

Determination of the Stability Constants for some First Transition Elements Complexes with 3-(2- hydroxy phenyl) -2 – Pyrazoline In Aqueous Solution

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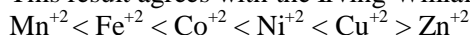
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ABSTRACT

Transition metal complexes Cr(III) , Fe(III) , Co(II) , Ni(II) & Cu(II) with 3-(2- hydroxy phenyl) -2– pyrazoline have been prepared and characterized in aqueous solution. The complexes were characterized by infrared (IR), UV-visible & molar conductivity measurements. The bidentate ligand was bonded from one of the nitrogen atoms of pyrazolien & oxygen atom phenoxide group. The molecular structure for the complexes was proposed. The stability constants of these complexes were found by measuring electric molar conductivity in different concentrations was also found. The determined values of the prepared complexes increases according to the following sequence:



This result agrees with the Irving Williamson series:-



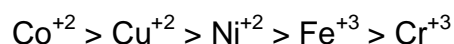
Keywords: Stability Constants, First Transition Elements Complexes, 3-(2- hydroxyl Phenyl) -2 – Pyrazoline.

قياس ثوابت استقرارية معقدات بعض عناصر السلسلة الانتقالية الاولى مع 3-2- هيدروكسي فنيل) -2- بايروزولين في الوسط المائي

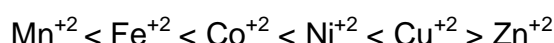
الخلاصة

تم في هذا البحث تحضير ودراسة معقدات Cr(III) , Fe(III) , Co(II) , Ni(II) , Cu(II) مع 3-2- هيدروكسي فنيل) -2- بايروزولين في الوسط المائي. شخّصت هذه المعقدات باستخدام القياسات الطيفية UV-visible ، IR ، وقياسات التوصيل المولاري. وقد تم الاستنتاج ان ارتباط الليكند الثنائي السن من خلال احدى ذرتي نيتروجين البايرازول و ذرة اوكسجين مجموعة الفينيل وتم اقتراح الصيغة التركيبية للمعقدات.

قد تم الاستنتاج ان ارتباط الليكند الثنائي السن من خلال احدى ذرتي نيتروجين البايرازول وذرة و اوكسجين مجموعة الفينيل وتم اقتراح الصيغة التركيبية للمعقدات. ثم حساب ثابت استقرارية المعقدات من قياس التوصيلية الكهربائية المولارية عند تراكيز مختلفة ووجد أزيد ثابت التكوين المعقدات المحضرة وفقا للتسلسل التالي:-



وهذا يتفق مع سلسلة ارفنج



الكلمات المرشدة: ثوابت ، معقدات العناصر الانتقالية الاولى، 3-(2-هيدروكسي فينيل) -2-بايروزولين. الاستقرارية

INTRODUCTION

Metal complexes of 2-Pyrazoline ligands have played a central role in the development of coordination chemistry⁽¹⁻⁵⁾.

From the survey of existing literature, it appears that 2-pyrazoline and pyrano, pyrazole and its related metal (II), (III) complexes have been extensively used as biological activity reagents agents as well as analytical reagents⁽⁶⁻¹¹⁾.

Pyrazolines are an important class of heterocyclic compounds. They are used industrially as additives for dyes, lubricating oils and antioxidants, and in agriculture as catalysts for decarboxylation reaction as well as inhibitors for plant growth.^(12- 14) Therefore, the determination of stability in aqueous solutions of these compounds is highly encouraging.

