Thermodynamic Parameters, Electrical Conductivity and Spectrophotometric Measurements of Mn^{2+}, Co^{2+}, $Ni^{2+}Cu^{2+}$, Zn^{2+}, Cd^{2+}, and Fe^{3+}-Complexes with Some Schiff Base Hydrazones Containing Quinoline Moiety

M.El Batouti[1] and G.Nawmosy[2]

[1]Chemistry Department, Faculty of Science, Alexandria University.

[2]Chemistry Department, Faculty of Science and Arts, Al Qassim University.

ABSTRACT

A new hydrazone Schiff base consisting of 7-chloro-4-(o-hydroxy benzilidenehydrazo) quinoline, with metal complexes of some divalent metal ions, Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) were investigated Conduct metrically and thermodynamically. We have used molar ratio method to determine the stoichiometric of the formed complexes, The results obtained confirmed the formation of 1:1 and 1:2, M: L complexes. In order to get information about the composition of complexes electrical conductivity were determined. The standard thermodynamic parameters viz. ΔG, ΔH and ΔS, for the proton-ligand and the stepwise metal-ligand complexesluated. Thermodynamic functions were analyzed in terms of the electrostatic (el) and non-electrostatic (cratic, c) components. ΔH_c was found to be linearly correlated with the acceptor number of the metal ion (AN_M), and ΔH_{el} was linearly correlated with the ionic radii of the metal ion. The calculated values for ΔG^o, ΔH^o and ΔS^o concluded that the complexion process processed spontaneously. Spectrophotometric measurements of Co (II), Ni(II) complexes obeyed Beer's law up to certain values, 6.6×10^3, 8.0×10^3 $dm^3 mol^{-1} cm^{-1}$, respectively, indicating that the ligand HL could be used to detect Co(II) and Ni(II) in such concentrations. The study was performed also for Fe (III)-complexes.

Introduction

Hydrazone Schiff base compounds containing quinoline moiety are well known in natural materials, and show interesting biological and antiviral activities [1-3]. Many derivatives of hydrazon compounds form colored complexes with different metal ions and can be used as analytical reagents for their determinations [4-9].The coordination compounds of aroylhydrazones have been reported to act as enzyme inhibitors [10] and are useful due to their pharmacological applications [11-13]. . The study of Schiff base hydrazones has been growing interest because of their antimicrobial, anti-tuberculosis, and anti-tumour activity [1-12].The azomethine (C=N) linkage in Schiff bases imports in elucidating the mechanism of transamination and resamination reactions in biological system [14]. The importance of metals and transition elements are formed organic compound due to its presence in many of the enzymes associated with mineral particles of large ring molecules such as hem [15]. Effect of the nature of the center metal ion and the medium, composition of fixed factors on the stability of the complexes formed Hydrazones of Schiff bases with ions transition elements were studied by using, spectral studies of solutions, and reduced the pollution of both heavy metals or organic compounds unwanted .

Thermodynamic parameters are computed and analyzed in order to investigate the bond character between the metal ligand. The magnetic moments and electrical conductance of the complexes were also determined.

Experimental

Reagents and materials

All chemicals used were for Anal. Grade and the solutions of metal nitrates of, Mn (II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) ions were prepared in carbonate free double distilled water and they were stabilized using EDTA titrations[16]. The HL ligand was prepared as described previously [17]. The structure of the ligand was elucidated by IR, Mass, ^{1}H-NMR and electronic (UV-VIS) spectroscopy, as well as micro analytical analyses [17]. The results have been previously published [17] and weighed quantity of the ligand was dissolved in 75% (v/v) ethanol-water medium. Ethanol-water was freshly refluxed and distilled over magnesium powder and iodine [16].

Potentiometric measurements

A Hanna pH-meter Model 302 digital with conventional pH-electrode assembly was used for pH measurements at 10, 20, 30 and 40°C. The ionic strength of the medium was kept virtually constant at 0.05 $mol.dm^{-3}$ with KNO_3 as background electrolyte. The temperature was maintained constant by use of double –jacket cells with water circulated from a constant-temperature bath. Purified nitrogen gas was bubbled through the solution before and during the titrations Multiple titrations were carried out for each system and the pH meter readings were recorded [6-9]. Electronic absorption spectra of the free ligand and its complexes in 75% (v/v) ethanol-water were recorded using a Shimadzu Model Uv-probe spectrophotometer. The composition of the complexes in solutions were determined by the molar ratio method [18,19]. The pH metric titrations in 75 %(v/v) ethanol -water of the free ligand and its mixtures with the metal ions were carried out as described previously [6-9].
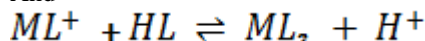
Using equations of Irving and Rossoti[20] the curves were used to calculate the formation constants of the following equilibria:

$$M^{2+} + HL \rightleftharpoons ML^+ + H^-$$

And

$$ML^+ + HL \rightleftharpoons ML_2 + H^+$$
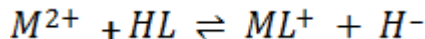
The experimental reading was used to calculate the values of $\bar{n}$ and PL. From which the stability constant log K_1 and log K_2 were calculated with the help of the following equations given by Irving and Rossoti [20].

