

## SPECTROPHOTOMETRIC STUDIES OF THE COMPLEXES OF 5-[2,3-DIHYDRO-1,4-PHTHALAZINEDIONAZO]8-HYDROXY QUINOLINE WITH SOME GROUP [IIB] METAL IONS.

Khawla S. Abd Al-Rassol

College of pharmacy –Dept. of pharma. chem.and the chem. of nat. products

Basrah university – Basrah - Iraq

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### ABSTRACT

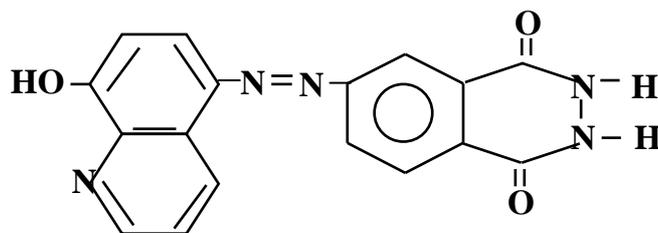
The reactions of 5[2.3-dihydro –1.4-phthalazindionazo] 8-hydroxyquinolin with Sc,Y and La ions have shown that 1:1and 1:2 complexes were formed in solution. The complexes were found to be suitable reagents for direct spectrophotometric microdetermination of scandium. Yterium and Lanthanium, the stepwise stability constants were evaluated applying corresponding solution method.

**Key words :** Spectrophotometric studies , azo dyes , rare earth.

### INTRODUCTION

Azo compounds are a very important class of chemical compounds receiving attention in scientific research <sup>(1)</sup>. They are highly colored and have been used as dyes and pigments for a long time<sup>(2,3)</sup>.Furthermore ,they have been studied widely because of their excellent thermal and optical properties in application<sup>(4-6)</sup> .The rare earth elements (REE)or Lanthanides , constitute a group of fourteen elements from Lanthanum to Lutetium , that are found in trace amounts in terrestrial and extraterrestrial samples .Several analytical techniques such as neutron activation analysis and isotope dilution mas spectrometry are generally used for determining REE <sup>(7-9)</sup>.The reported methods for determining of some group [IIB] elements include, spectrophotometrical methods based on a complex formation with some azo

dyes<sup>(10,11)</sup>.The azo dyes 5[2.3-dihydro-1,4-phthalazinedionazo] 8-hydroxy quinolin have been used for the spectrophotometrical determination of Aluminum and mercurious <sup>(12)</sup>.The present investigation deals with the spectrophotometric determination of Sc [III], Y[III]and La[II] ions with azo dye5-[2,3-dihydro-1.4-phthalazinedionazo]8-hydroxy quinolin [L] and the determination of stability constants of complexes ( $\text{Log}\beta_1$  and  $\text{Log}\beta_2$  ) by using corresponding solution method in ethanol medium.



(L)