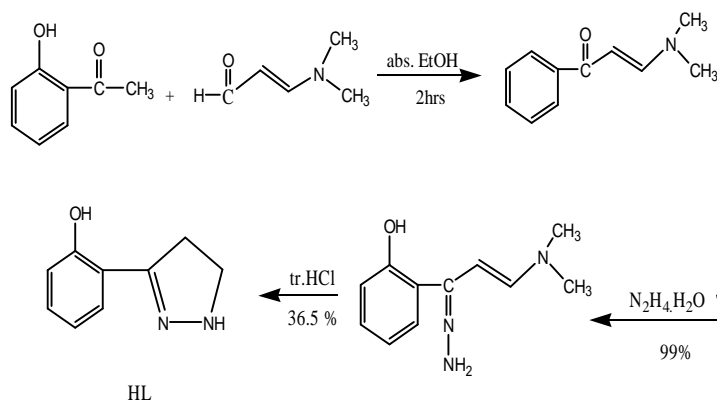
A number of measurements of stability constants of the amino acids⁽¹⁵⁾, 2-mercaptobenzothiozole, 2-amino-Pyrano-pyrazole⁽¹⁶⁾ complexes have been reported by Potentiometric techniques. Benzil-2, 4-dinitro phenyl hydrazine pyrazole complexes of La (III), Cr (III), Co (II) and Cu (II) Have been also reported⁽¹⁷⁾.

In the present paper we reported the synthesis, characterization and determination of the Parameters of metal complexes of Cr(III), Fe(III), Co(II), Ni(II) and Cu(II) with 3-(2-Hydroxy phenyl)-2-pyrazoline(HL)⁽¹⁸⁾ The stability constants were determined by electrical conductivity methods.

EXPERIMENTAL

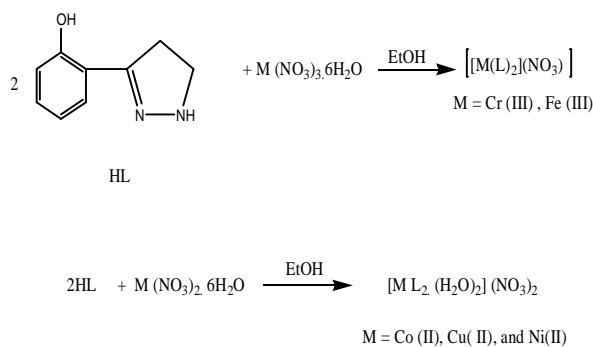
All the chemicals used were of Analytical grade. N,N-dimethyl formamide acetal was distilled prior to use .

The solvents were dried and distilled before use according to standard procedures. The ligand 3-(2-hydroxy phenyl)-2-pyrazoline was prepared according to a method published in the literature⁽²⁰⁻²³⁾, according to following scheme. (1).



Scheme (1)

The metal complexes of Cr(III), Fe(III), Co(II), Ni (II) and Cu(II) with HL were prepared according to the literatures^(24,25,26) by mixing (0.64g, 4mmole) of HL ligand in (50ml) absolute ethanol and 2mmole of (0.581gmNi(NO₃)₂.6H₂O)(0.692g, Cr(NO₃)₃.6H₂O), (0.70g,Fe(NO₃)₃.6H₂O), (0.582gCo(NO₃)₂.6H₂O) and (0.447g Cu(NO₃)₂.2H₂O) keeping the ligand metal ratio of 2:1 followed by few drops of (2%) sodium acetate at (pH=8). The mixture was then refluxed at 0.5hr. On a water bath, until the formation of the precipitated complex. The precipitate was dried over KOH pellets. The solid product obtained was filtered, washed with distilled water and dried under vacuum, Scheme (2):



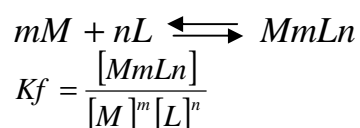
Scheme (2)

IR spectra were recorded in KBr medium on F.T.IR shimadzu 830 spectrophotometer .The absorption spectra (UV-Vis) of all the complexes were recorded in ethanol on a shimadzu UV-visible recorded spectrophotometer, UV-160. The molar conductivity of

10^{-3} M solutions in ethanol was measured by Phillips PW 9526 digital conductivity meter.