$$\log \frac{\bar{n}}{1-\bar{n}} = \log K_1 + PL$$

$$\log \frac{\bar{n}-1}{2-\bar{n}} = \log K_2 + PL$$

The metal-ligand stability constant was obtained using linear plot method by plotting $\log \frac{\bar{n}}{1-\bar{n}}$ or $\frac{\log(\bar{n}-1)}{2-\bar{n}}$ against PL . where $\bar{n}$ is defined by Irving and Rossetti [20] as the average number of the reagent molecules attached per metal ions. It can be obtained from the following relations

$$\bar{n} = \frac{(V_3 - V_2)(N^0 + E^0)}{(V^0 + V_2)\bar{n}_A \, TC_M^0}$$

And

$$PL = \log_{10} \frac{\sum_{m=0}^{n=1} \beta_n^H \left(\frac{1}{anti \log pH}\right) V^0 + V_2}{TC_L^0 - \bar{n} TC_M^0}$$

Where V_2 and V_3 are the volumes of alkali required to reach the same pH value, V_0 is the total volume of titrating mixture, N^0 and E^0 are the concentration of free acid, respectively, TC_L^0 and TC_M^0 are the total concentration of ligand and metal ion, respectively and pL, is the free ligand exponent. The experimental reading were used to calculate the values of $\bar{n}$ and PL . From which the stability constant log K_1 and log K_2 were calculated with the help of the following equations given by Irving and Rossetti [20].

The variations of pKH, log K_1 and log K_2 vs. 1/T gave straight lines which enable us to calculate the thermodynamic parameters ΔG^o, ΔH^o, and ΔS^o of the complex formation by the Vant -Hoff equation and other relationships [21-22].Conduct metric titrations were carried out at room temperature by titrating 30ml metal ion solution (1×10^{-3} mol dm^{-3})with the ligand solution (1×10^{-2} mol dm^{-3}) as titrant using WTWD-812 Weilneium- conductivity meter, model LBR, fitted with a cell model LTA100.

Synthesis of the Organic Ligand

7-chloro-4-(o-hydroxy benzilidenehydrazo) quinoline, HL The ligand (HL) was synthesized as follows.7-chloro-4-hydrazinoquinoline; 2g (1mmol) was dissolved in 10ml absolute ethanol. To this solution salicylaldehyde, 13ml (1.1mmol) was added. The reaction mixture was refluxed for 2h. After cooling, the formed yellow precipitate was collected, filtered, and finally washed with 5-10ml absolute ethanol and purified by recrystallization from ethanol (80%m mp 235° C)

Measurement of electrical conductivity

Electrical conductance conducted measurements using a WTW. D 8120 Weilheim LF. 42

Spectral measurements

Spectral measurements were conducted, on a Shimadzu Model Uv-probe.

7-chloro-4-hydrazinoquinoline + salicylaldhyde
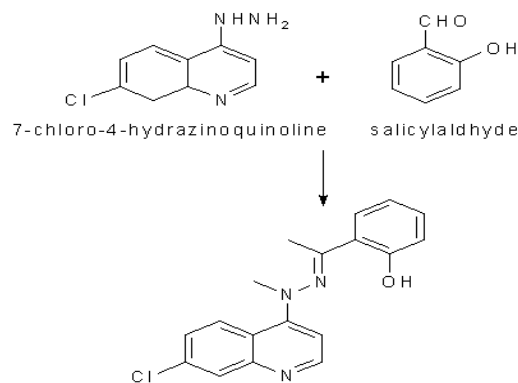
7-chloro-4-(o-hydroxybenzilidenehydrazo) quinoline

Result and Discussion

Thermodynamic parameters

Thermodynamic parameters, Table 1 are calculated from the formation constants in a mixture of 75% ethanol - water, at different temperatures as follow:

1-Free energy change ΔG^o

$-\Delta G^o = 2.2303T \log K$ --------- (1)

Vant- Hoff isotherm ΔH^o

$d\log K/dt = \Delta H^o/4.57T$ ---------- (2)

By solving (1) and (2) we obtained

Log $K = -\Delta H^o/4.47T$ + constant

By plotting the relation between log K vs. 1/T we obtained a straight line its slope is equal to $= \Delta H^o/4.57T$ and ΔH^o is in cal.mol^{-1}.

The change in entropy ΔS^o is calculated from Gibbs_Helmhoholtz equation:

$\Delta G^o = \Delta H^o - T\Delta S^o$

Thermodynamic parameters provides valuable information about nature of formed complexes, the degree of covalent bonding, and the change in hydration. The thermodynamic parameters results and the stability constants of the metal ions at a temperature 30°C in 75% (v /v) prove that the stability constants of complexes ligand logK_1 would be in the following order:

Ni (II)> Co (II)> Mn (II)> Cd (II)> Zn

The Fe (III) ion was excluded because it must be compared with Triple charges ions. If we compare {Zn (II), Cd (II)} ions and {Co (II), Ni (II)} ions, we find that their positions are consistent with previous publication research [21-24]. Fig. 2 illustrates the form of a linear relationship between the dissociation constant of ligand and static stability of the complexes logK_1. This linear relationship reflects the similarity of the ionic nature of the reaction between the metal and ligand [21].
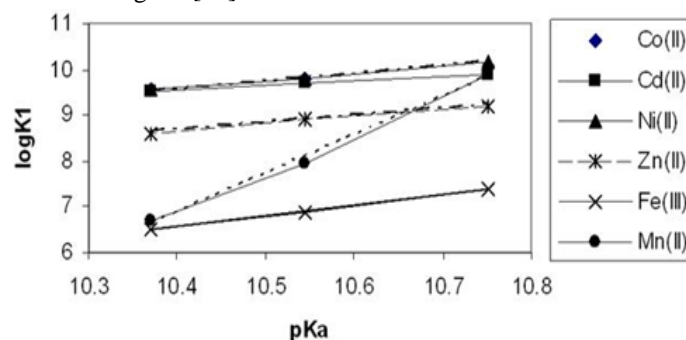

Fig 2. Relationship between the values of logK1 and pKa at 30 ^{o}C in 75% (v/v) ethanol-water

We can also use functions to distinguish between thermodynamic parameters formed inside the outer sphere and inner sphere complexes. According to Choppin [25] reflects the functions thermodynamic parameters and any type of these complexes may be as follows:

Therefore, the results confirm thermodynamic parameters which are internal complexes. Also, the table shows that the complexion process decreased with the increase of temperature, indicating that the temperature at least is the favorite for the complexion process and leading to negative values for ΔH^o which means that the interaction between the metal ion and ligand molecule reaction is exothermic.