## EXPERIMENTAL

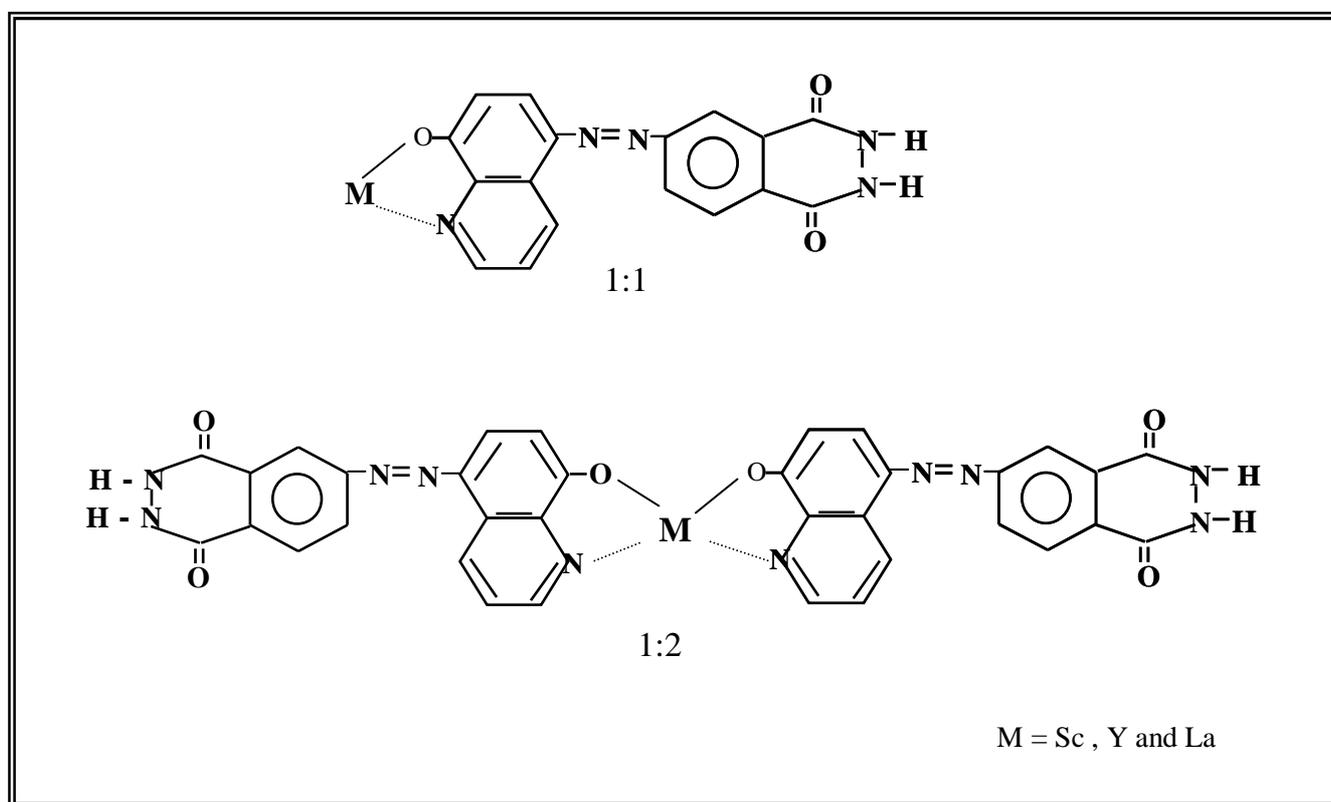
The azo dye [L] was prepared by coupling the diazotized 3-amino phthalhydrazide with 8-hydroxy quinoline in alkaline medium<sup>(13)</sup>. The 0.001M solution of the azo dye [L] was prepared by dissolving the accurate amount of the acid form in the proper volume of ethanol. A 0.001M of stock solutions of  $\text{ScCl}_3$ ,  $\text{Y}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{La}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  were prepared in water and standardized with EDTA by recommended procedure<sup>(14)</sup>. Distilled water and chemicals of the highest purity were used in all experiments.

I.R. spectra of complex (Sc[III]-ligand) were recorded in KBr disk using Buck model 500 spectrophotometer.

The absorption spectra of the azo dye [L] and its complexes with Sc[III], Y[III] and La [III] ions were

scanned within the range 360-700 nm in ethanol using the spectrophotometer [LKB(Biochrom) ultraspec II 4050 UV/visible].

For the determination of Sc, Y and La ions, a series of solutions were prepared containing up to 5, 10 and 15 ppm of Sc, Y and La respectively. A (0.1—1.0 ml) of 0.001M of azo dye [L] was added and the mixture was completed up to 5 ml with ethanol. The absorbance at 480 nm for Sc, 470 nm for Y and La respectively was measured against a blank containing the same ingredients except metal ion. The concentration of the metal ion was computed by extrapolation from a standard calibration curve prepared in the same manner.



Suggestion formula of complexes

## Results and discussion

Fig.(1) and Fig.(2) show the IR spectra for ligand [L] and complex (Sc(III) and ligand). Fig.(1) shows the infrared spectra of ligand, it shows an intense band appearing at  $(1700 \text{ cm}^{-1})$  these peaks are attributed to the carbonyl group (stretching vibration). The peaks appearing in the region  $(1560-1635 \text{ cm}^{-1})$  are attributed to  $(\text{C}=\text{C}$  and  $\text{N}=\text{N}$

)(stretching vibration). The peak appearing in the region  $(3300-3460 \text{ cm}^{-1})$  are attributed to the hydroxyl group (stretching vibration). Fig.(2) shows the infrared spectra for the complex (Sc(III)-[L]), the IR spectra of the complex showed significant differences from the free dye, general shift of vibration bands in some groups like the increase of

wave number of carbonyl group position in complex (20 cm<sup>-1</sup>) compared to that free dye. The broad band of hydroxyl (-OH) (stretching vibration) is not appear in complex spectra, and the broad band appearing in the region (3150-3650 cm<sup>-1</sup>) are attributed to (-NH) group hydrogenic bonding.

The absorption spectra of the azo dye [L] and its complexes with Sc, Y and La ions were recorded within wavelength range 360-700nm. It was found that the suitable medium for developing the violet colour is ethanol. The complexes are characterized by absorption bands with their maximum allocated at 480nm to Sc and 470nm to Y and La, respectively, and the λ<sub>max</sub> of the free dye is 500nm. The absorption of dye [L] and its complexes [1:1 and 1:2], against ethanol and against dyes, are shown in Figs(3,4 and 5) for Y, Sc and La ions, respectively ([M]=0.8x10<sup>-4</sup>m).