Stability Constant of the Complexes

Stability constants [Formation constant (K_f)] is an equilibrium constant for the formation of a complex in solution ⁽²⁷⁻²⁸⁾



Where:-

[M]=concentration of the metal ion

[L] = concentration of the ligand

[M_mL_n] = C = concentration of the formed complex.

Molar Conductivity

Conductance is a measure of ionic mobility in solution when the ions are subjected to electric potential gradient. The molar conductivity (Λ_m) of the electrolytic solution containing one mole of the solute in the solution (mole/cm^3) was recorded. The conductance of solution is the sum of conductances of all the ions in the solution. It is related to the electric charge, size and concentration of the ion ⁽²⁹⁾.

RESULTS AND DISCUSSION

The physical and analytical data of the ligand and its metal complexes are given in Table (1). Results obtained from elemental analyses are in satisfactory agreement with the calculated values.

The characteristic stretching modes for the ligand and its metal complexes are described in Table (1) .IR spectrum of the free ligand exhibited strong band at 1610 cm^{-1} which is attributed to C=N of pyrazoline ring ⁽³⁰⁾, while the O-H phenolic group appears at 3500 cm^{-1} . The shift in shape and position of the medium as well as new bands in the region $(350-510) \text{ cm}^{-1}$ (which referred to ν_{M-N}) might be due to the complexation of metal ion with the (HL) ⁽³¹⁻³⁴⁾. The appearance of these new bands and the absence of a hydroxyl band suggest that the pyrazoline behaves as a monobasic bidentate ligand.

The electronic spectrum of the ligand in absolute ethanol showed two distinct peaks at 250 and 315nm, these are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions ⁽³⁵⁾. However the electronic spectra of metal complexes in ethanol showed a change in positions of transitions (both hypsochromic shift) and showed new bands in the visible region, which indicates the formation of the complexes ⁽³⁶⁾. Figure (1).

The molar conductivity (Λ_m) of the prepared transition metal complexes dissolved in absolute ethanol with different concentration was determined.

Table (1) The conductometric measurements may distinguish whether certain group in solution are ionic or it is coordinated directly to the transition metal ions ⁽³⁷⁾ also to get another formation about the coordination sphere of the complex plotting the values of

(Λ_m) against the square root of the concentration according to the Kohlraush's equation⁽³⁸⁻⁴⁰⁾

$$\Lambda_m = \Lambda_\infty - K_c(C)^{1/2}$$

Where Λ_∞ = infinite dilution

C = concentration

K_c = constant

As shown in Figure (1) a slope line of the weak electrolyte for the prepared complex is a result of the relation between negative ion (NO_3^-) and the positive (Complex, Cation), which could indicate as well that the solvent may replace the (NO_3^-) in coordination with metal ion⁽⁴¹⁻⁴²⁾

These results agreed with the expected values once helped in having a good idea about the expected molecular formula and the geometry of the prepared complexes⁽⁴³⁻⁴⁴⁾. The measurement of (Λ_m) at different concentrations showed an increase in the (Λ_m) value with dilution due to increasing the number of mobile ions in solution and this was investigated by Kohlraush's equations see Table(1). The determination of the dissociation constant (K_d) is one of the most useful properties for a weak electrolyte. (K_d) for the complexes can be revealed by using Cruze rearrangement, which was derived from Ostwald equation of dilution⁽⁴⁵⁻⁴⁶⁾.

$$\Lambda_m \cdot C = K_d \Lambda_0 \frac{1}{\Lambda_m} - K_d \Lambda_0^2$$

Where: - Λ_0 infinite dilution molar conductivity

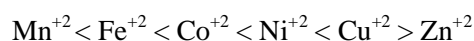
A straight line with slope of $K_d \Lambda_0^2$ was obtained by plotting ($\Lambda_m \cdot C$) against ($1/\Lambda_m$) and the intercept of that line with X – axis will obtain ($1/\Lambda_0$) then the value (K_d) can be calculated⁽⁴⁷⁾ as shown in Figure (3) to Figure (7) and k_f can be calculated⁽⁴⁸⁻⁴⁹⁾.

$$K_f = \frac{1}{K_d}$$

It was found that the values of (k_d) of the prepared complexes increased according to the following sequence:



This result agrees with the Irving Williamson series⁽⁴³⁾:-



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Table (1) Physical Properties and FT-IR, UV-Vis Spectra of the Ligand (HL) and its Metal Complexes.

