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Analytical studies of the complexes of 5-(X-NO_2 phenylazo)-8-hydroxyquinaldine with Indium ion

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Abstract

The reaction of 5-(X-phenylazo)-8-hydroxyquinaldine derivative [X=m-NO_2(I) and p-NO_2 (II)] with In^{+3} ions in solutions showed that 1:1 and 1:2 complexes were formed. The formed complexes were found to be a suitable method for direct spectrophotometric micro determination of indium ion .

Beers law was obeyed over the range (2-16) and (2-14) ppm of In^{+3} with complexes (I) and (II) respectively. The molar absorptivity is 14000 and 35000 mol^{-1} cm^{-1} for (I) and (II) respectively.

The stepwise stability constants of complexes were calculated by applying the corresponding solutions method

The melting point of complexes were measured [(158-160)C^0 for I and (201-203)C^0 for II] respectively, and the infrared spectra of the formed complexes were measured using (KBR) disk.

Key wards: Absorption, Sequence of addition, Isopestic point, Stoichiometry, Colman's graphical method and Stability constants.

List of symbols and notations:

M: Metal	In^{+3}: Indium ion
L: Ligand	A: Absorbance
C_M: Metal concentration	a: Specific absorptivity
C_L: Ligand concentration	ε : Molar absorptivity
$\bar{n}$: Complex formation function	S: Sandell sensitivity
E: Ethanol	λ : Wave length

دراسات تحليلية لمعقدات 5-(X-NO$_2$ phenylazo)-8-hydroxyquinaldine مع آيون الأنديوم

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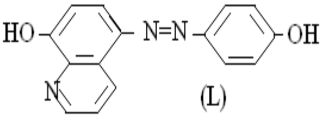
الخلاصة

البحث يتضمن تحضير و دراسة معقدي الانديوم (In^{+3}) مع الصبغتين الآزويتين 5-(X-NO$_2$ phenylazo)-8- hydroxyquinaldine، حيث [X=m-NO$_2$(I) and p-NO$_2$ (II)] . وبعد اعادة بلورة هذين المعقدين باستخدام الكحول الاثيلي تم حساب نقاط الانصهار لهما، و تم اختيار الظروف المثلى لتكوين هذين المعقدين من حيث تحديد التركيب ألجزيئي لهذين المعقدين باستخدام طريقة النسبة المولية و طريقة التغيير المستمر و كانت النتائج تشير إلى أن كل من المعقدين يتكون بنسبة (1:1) و(1:2) (فلز: ليكاند). لقد أخترنا الطول ألموجي الأقصى للمعقدين و درسنا كل من تأثير الزمن و تأثير تعاقب الإضافة على هذين المعقدين و من قيم الامتصاص المستحصله من طريقة النسبة المولية ، تم حساب عدد الأصناف الماصة في الطيف لهذين المعقدين و ذلك باستخدام طريقة كولمان البيانية وأشارت النتائج إلى وجود ثلاثة أصناف ماصة لكل من المعقدين وهي كل من الليكاند الحر(الصبغة) ،المعقد ذي النسبة الجزيئية (فلز:ليكاند) مساوية إلى (1:1) و المعقد ذي النسبة الجزيئية (1:2). كما تم دراسة مدى انطباق قانون بير على محلولي معقدي الأنديوم مع الصبغتين الآزويتين (I)and(II) على التوالي، ثم رسم منحني المعايرة للمعقدين المدروسين و عينت القيم القصوى لتركيز الأنديوم (جزء بالمليون) و حددت قيمة معامل الامتصاص المولاري (ε) و قيمة الامتصاصية النوعية (a) و قيمة حساسية الطريقة الطيفية باستخدام قيمة حساسية ساندل (δ) لكل منهما. و باستخدام طريقة المحاليل المتناظرة المتضمنة طريقة نصف قيم دالة التكوين تم حساب ثابتي تكوين المعقدين المحضرين $\log\beta_1$ و $\log\beta_2$.

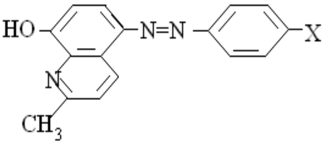
وبأخذ أطياف الأشعة تحت الحمراء لهذين المعقدين ومقارنتها مع الأدبيات تبين أن وبأخذ أطياف الأشعة تحت الحمراء لهذين المعقدين ومقارنتها مع الادبيات تبين ان الارتباط ما بين ايون الانديوم (In^{+3}) مع جزيئة الصبغة يتم من خلال تكوين اصرتين احدهما تساهمية بين الايون و ذرة الاوكسجين العائدة لمجموعة الهيدروكسيل الكوينالدينية و الاخرى تناسقية مابين الايون و ذرة النيتروجين الكوينالدينية.