According to Nancollas et al [26], the values of ΔH^o reflect the change in the number and strength of the bonds that are formed by breaking during the interaction between the metal ion and ligand. The composition of the complex and hence the values of ΔH^o is directly related to the type of inter dependence between the metal ion (M^{n+}) and ligand molecules, as well as with the structure of Complex formed. If we take into account the fact that the areas of crystal-fields produced by the consistency of oxygen centers O-coordinating sites are similar to the consistency of molecules [27], including water, ΔH^o conclude that the effect is not affected by moving the replacement of water molecules. Therefore, the negative value of ΔH^o is due to N-coordinating sites in the ligand molecule as described in the following structure.
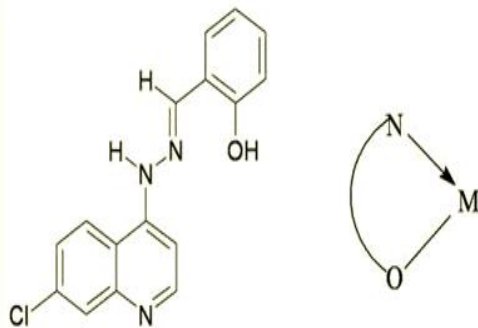
The table shows the values of $\Delta H^o_1 > -\Delta H^o_2$ of the ligand complexes with ions Co (II), Ni (II), Fe (III), and Mn (II).This demonstrates that there is a change in the properties of x-rays of the ligand, change in the dentate character. In other words, the decline in values $-\Delta H^o_2$ indicated to change donor centers in ligand of tridentate (ONN) donor in 1:1 complexes to bidentate (ON) donor complexes to 1:2 (M:L) to overcome the steric hindrance in the complexes 1:1 (M: L). Which is identical to the published Evans et al [28], where he obtained the same results. On the contrary, illustrates Table 2 that the values of $\Delta H^o_2 > \Delta H^o_1$ for complexes with ions of Cd (II) and Zn (II) and takes this as a sign characteristic of the effect of Trans influence [29] of the second coordination.

valuable thermodynamic parameters probably due to the change in the electron affinity to ions Metals In contrast, high negative values for ☐Go indicates that the complexity is spontaneously, and that the positive values of ☐So for all complexes are consistent with the hypothesis that during the process complexity remove a large number of water molecules with the possibility of changes in the number of coordination [29] This shows that the change in entropy reflects the formation of complexes. Fig. 3 shows the relationship between the change in ☐Go1 ، ☐Ho1, ☐So1 and the number of electrons3d and found that relationship is between metal ions and the number of electrons 3d, which indicates that the change

is a valuable thermodynamic parameters probably due to the change in the electron affinity to ions Metals.
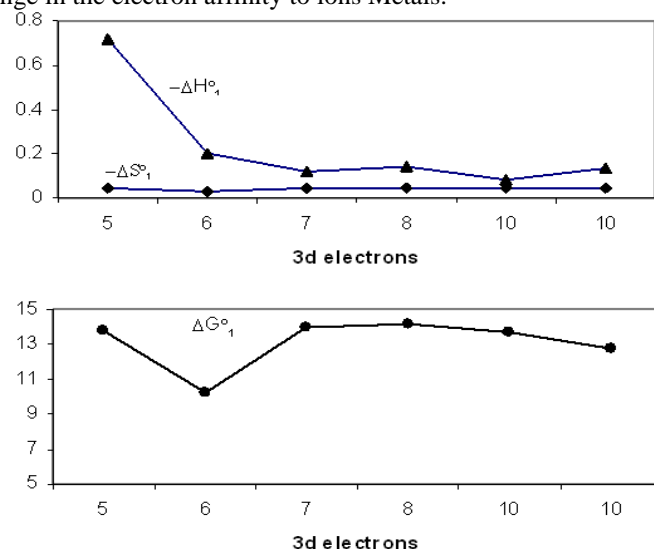
Fig 3. Relationship Between the Thermodynamics Functions, (Δg^o_1 , Δh^o_1, k. Cal. Mol^{-1}) and Δs^o_1 (cal. Mol^{-1} k^{-1}) and the 3d Electrons