Comp.	m.p./C°	Yield%	M% Calc.(form.)	I.R v/cm ⁻¹	UV-Vis. λ _{max} /nm	ε cm ⁻¹
HL	185-187	80	—	3500(O-H), 1610(s) 1410(m)	250,315	(450)
[Cr(L) ₂]NO ₃	252-254	70	12.28 (11.92)	1590,1450, 450,420(w)	260 420 ^a ,715 ^a	(19500) ^c (90)
[FeL ₂]NO ₃	275 ^d	75	12.70 (12.01)	1585,1435, 395,415(m)	280 550 ^a	(20500) ^c (90)
[Co(L) ₂ (H ₂ O) ₂]	310-312	85	11.74 (10.85)	3280(br.),1610(s) 480(m),410(w)	220,560 460 ^a	(90) (120)
[NiL ₂ (H ₂ O) ₂]	345 ^d	82	12.13 (11.77)	3180(br.),1605(s), 450,390(w)	290, 519 ^a	(30,000) ^c (100)
CuL ₂ (H ₂ O) ₂]	350-352	90	13.09 (12.91)	3150(br.),1610(s), 415,510(m)	220,305, 601 ^a (br.)	(90)

d=Decomposed

m=Medium, s=strong, w=Weak, br=Broad and c=Charge Transfer

a=D-d transition in the Visible Region.

Table (2) Determination of Stability Constants for the Prepared Metal Complexes in Absolute Ethanol.

Comp.	Λ _m (ohm ⁻¹ .cm ² .mol ⁻¹)			
	1×10 ⁻³	0.5×10 ⁻³	0.2×10 ⁻³	0.05×10 ⁻³
CrL	80	120	162	200
FeL	95	130	220	270
CoL	40	55	110	205
NiL	60	80	120	198
CuL	40	60	115	181

Table (3) Measurement of K_f & K_d for the Complexes.

Comp.	$1/\Lambda_0$	$K_d \Lambda_0$	K_d	K_f
CrL	0.0033	0.029	9.5×10^{-5}	0.1×10^5
FeL	0.002	0.019	3.8×10^{-5}	0.26×10^5
CoL	0.003	0.005-	1.5×10^{-5}	0.6×10^5
NiL	0.003	0.011	3.3×10^{-5}	0.3×10^5
CuL	0.004	0.007	2.8×10^{-5}	0.35×10^5