Introduction

An investigation deals with spectrophotometric determination of Al(III) , Ga(III) and In(III) ions with azodyes 5-(p-hydroxyphenylazo)-8-hydroxyquinoline (L) and the determination of stability constants in methanolic solution was done by Ali and Al-Issa (1994).



The spectrophotometric studies of complexes of 5-(p-hydroxyphenylazo)-8-hydroxyquinoline with some group (III A) metal ions were also studied. Some azodyes which are derived from 8-hydroxyquinaldine can prepared by Ali (1997) and which have the following general structure:



where X represents the substituted group ,namely, –H, –Br, $–COCH_3$, $–CH_3$, and –OH. The analytical studies of these azodyes and their complexes with zinc ion has been done. The Infrared spectra of formed complexes reveal that the bonding of zinc ion with any of investigated dyes takes place through the formation of two bonds.

The spectrophotometric studies of complexes of 1-(o-Carboxyphenylazo)-2-Naphthol with Cobalt (II) and Iron (III) were done by Abed Al-Kareem (1996).

The spectrophotometric analysis of α- and β-Naphthol mixtures applying partial least-squares method was studied by Revilla (1999), and the Kinetic spectrophotometric determination of nanogram levels of manganese (II) by azodye potassium periodate-1,10-phenanthroline system was studied by Mutaftchiev (2002).

The reaction of 5-(o- phenylazo)-8- hydroxyquinaldine with In^{+3} ions was studied by Ali (2006)

Experimental:

All reagent were of analytical reagent grade solutions. A 0.01 M indium (III) stock solution was prepared by dissolving 0.304 g of $In_2(SO_4)_3 \cdot 5H_2O$ in 50 ml. The indium calibration solution were prepared from the stock solution, Ali (2006). The absorption spectra of the azodye complex with In^{+3} ions was measured with the range (360-650 nm) in ethanol using the [LKB (Biochrom) ultraspec II 4050 UV/Visible].

The Ethanol used to recrystallize the formed complexes and then the melting point of complexes were measured [(158-160) I and (201-203) II] respectively.

The infrared spectra of complexes recorded in the rang (600-4000) cm^{-1} by using Potassium Bromide (KBr) disk.

Procedure:

The solutions of azodyes with concentrations (0.001 M) was prepared by dissolving weight (0.023 g) in 75 ml Ethanol. The complexes formed was recrystallize in Ethanol and the melting points of complexes were measured. The two series of complexes solutions were prepared to studied the maximum wavelength ,in the first series the ratio [1:1] complexes of In^{+3} ions with azodye (4×10^{-5} M), and the [1:2] complexes [4×10^{-5} M(In^{+3}): 8×10^{-5} M(L)] were prepared by using ethanol and ligand as blanks respectively. In molar ratio method the series of complexes solutions were prepared with In^{+3} ion of constant concentration (1.5×10^{-5} M) and variation in azodyes concentrations in the range[(0.45×10^{-5})-(5×10^{-5}) M] and the absorption spectra of the complexes was computed using ligand as a blank. In continuous variation method the series of the complexes solutions with variation concentration of In^{+3} ions in the range [(0.2×10^{-5})-(1.41×10^{-5}) M] and variation concentration of azodyes in the range [(0.6×10^{-5})-(1.8×10^{-5}) M], the total concentration of complexes remains un changed, using ligand as a blank.

The sequence of addition effect was studied by preparing the following complexes [(M,L,E), (M,E,L), and (L,E,M)]. The complexes (4×10^{-5} M) was prepared to study the time effect during (0.5-120) minutes.

To know the number of absorbing species in solution mixture of complexes, the solution of In^{+3} ions (1.5×10^{-5} M) was prepared, as well as the variation concentration of azodyes (I) and (II) respectively was also prepared at the rang (0.9×10^{-5} - 3.9×10^{-5} M)in complexes.