In order to get information on the nature of the bonds in the complexes,Table2 would be advisable to analyze the values of ΔG^o,ΔH^o,ΔS^ointo two parts: Part-a, the part that temperature-dependent ΔX^o_{el}, , electrostatic (el) interaction due to reaction of dipole or ion with long-range electrostatic forces of the powers of the electrostatic solvent medium.Part-b, which does not depend on temperature ΔX^o_{non} non-electrostatic or also called Kratk ΔX^o_cwhich is due to the molecule or ion is produced from a short term or short range of covalent bonds with the surrounding environment and hence the

$$\Delta X^o_{non=}\Delta X^o_{el +} \Delta X^o_c$$

If we look at the degree of covalent bonding, we find that the ion metal has a softener donors [30] and figure 4 shows the relationship between ΔH^o_{non} d quantity $E_n^{\#}$ described at Klopman [30] as a measure of hardness and a softness, where we note that the metal ion soft features With negative values of high-value $E_n^{\#}$ and vice versa.
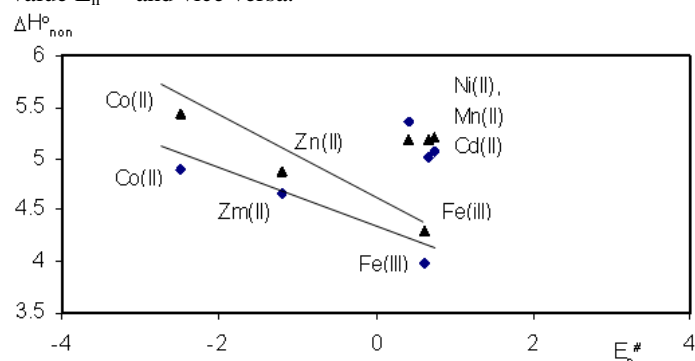
Fig 4. Relationship of hardness and softness, en# (ev), of metal ions and non-electrostatic heat change, Δh^o_{non} , of the formation of the complex

As is clear from the figure4 that there is a linear relationship between ΔH^o_{non} and the number of En # ΔH^o_{non} in the sense that increases as the increased softness of the softer metal ion. According to many authors [31-33],the change in electrostatic enthalpy ΔH^o_{non} arises from changes that occur in the area of changes in the ligand field (LSF) associated with the composition of the complex. The following forms (Figs. 5 a, b, 6, 7 and 8), and after excluding the ion Fe (III),show the relationship between each of the electronegativity (X_m) and

second ionization potential (2Ip) for ions metals with a fixed configuration $\log K_1$ as well as with a fixed configuration $\log(K_1 K_2)$ and note that the constants of the configuration $\log(K_1 K_2)$ of the complexes are growing linearly with the increase electronegativity (X_m) or increase the ionization potential of the metal ions bilateral charge (2Ip).
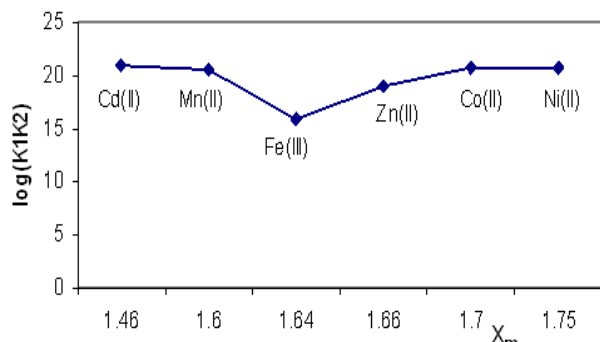

Fig 5a. Relationship of the x_m of the metal ions with $\log(k_1 k_2)$
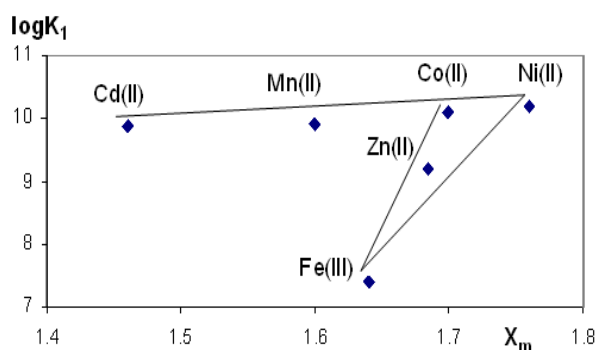

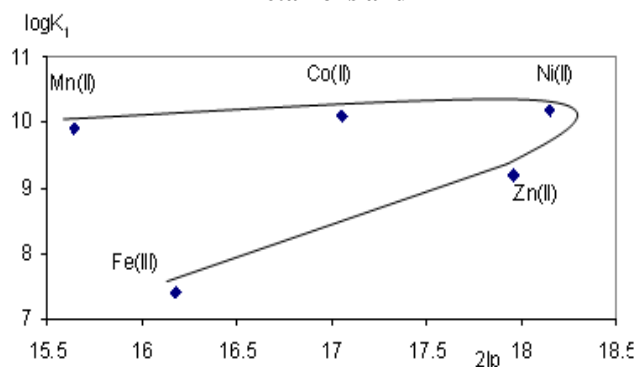**Fig 5b. Relationship between the electronegativity of the metal ions and**

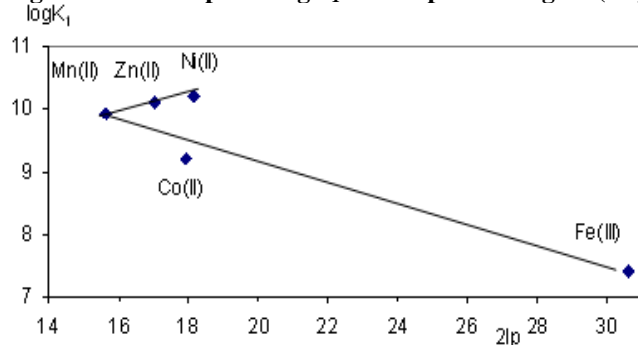**Fig 6. Relationship and $\log K_1$ with 2Ip including Fe (III)**

Fig 7. Relationship and $\log K_1$ with 2Ip including 3Ip of Fe (III)