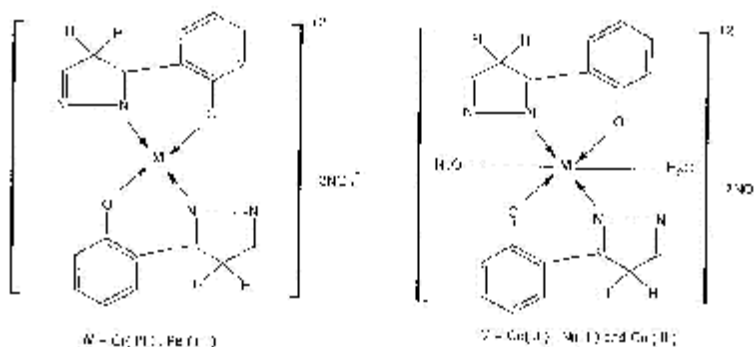


Figure (1) Molecular of $[ML_2]$

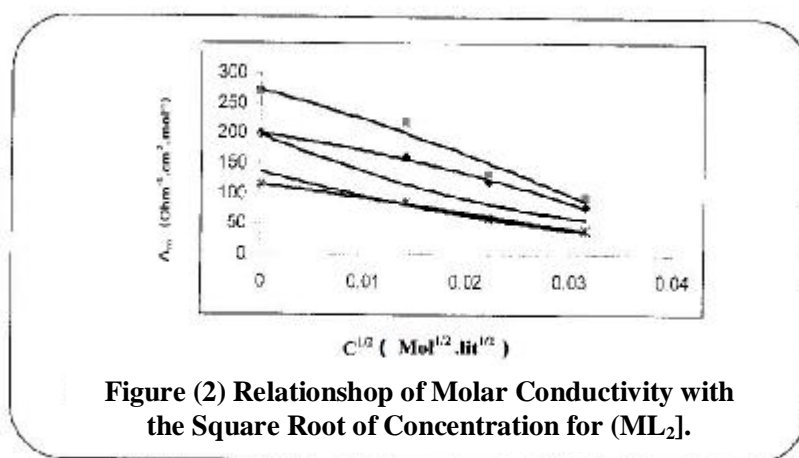


Figure (2) Relationship of Molar Conductivity with the Square Root of Concentration for (ML_2) .

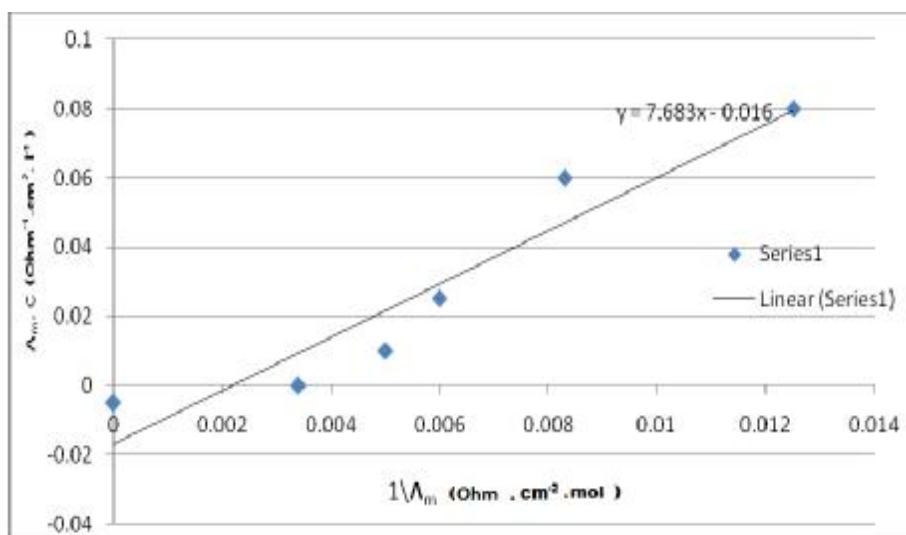


Figure (3) Relation between $\Lambda_m \cdot C$ & $1/\Lambda_m$ for Fe.L Complex.