The stability constants of formed complexes were calculated by preparing two series of complexes solutions. In the first series a constant concentration (1.5×10^{-5} M) of In^{+3} ions, while variation the concentration of dyes solutions (I) and (II) in the range [(0.45×10^{-5})-(5×10^{-5}) M], the second series a constant concentration at (0.8×10^{-5} M) of In^{+3} ions, and variation concentration of dyes solutions (I) and (II) was prepared in the range [(0.4×10^{-5}) -(3×10^{-5}) M]. The spectra of the complexes solutions were computed using ligand solution as a blank.

The formed complexes recrystallize in the Ethanol and the melting points of complexes were measured. The infrared spectra of complexes were investigated using (KBr) disk.

Results and discussions

The absorption spectra of the complexes was recorded the range λ=(350-600) nm, it was found that the complexes have an absorption broad band with maxima at [(420 nm) for complex (I) and (460 nm) for complex (II)] (Fig. 1). These pond in complexes I and II seems to be belong to (π - π^*) transition. The effect of time was studied (table 1), it was found that the complexes is almost formed instantaneously and remain stable for more than 24 hours.

The sequence of addition (Table.2) was studied, it was found that the complexes of In^{+3} ions with azodyes (I) and (II) respectively remain stable by using sequence dye, ethanol and metal.

The stoichiometry was investigated using the molar ratio method Ali and Al-Issa (1994) and the continuous variation method Budesinsky (2007), the results indicates the formation of [1:1] and [1:2] [M:L] complexes is noticed, (Fig.2) and (Fig.3) respectively.

The presence of that complexes was confirmed by calculating the number of absorbing species using Colman's graphical method Boella (2005), as applied to the results of the molar ratio method for the complexes. This method shows that three species exist, (Fig.4).

Beer's law was obeyed to the complex under investigation for the spectrophotometric determination of indium, it was found that Beer's law is satisfactorily obeyed up to 16.06 ppm(I) and 13.78 (II), (Table.3). A better results and higher values were obtained by applying the optimum blank compensation technique Ali and Al-Issa (1994), i.e. using amount of unreacted dye as the blank from the knowledge of the stoichiometry of the complexes (Fig.5).

lists the molar absorptivity ε, , specific absorptivity Boella (2005), (a correspond to the absorbance of 1 ppm in a cell with optical path length of 1 cm), and Sandell function for sensitivity Sandell (1959), (represents the number of micrograms of the determined matter per ml of solution having an absorbance of 0.001 for a cell with path length of 1 cm), were given in (Table.3).

The number of absorbing species in solution mixture of In^{+3} ions with azodye is determined using Coleman's graphical method based on the data obtained by the molar ratio method. The number of absorbing species obtained confirm the formation and molecular structure of the complexes as indicated by the stoichiometric studies, (Fig.4).

By the corresponding solutions method Ali and Al-Issa (1994), the stability constants of the complexes of In^{+3} ions with dyes (I) and (II) were calculated using half values method. This method required two series of solutions of total metal In^{+3} ions concentration C_1M and C_2M of each of the complexes (Fig. (6-a)), and of varying legands [dyes (I) and (II)] concentrations C_1L and C_2L. The corresponding solutions method is that having the same absorbance at different ligand concentration from the absorbance-CLplots many pairs of C_1L and C_2L consequently $\bar{n}$ (complex formation function) and [L] can be determined:

$$\bar{n} = \frac{C_1L - C_2L}{C_1M - C_2M}$$

$$[L] = \frac{C_1M \cdot C_2L - C_2M \cdot C_1L}{C_1M - C_2M}$$

By using the half value method, $\log\beta_1$ and $\log\beta_2$ are obtained by ploting $\bar{n}$ against PL, (Fig.(6-b)), it was found that $\log\beta_1$ of (I)=5 and $\log\beta_1$ of (II) =5.2, $\log\beta_2$ of (I) =10.2 and $\log\beta_2$ of (II) =10.25.

To know the natural bonding of the azodyes with In^{+3} ions the infrared spectra of complexes were recorded in the range (4000-600) cm^{-1}, (Fig.7).This spectra shown the differences between azodyes spectra and complexes spectra which can be represented by the absorption bands which are related to O-H group where disappearance of the analogues bands of the stretching vibration can be expected at 3300 cm^{-1} and the analogues bands of the bending vibration out the plane in the range (825-850) cm^{-1}, but the possibility of entered of Ethanol molecules in formed complexes structure make the band at 3300 cm^{-1} appears in complexes spectra .But the different is seemed to be clear in the relative strength of the bending vibration bands to O-H bond which appear in the range (1120-1080) cm^{-1}, where the relative strength of this band related to the O-H group is increased when it is moved from azodye to the complex.