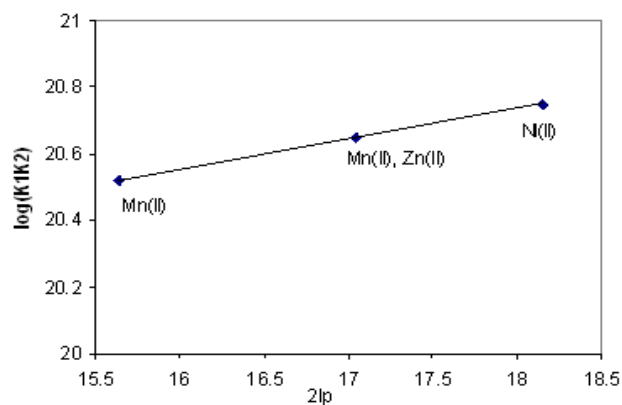**Fig 8. Relationship and $\log(K_1 K_2)$ with 2Ip of divalent cations excluding Fe(III)**
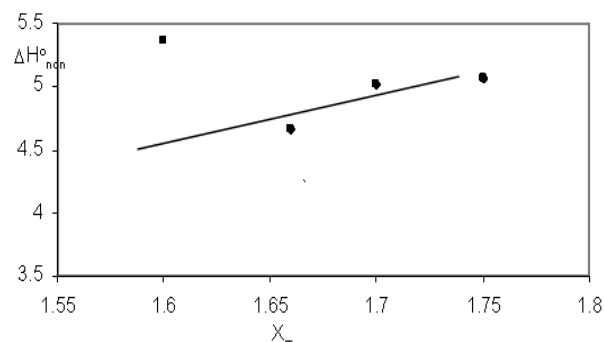
Fig 9. Relationship of the Xm of the metal ions with ΔHonon

On the other hand, the property of the bond in covalent complexes can inferred from the linear relationship (Fig. 10) between ΔH_{non} and ANm acceptor number of the cations[34].
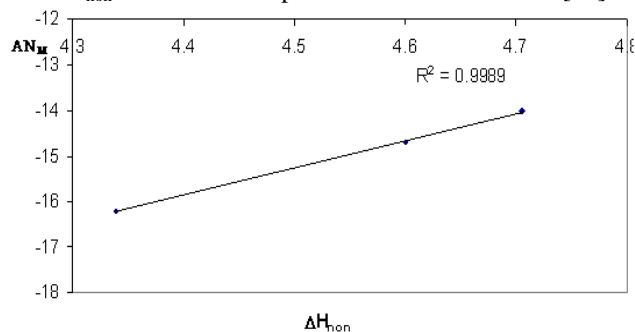
Fig 10. Relationship of acceptor number of metal ions, AN_M, with $\Delta H°_{non}$

Acceptor number (AN) Known as a quantitative measure of Lewis acidity according to the ability to form covalent bond with a pair of electrons. We can summarize the above, we found that the $\Delta H°_{non}$ associated with a positive relation with the donor acceptor number while $\Delta H°_{el}$ and $\Delta S°_{el}$ linked to a positive relation with half radii of metal ion (Figs. 11, 12)

Fig 11. Relationship of $\Delta S°_{non}$ with ionic radii of metal ions

Table 1. Thermodynamics functions and stepwise formation constants of 1:1 and 1:2 metal complexes at 30, 40, and 50 ^{o}C in 75 % ethanol-water

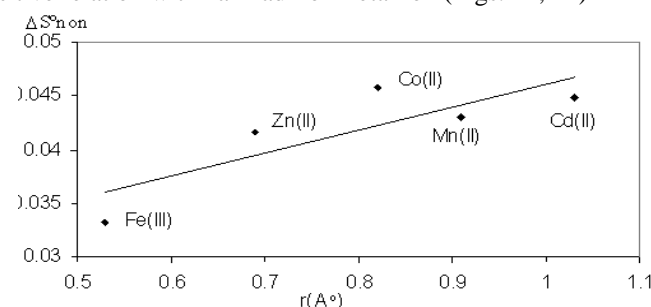| Complex (HL)	t ^{o}C						K. cal. mol^{1-}				K^{1-} cal. mol^{1-}	
	30		40		50		$-\Delta G^o_{30}$		$-\Delta H^o_{30}$		$-\Delta S^o_{30}$	
	logk1	logk2	logk1	logk2	logk1	logk2	ΔG^o_1-	ΔG^o_2-	ΔH^o_1-	ΔH^o_2-	ΔS^o_1	ΔS^o_2
(Co(II	10.09	10.56	9.79	10.4	9.55	10.2	13.9903	14.6419	0.120863	0.0803863	0.0457736	0.0480579
(Cd(II	9.88	10.99	9.69	10.6	9.52	10.1	13.6991	15.2381	0.080528	0.198704	0.0449457	0.0496351
(Ni(II	10.18	10.57	9.8	10.32	9.55	10.11	14.115	14.6558	0.141149	0.10293	0.0461185	0.0480296
(Zn(II	9.21	9.69	8.93	9.31	8.61	9	12.7701	13.4356	0.134038	0.15442	0.0417032	0.0438324
(Fe(III	7.41	8.4	6.9	8.1	6.5	7.9	10.2743	11.647	0.203699	0.112015	0.0332363	0.0380692
(Mn(II	9.91	10.61	7.96	10.47	6.7	10.3	13.7407	14.7113	0.719272	0.0692309	0.0429749	0.0483235
pka	10.751	--	10.544	--	10.371	--	14.9068	--	0.0850294	--	0.0489166	--