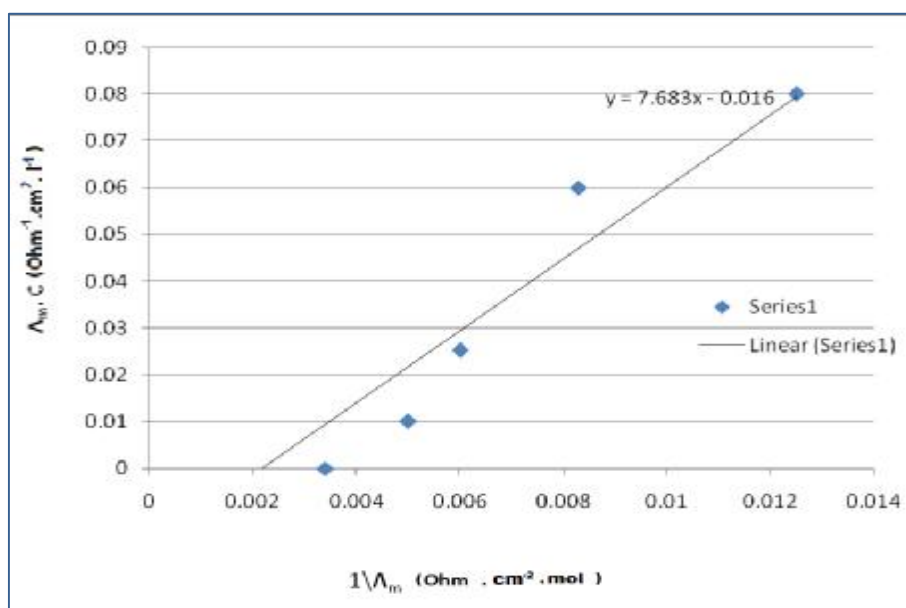


Figure (4) Relation between $\Lambda_m \cdot C$ & $1/\Lambda_m$ for Cr.L Complex.

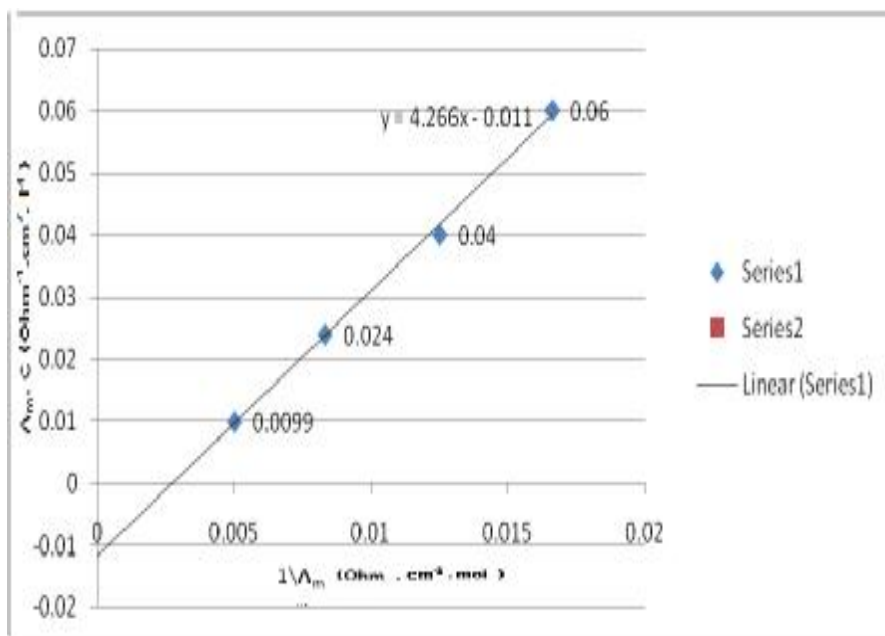


Figure (5) Relation between $\Lambda_m \cdot C$ & $1/\Lambda_m$ for Ni.L Complex.