Furthermore, it is expected to occur a shift in the position of the analogues band of the bond C=N in the quinaldine part as a consequence of connecting C=N with metal. On the other hand the absorption positions of the –N=N- group in the complexes are effected, as well as shifts occur for them towered the minimum frequency in range (10-45) cm^{-1}.

It can also be noted that there are two bands appeared in the spectra of the quinaldine molecule at 1590 cm^{-1} and 1560 cm^{-1} in spectra of complex and ligand, but when it is moved to the spectra of the analogues complexes, we see that the band at 1590 cm^{-1} remain without big change, while it is occur a shift towered the minimum frequency in the position of a second band in range (10-30) cm^{-1}, which can be approximately expressed as the occurrence of a coordination pond between nitrogen atom of C=N group and metal, and such a shift coincide with the values that mentioned in the literature Silverstien (1998). On the other hand the absorption positions of the group –N=N– are effected in the complex and a general shifts for them are occur toward low frequency in the range (10-45) cm^{-1}.

Table 1: The time effect .

Time (min.)	AI	AII
0.5	0.205	0.298
1	0.205	0.298
3	0.206	0.299
5	0.210	0.300
10	0.209	0.301
15	0.210	0.300
30	0.210	0.301
45	0.211	0.302
60	0.210	0.301
120	0.209	0.303
1440	0.209	0.299

Table 2 : Sequence of addition

Sequence of addition	AI	AII
E+dye+M	0.206	0.286
Dye+E+M	0.282	0.316
M+E+dye	0.208	0.293

Table 3 : The data obtained from Beer's law for the complexes at $\lambda_{\max}$ [420 nm (I)] and [460 nm (I)] respectively.

Complex In^{+3}_I	ε. cm^{-1} $mol^{-1}.l$	a. g. cm^{-1} *ml*	sMg. cm^{-2}	ppm up to
In^{+3} _ I	14000	0.12	0.008	16.06
In^{+3} _ II	35000	0.30	0.003	13.78

Table 4 :The data obtained by applying the Coleman's graphical method.

i	Wave length (nm)	Absorption						
		Number of dye solution (j)						
		1	2	3	4	5	6	7
AI								
1	410	0.13	0.22	0.30	0.49	0.51	0.60	0.61
2	420	0.14	0.26	0.35	0.53	0.50	0.61	0.63
3	430	0.10	0.25	0.31	0.49	0.56	0.66	0.68
AII								
1	450	0.249	0.507	0.594	0.813	0.712	0.795	0.888
2	460	0.25	0.51	0.60	0.82	0.72	0.80	0.89
3	470	0.18	0.45	0.53	0.62	0.70	0.78	0.86

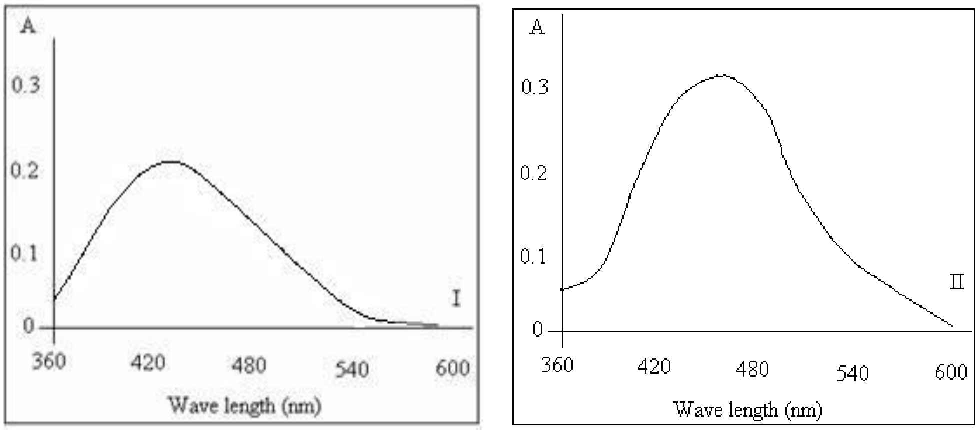


Fig. 1: Absorption spectrum of complexes I and II.