ΔH^o and ΔS^o	ΔG^o	Type of complex
Large positive	Large negative	inner sphere complex
Small positive	Small negative	outer sphere complex

Table 2.Thermodynamics functions and stepwise formation constants of 1:1 and 1:2 metal complexes at 30, 40, and 50 ^{o}C in 75 % ethanol-water

| Complex (HL)	t ^{o}C						K. cal. mol^{-1}				cal. mol^{-1} K^{-1}	
	30		40		50		$-\Delta G^o_{30}$		$-\Delta H^o_{30}$		$-\Delta S^o_{30}$	
	logk1	logk2	logk1	logk2	logk1	logk2	$-\Delta G^o_1$	$-\Delta G^o_2$	$-\Delta H^o_1$	$-\Delta H^o_2$	ΔS^o_1	ΔS^o_2
Co(II)	10.09	10.56	9.79	10.4	9.55	10.2	13.9903	14.6419	0.120863	0.0803863	0.0457736	0.0480579
Cd(II)	9.88	10.99	9.69	10.6	9.52	10.1	13.6991	15.2381	0.080528	0.198704	0.0449457	0.0496351
Ni(II)	10.18	10.57	9.8	10.32	9.55	10.11	14.115	14.6558	0.141149	0.10293	0.0461185	0.0480296
Zn(II)	9.21	9.69	8.93	9.31	8.61	9	12.7701	13.4356	0.134038	0.15442	0.0417032	0.0438324
Fe(III)	7.41	8.4	6.9	8.1	6.5	7.9	10.2743	11.647	0.203699	0.112015	0.0332363	0.0380692
Mn(II)	9.91	10.61	7.96	10.47	6.7	10.3	13.7407	14.7113	0.719272	0.0692309	0.0429749	0.0483235
pka	10.751	--	10.544	--	10.371	--	14.9068	--	0.0850294	--	0.0489166	--

Table 2. Electrostatic (el) and non-electrostatic thermodynamic parameters for the reaction of metal ions with HL ligand in 75 % a(v/v) ethanol – water at 30 oC

complex (HL)	ΔG^o_{30} (K. cal. mol($^{1-}$				ΔH^o_{30} (K. cal. mol($^{1-}$				ΔS^o_{30} (cal. mol^{1-} K($^{1-}$	
	$-\Delta G^o_{el}$		$-\Delta G^o_{non}$		$-\Delta H^o_{non}$		ΔH^o_{el}		ΔS^o_{el}	
	Log K $_1$	Log K $_2$	Log K $_1$	Log K $_2$	Log K $_1$	Log K $_2$	Log K $_1$	Log K $_2$	Log K $_1$	Log K $_2$
Co(II (	11.3959	11.8801	2.5944	2.76177	5.01251	5.17988	4.89164	5.09949	53.7543	56.0383
Cd(II (	11.2204	12.2145	2.4787	3.0236	4.89681	5.44171	4.81629	5.24301	52.9262	57.6155
Ni(II (	11.4689	11.8741	2.64602	2.78171	5.06413	5.19982	4.92298	5.09689	54.0987	56.0097
Zn(II (	10.533	10.9843	2.23716	2.45127	4.65526	4.86937	4.52123	4.71497	49.6838	51.8128
Fe(III (	8.73795	9.76253	1.53631	1.88442	3.98	4.30252	3.75072	4.19052	41.2168	46.0497
Mn(II (	10.8026	11.9365	2.93815	2.77479	5.35626	5.19289	4.63697	5.12367	50.9557	56.304
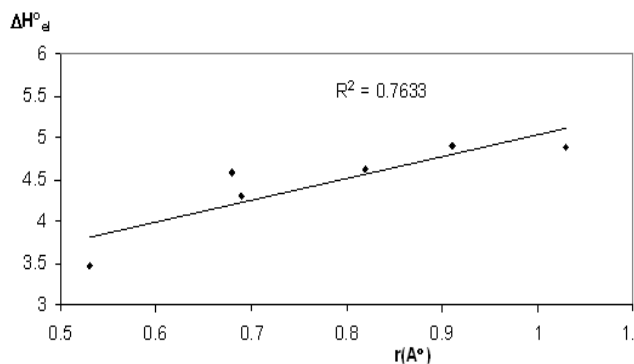
Fig 12. Relationship of ΔH°$_{el}$ with ionic radii of metal ions

Conductometric Titration

In order to get information on the composition of complexes we have had adjustments electrical conductivity. It is known that this measurement shows that the measured amount reflect and directly proportional to the concentration of one or more of the ions. When the interaction between metal ions and ligand we get calibration curve, which consists of two or more lines transmit at the equivalent point (the point that determine the structure of the complex) [35].
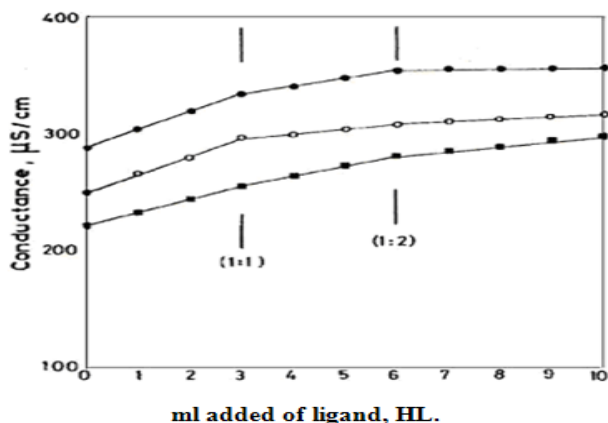
Fig. 13

Fig. 13. Showed conductometric titration curve of the ligand, HL, with metal ions, in which electrical conductivity increases continuously whenever we add ligand to the metal ion and continue to increase until we reach the equivalence point for titration. It is also clear that this behavior was attributed to the replacement of some metal ions with some of complex molecules. When you add the following drop of ligand we note that there is a slight increase in the values of electrical conductivity, which reflects that the added ligand remains without reaction and that increase could be due to the accumulation of ligand molecules. Titration curve and electrical conductivity appears to be complex double transmitance which reflects the percentage of M: 2L and M: L, and corresponds with the results of potential titrations. Titration electrical conductivity has been made under the same conditions of potential titration.

