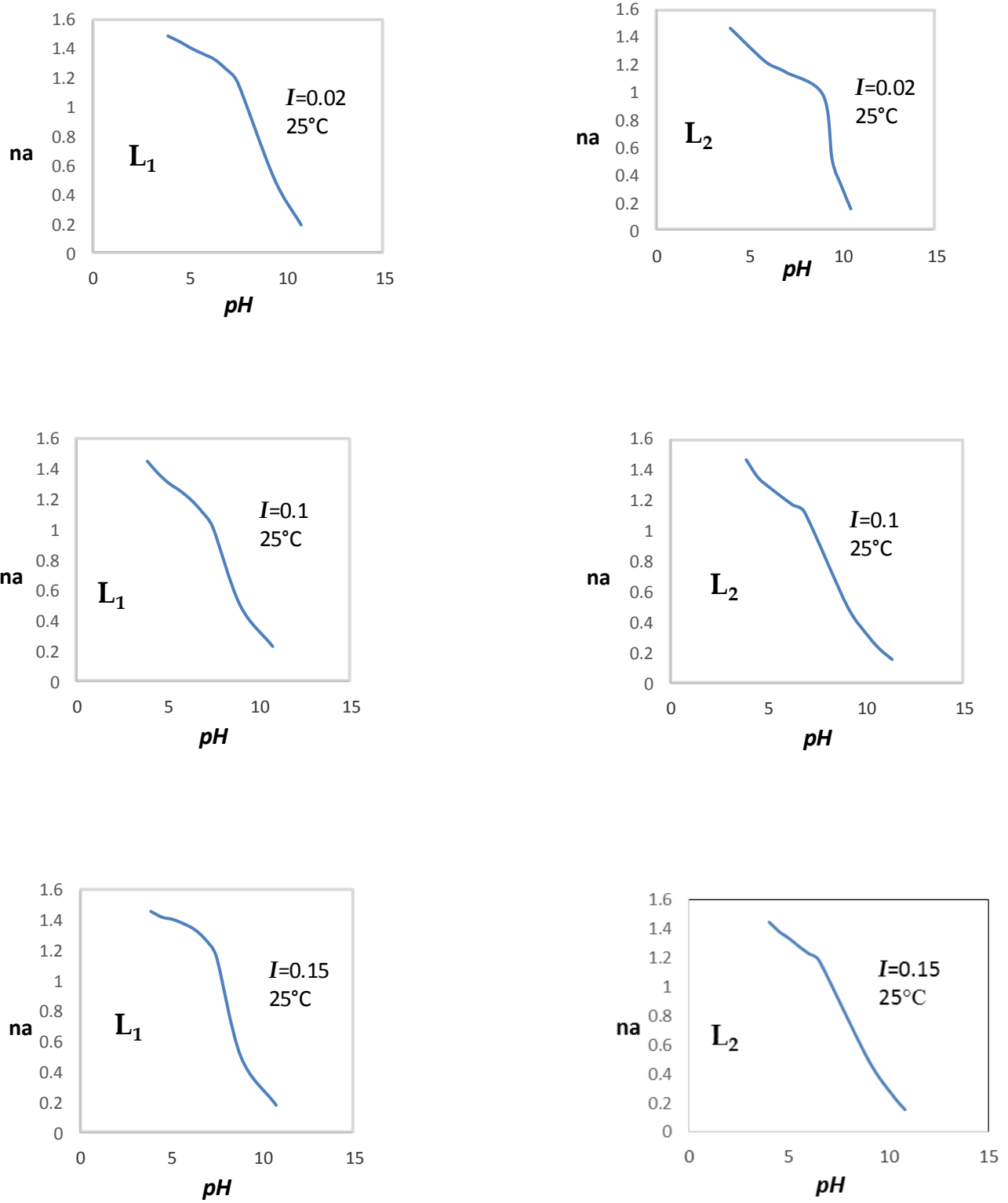


Figure (1): na - pH relation for L_1 and L_2 at different ionic strengths at $25^\circ C$.