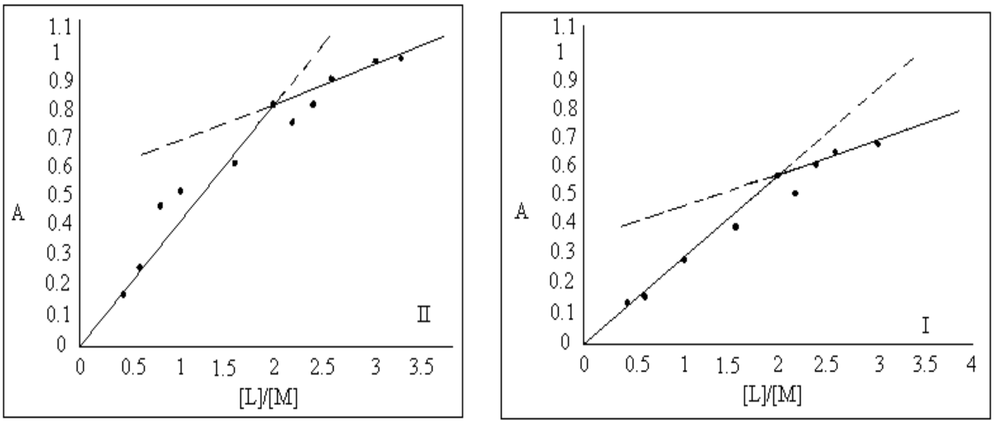


Fig. 2: Molar ratio method for the determination of the complexes (M:L I) and (M:L II).

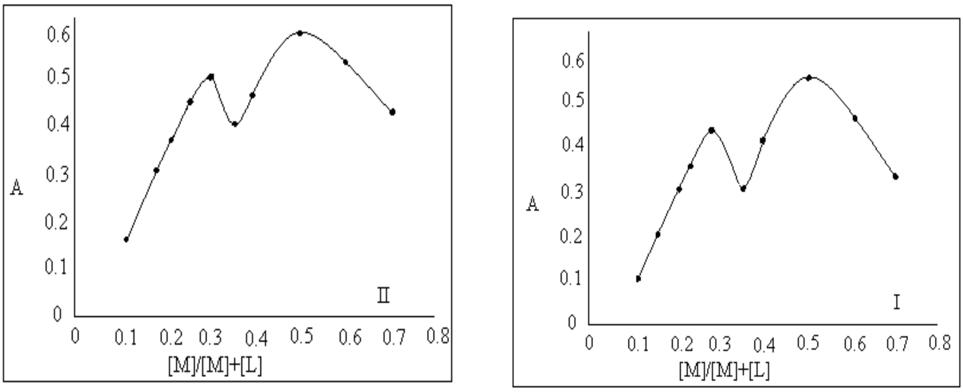


Fig. 3: Continuous variation for the determination of the complexes (M:L I) and (M:L II).

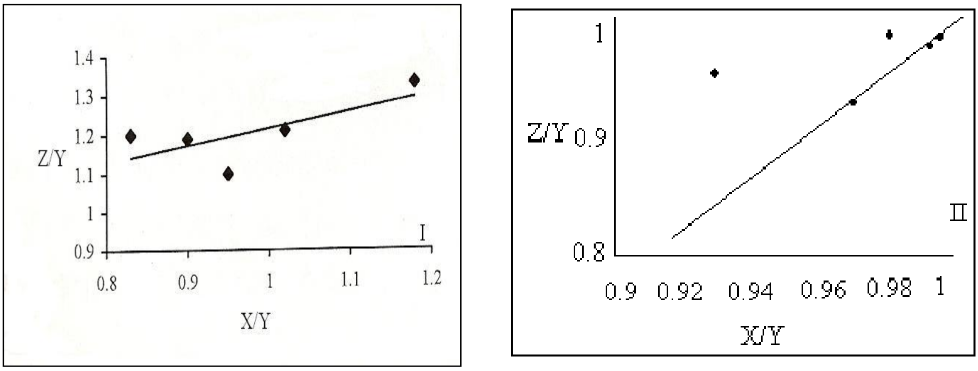


Fig. 4: The Coleman's graphical method to determined number of absorbing species of the complexes.