Spectrophotometric Measurements

The spectra of organic molecules are usually affected by the nature of the solvent and observed the influence of peaks intensity and position of the absorption top λ$_m$. . The influence depend on several factors, including, for example, the physical properties of solvent such as dielectric constant and the determination of dipole moment and refractive index as well as the ability of the solvent on the interaction through the formation of hydrogen bonds

Determination of stoichiometric of the formed complex

The method used to determine the percentage molar ratio to form the complex.

$$M^{n+} + nHL \leftrightarrow ML_n + nH^+ ....1$$

$$K = \frac{[ML_n[H^+]^n}{[M^{n+}][HL]^n}$$

1 - Job's method [35-38] derived from equation (1), the interaction between the metallic ion M^{n+} and organic ligand.
2 - Molar ratio method [40-43], where the metal ion concentration was constant while changing the concentration of [ligand]/Metal ion] and when we plot the valuesof absorption of these solutions against molarity ratio we get the straight lines intersect each two of them at a certain rate. And contrary to the method that we can make ligand concentration fixed and change the metal ion concentration was measured [metal ion] / [ligand] absorption of solutions at required pH.
3 – Slope- ratio method [44] in this way prepares two series of solutions. Saves in the first series ion concentration element constant while changing the ligand concentration. In the second series saves the ligand concentration ion concentration fixed and changes the element. The pH value of the two methods was constant and measured the absorption using both the contents of the standard solution except the ion element.

We used the Molarity ratio method to determine the Molarity ratio of the complexes Co (II)-ligand, and Ni (II)-ligand as follows preparation of a series of solutions, size 10 ml consisting of 0.2 ml of a solution of concentration [2-10M] of the ions Co (II), Ni (II) and Mn (II). Then added 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 ml of a solution focus ligand [2-10 M] added buffer (3 ml) and then to complete the 10 ml by 70% (v / v) Ethanol - water, when ionic strength m = 0.5 M and then measured the spectrum of the figure turns out to be ML1 and ML2 (Fig 15). We will discuss the spectra of the complexes Co (II)-ligand (as an example to the rest of the complexes) as a function of ligand concentration and analysis of the results at wavelengths different that the ions Co (II) and Ni (II) are two entities essential Two maim complex species are 1:1 and 2 : 1metal to the ligand.


n (CL) / n (CM)
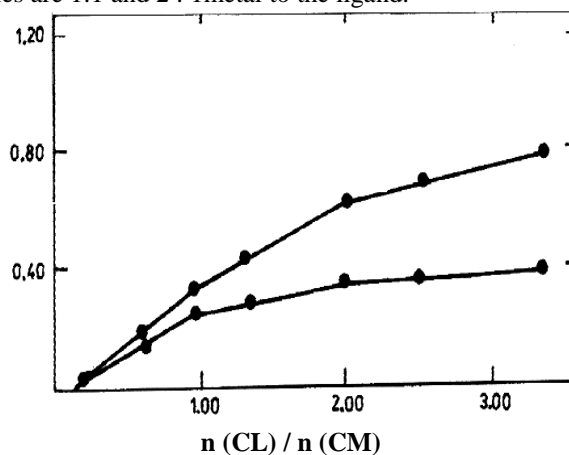
Fig 15 . Mole ratio method for Co (II)-ligand (a) and Ni (II)-ligand (b)

The results of this method agreed with the results of measuring the pH adjustments previously discussed, where the Co (II), Ni (II), as an example to the rest from complexes, ML and ML$_2$ overlapped with ligand HL.

Validity of Beer's laW

Using a constant concentration of ligand HL (1 x 10^{-3} M) and change the concentration of ions Co(II), Ni(II) and Mn(II) in a mixture of ethanol - water percentage of 75% (v / v)and when ionic strength μ = 0.05 using potassium nitrate and Ligand reference when λ= 500 nm and found that they all follow the Beer law of Standard deviation 0.002, 0.006 and 003 respectively during the concentration of metal ion complexes with Co (II) of 1 x 10^{-5} to 4 x 10^{-4} M With Ni (II) and the values of molar absorptivity (ε)at 500 nm for the complexes of Co (II), Ni (II), Mn (II) are respectively 6.6 x 10^3, 8.0 x 10^3 and 1.4 x 10^3 dm^3 $mol^{-1}cm^{-1}$, indicating that HL can be used as a sensitive factor in the specific analysis to determine the copper (II) and nickel (II) form (Fig. 14)
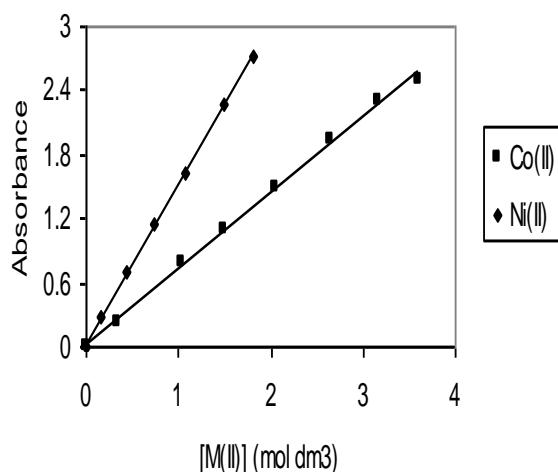
**Fig 14 .Validity ob Beer's law, a) Co (II)-ligand at pH=8;
b)Ni(II)-ligand at pH=8 and**

References
1-P.W.Heilman, R.D. Geilman,A.J.Scozzie, R.J.Wayner, M.J.Gullo and S.Z.Aryan, J. Pharm.Sci. 69(1980)282.