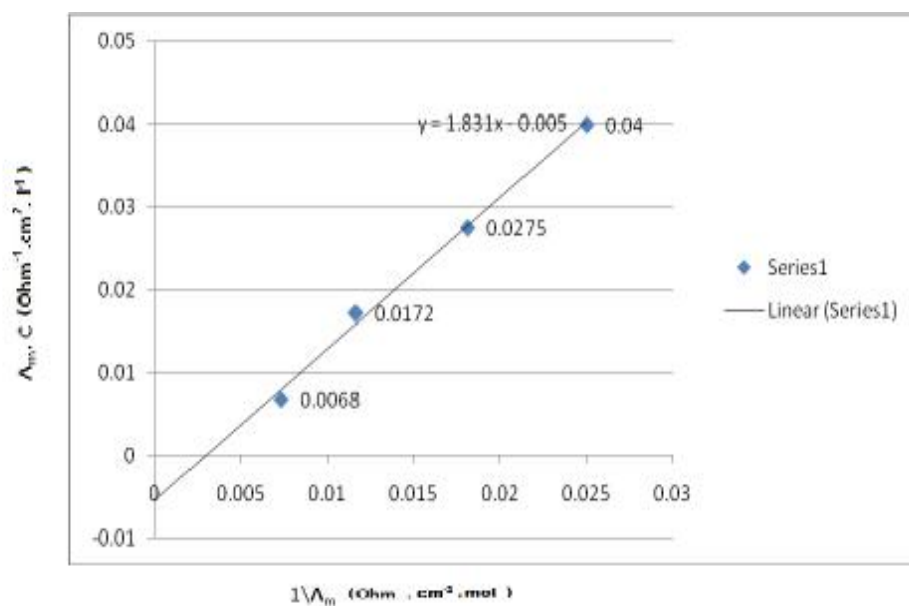


Figure (6) Relation between $\Lambda_m \cdot C$ & $1/\Lambda_m$ for Co.L Complex.

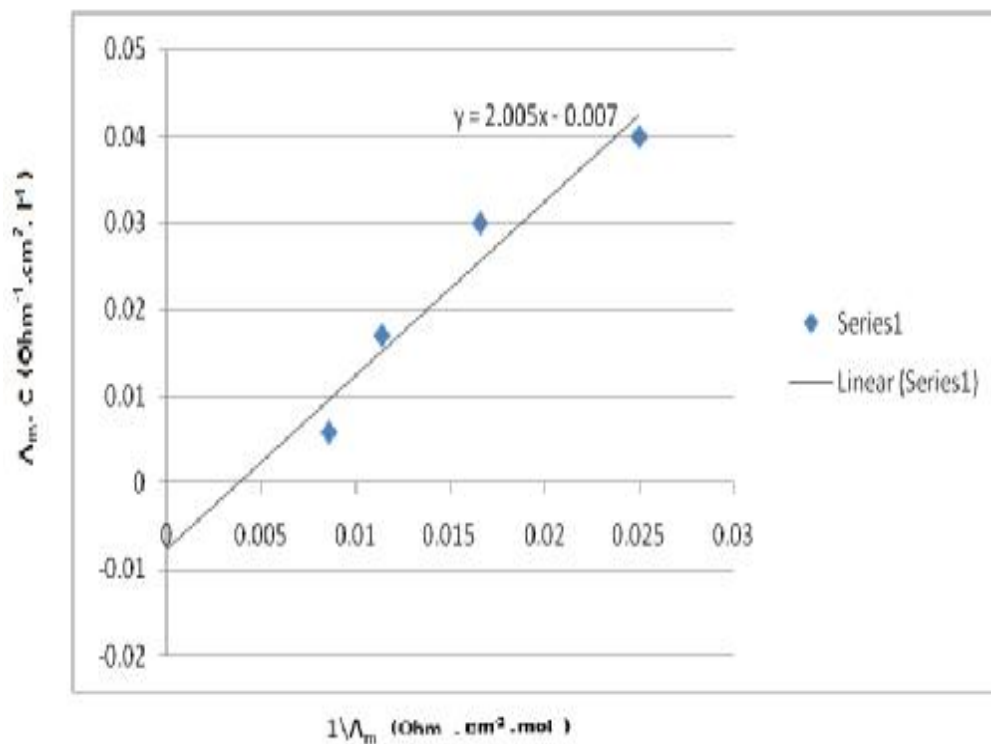


Figure (7) Relation between $\Lambda_m \cdot C$ & $1/\Lambda_m$ for Cu.L Complex.