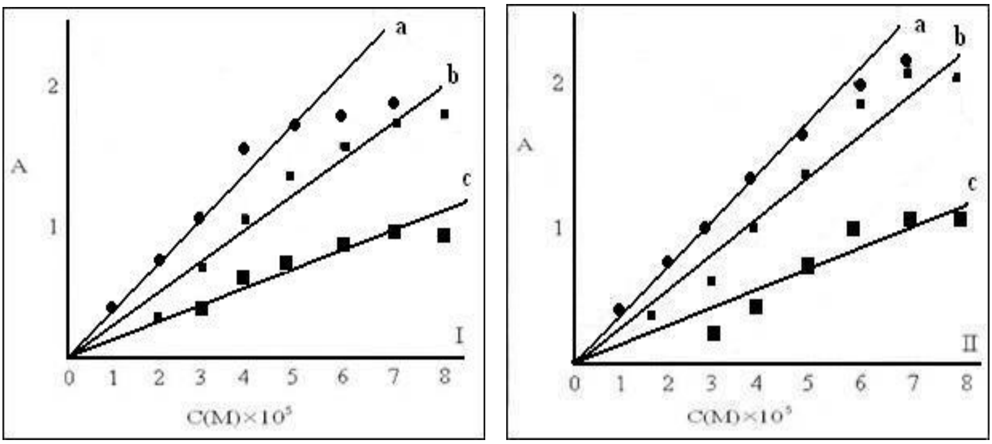


Fig. 5: Calibration curve of the complexes I and II at 420 nm and 460 nm respectively.

● a : Ethanol as a blank (E).

▪ b : Un reacted dye as a blank (Lun).

■ c : Dye as a blank (L).

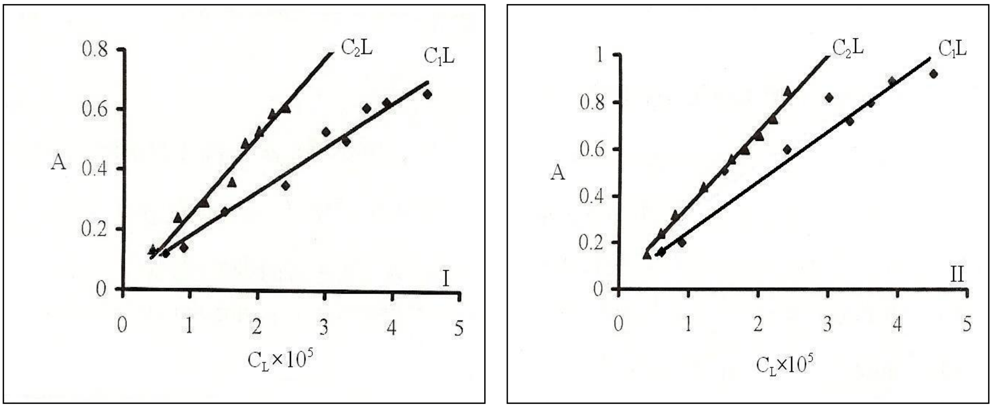


Fig. 6-a: Absorbance curve (1×10^5) M – Azodyes concentration(1×10^{-3} M). ♦ C_1L , ▲C_2L [(I) and (II) respectively].