2-A.A.Schilt and W.E.Dunbar, Talanta 16(1969)519.

3-A.K.Sen Gupta N. Srivastava and A;A; Gupta, Indian J.Chem., Sect.B21(1982)793.

4-S.Kirschner, Y.K.Wein francis and J.G.Bergman, J.Med.Chem.9(1966)369.

5-R.Fusco and R.Trave, Rend. Lomnardo Sci.Pt. I.91(1957)202.

6-A.A.T. Ramadan, M.A.El –Behairy, A.I.Ismail and M.Mahmoud, Monatsh.Chem.125(1994)1171.

7-A.A.T.Ramadan, R.M.Abdel Rahman and M.H.Seda, Asian J. Chem. 4(1992)569.

8- A.A.T.Ramadan, R.M.Abdel Rahman, M.A.El –Behairy, A.I.Ismail and M.Mahmoud, Thermochim. Acta222(1999)291.

9-A.Taha B.El-Shetary and W. Lnert, Monatch. Chem.124 (1993)135.

10- J.R.Dilworth, Coord. Chem. Rev., 21(1976)29.

11- J.R.Merchant and D.S.Clothia, J.Med. Chem., 13(1970)335.

12- N.S.Biradar andB.R.Havinale, Inorg.Chim.Acta, 17(1976) 157.

13- H.N.Fox, Science,116(1952)129.

14- K. Y. Lau, A. Mayr, K. K. Cheung, Inorg. Chim. Acta., 1999, 285, 22

15- Mansour, A. K.; Eid, M. M.; Khalil, N. S. A. M. Synthesis and reactions of some new heterocyclic carbohydrazides and related compounds as potential anticancer agents. Molecules 2003, 8, 744-755.

16- A.I.Vogel, "quantitative Inorganic Analysis"Longman, London, 1978.

17- Mostafa El-begery and Hefaa El-Twigry Spectrochimica Acta PartA Molecular Spectroscopy, 66(1)(2007) 28-36

18- Yoe J.H. and JonesA.L., Indust. Eng. Chem. Anal., Ed. 16, (1944) 111.

19- Job, P., Indem. Anna. Chim., 6, 97 (1936).

20- H.M. Irving and H.S.Rossotti, J.Chem.Soc.(1954)2904.

21- Ramadan, A. A. T.; El Shetary, B. A.; Abdel-Moez, M. S. andSeleim, H. S, Acta Chim. Hung., 130, 25 (1993)

22- Kole,Nand Chaudhurg; A.K., J. Inorg. Nucl.Chem., 43,2471 (1981)

23- Gergely,A., and Kiss, T., J. Inorg. Nucl.Chem., 39,109 (1976)

24- Schubert, W.M.,and Ronins, J., J. Am. Chem. Soc.,82, 1353 (1960)

25- Choppin, G. R. and Strazik, W. F., Inorg. Chem., 4, 1250 (1965)

26- Degischer, C. and Nancollas, G. H., J. Chem. Soc. A., 1125 (1970)

27- Nancollas, G. H., "Interaction On Electrolytic Solutions" Elsevier, Amsterdam (1966)

28- Rowlands, C. C.and Morgan, P. H., J. Coord. Chem., 9, 19 (1979)

29- Linert W. and Taha A., J. Coord. Chem., 29, 265 (1993)

30- Klopman,G.,J.Am.Chem.Soc.,90, 233(1968)

31- Paoletti, P. and Vacca, A., J. Chem. Soc., 5051 (1964)

32- Ciapolini, M.; Paoletti, P. and Sacconic, L.,J. Chem. Soc., 4553 (1960)

33- Jorgenson, C. K., Ada Chem. Scand, 10, 887 (1956)

34- Linert, W., Jameson, R. F., Bauer, G., and Taha, A., J. Coord. Chem. 42, 211 (1997)

35- D. Kealy, "Principle and Practice of Analytical Chemistry", Blackie Academic and Professional, London, 261, 371(1995)

36- Job,B., Anna.Chim., 9, 133(1928)

37- Job, B., Comp. Rend., 180, 928 (1925)

38- Job, B., Indem. Anna. Chim., 6, 97 (1936)

39- Vosburgh, W. C. and Cooper, G. R., J. Am. Chem. Soc., 63, 437(1941)

40- Yoe and Jones, Indust. Eng. Chem. Anal., Ed. 16, 14 (1944).

41- Babko, A. K., Fizikochimiczeskii Analiz Kompleksykh ScjedineniJ\v Rastvorach Keiv, pp. 137 (1955)

42- Babko, A. K., Zh. Spirkl. Khim., 8, 375 (1935)

43- Babko, A. K., Zh. Spirkl. Khim., VI, 1560 (1939)

44- A. E. and Manning, D. L., J. Am. Chem. Soc., 72, 4488