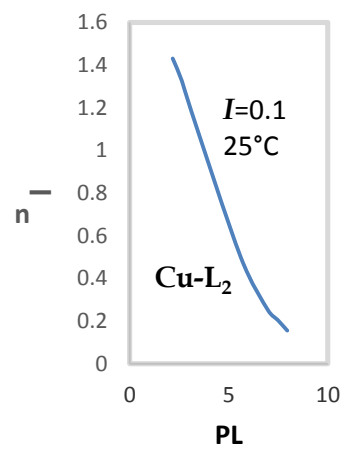
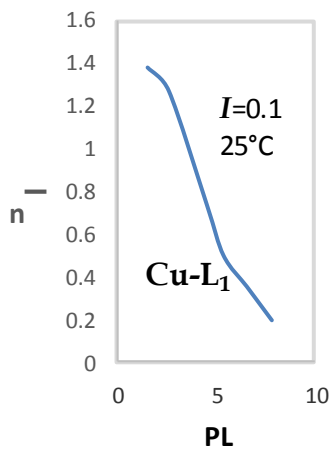
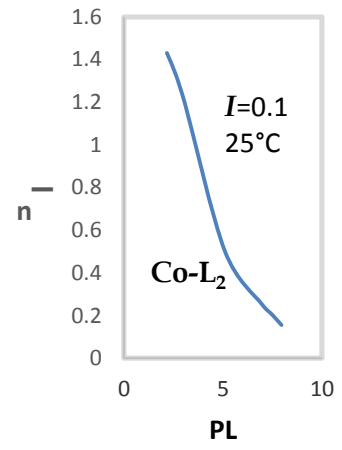
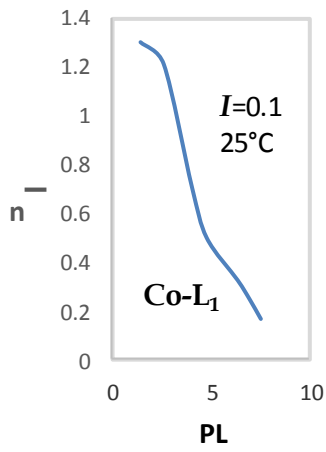
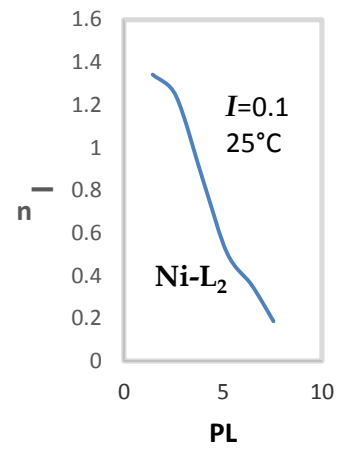
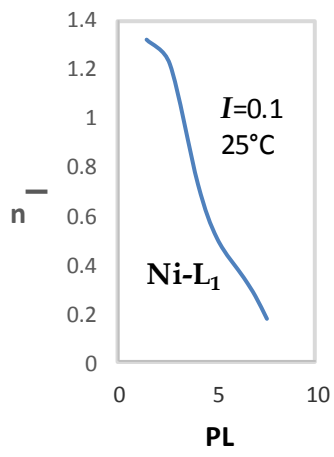


Figure (2): \bar{n} - PL relation for L₁ and L₂ with Ni, Co, Cu at 0.1M ionic strength and 25°C.

It has been found from Table (1) that the values of the stability constants decrease as the ionic strengths decrease for complexes which is in agreement with Debye's [14].

The overall changes in ΔG° , ΔH° and ΔS° were calculated at 25°C. Negative values of ΔG° (free energy) were obtained, indicating that these reactions are spontaneous. Also, the lower values of ΔG° at higher temperature (35°C) indicate clearly that the rate of the reaction decreases as the temperature increases. ΔH° values were calculated and it was positive, indicating that the complexation reactions are endothermic.

ΔS° values are negative for all chelates, indicating that the instability of the chelate is very low [15].

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