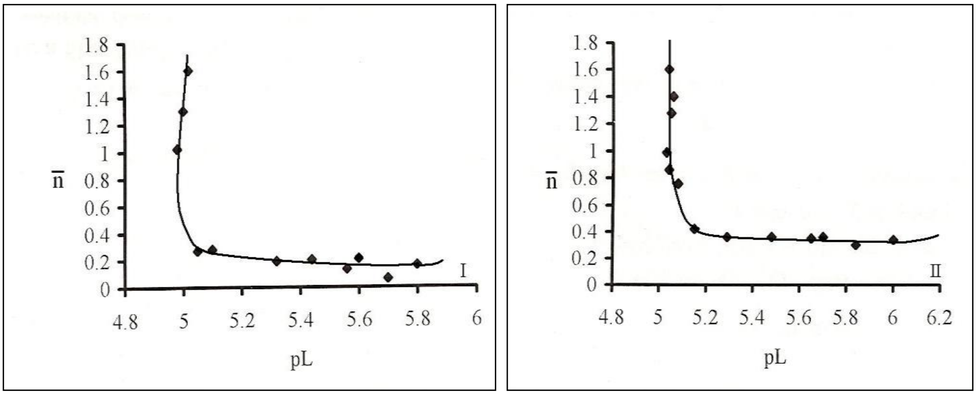
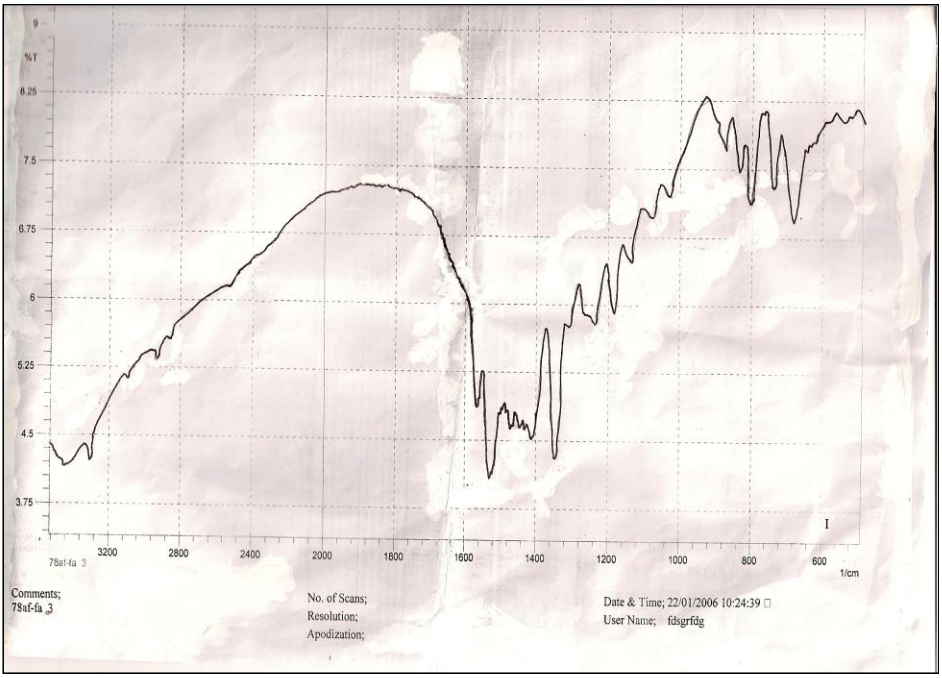


Fig. 6-b: Half value method for calculation the complexes (I) and (II) formation constants.



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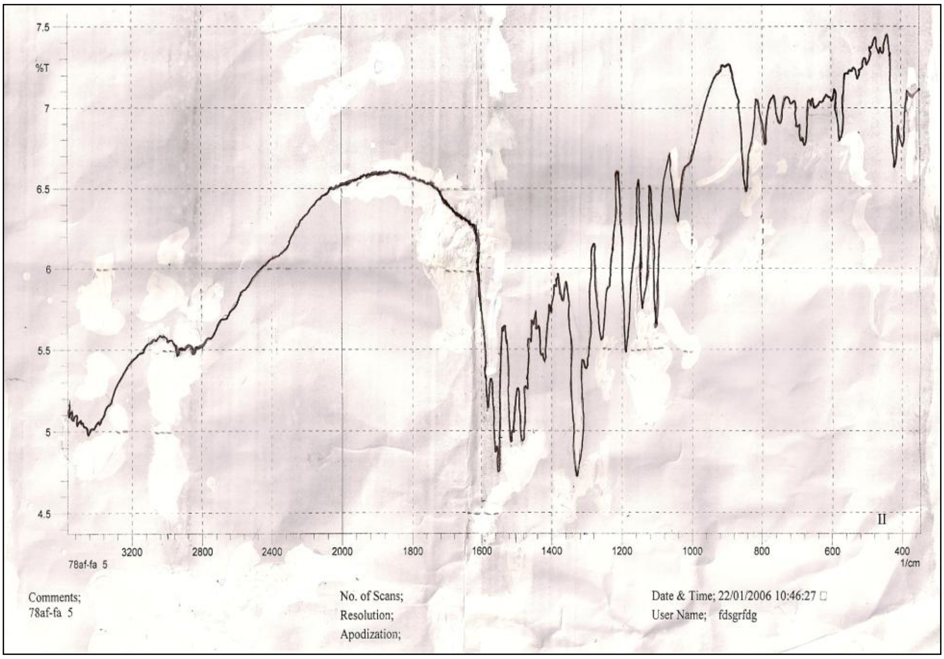

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Fig. 7: The infrared spectra of complexes (I and II) in the range(600-4000) cm^{-1} .

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