The effects of time, sequence of addition and pH on the stability of the complexes were studied in detail. It was found that all complexes are formed instantaneously and remained stable for more than 20 hours using the sequence, dye, metal, ethanol.

The suitable pH values for complex formation were found to be in the range of 11-12 by using a universal buffer solution<sup>(15)</sup>, but a pure ethanolic medium was preferred for use (since there was no difference in absorbance) instead of a buffer solution. This was because the complexes in a buffer solution were unstable due to hydrolysis and formation of a turbid solution.

The stoichiometry of the formed complexes was investigated using standard spectrophotometric methods such as, the molar ratio and continuous variation methods. The results indicate the formation of 1:1 and 1:2(M:L) complexes. The presence of these complexes was confirmed by calculating the number of absorbing species using Coleman's graphical method<sup>(16)</sup> as applied to the results of the molar ratio method for the complexes. This method shows that three species exist in solution.

Beer's law was obeyed to the complexes under investigation for the spectrophotometric determination of Sc, Y and La. It was found that Beer's Law is satisfactorily obeyed up to 8, 16 and 22 ppm of Sc, Y and La respectively (Table 1). A better results and higher values were obtained by applying the optimum blank compensation technique<sup>(17)</sup> using the amount of unreacted dye as the blank from the knowledge of the stoichiometry of the complex. Table (1) lists the molar absorptivity (ε) (L. mol<sup>-1</sup>.cm<sup>-1</sup>), specific absorptivity (a) (ml.g<sup>-1</sup>.cm<sup>-1</sup>) (corresponding to the absorbance of 1 ppm in a cuvette with optical path length of 1cm), sandell function for sensitivity

(S)(μg.cm<sup>-2</sup>), (represents the number of micrograms of the determined per ml of solution having an absorbance of 0.001 for a path length of 1cm), detection limit (DL) and correlation coefficient (r)<sup>(18)</sup>. A systematic study of the influence of foreign ions led to the conclusion that the presence of the following ions in 20 fold excess relative to Sc, Y or La do not interfere: Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Be<sup>++</sup>, Mg<sup>++</sup>, Ca<sup>++</sup>, Sr<sup>++</sup>, Cd<sup>++</sup>, Nd<sup>++</sup>, Al<sup>+++</sup>, Sm<sup>+++</sup>, Eu<sup>+++</sup>, Cu<sup>++</sup> and Ho<sup>+++</sup>. On the other hand, the following ions should not be present: Co<sup>++</sup>, Ni<sup>++</sup>, Cr<sup>+++</sup>, Fe<sup>+++</sup>, Ir<sup>+++</sup>, Sn<sup>++</sup>, Pb<sup>++</sup>, EDTA, Oxalate, Tartaric and CDTA. The present method affords a new means for the rapid spectrophotometric microdetermination of Sc, Y and La in a pure solution or in the presence of a variety of cations and anions, which do not interfere with such determination with fair accuracy and precision, as indicated by the low standard deviation values (SD) amounting to 0.004, 0.004 and 0.005 in the determination of 4, 9 and 14 ppm of Sc, Y and La respectively (5 determinations).

By the aid of the corresponding solutions method, the stability constants of the complexes of the dye [L] with Sc, Y and La ions were calculated using Olerup, Half values and Rossotti-Rossotti methods<sup>(12)</sup>. These methods require a series of solution of total metal ion concentrations C<sub>1</sub>M and C<sub>2</sub>M and of varying ligand (dye) concentrations C<sub>1</sub>L and C<sub>2</sub>L. The corresponding solutions are those which have the same absorbance at different ligand concentration. From the absorbance-CL plots, many pairs of C<sub>1</sub>L and C<sub>2</sub>L consequently, n̄ (complex formation function) and ligand concentration [L] can be determined by using the equation 1 and 2 respectively.

$$\bar{n} = \frac{C_1L - C_2L}{C_1M - C_2M} \dots\dots\dots 1$$

$$[L] = \frac{C_1MC_2L - C_2MC_1L}{C_1M - C_2M} \dots\dots\dots 2$$

For the Olerup method, Logβ<sub>1</sub>(LogK<sub>1</sub>) and Logβ<sub>2</sub>(LogK<sub>1</sub>+LogK<sub>2</sub>) are obtained by plotting n̄/[L] against [L] where a curve is obtained the slope of the initial part of which gives β<sub>2</sub> and the intercept yield β<sub>1</sub>. Figs( 6,7 and, 8) show the Y, Sc and La ions curves respectively. By using the half value method Log β<sub>1</sub> and Logβ<sub>2</sub> are obtained from a plot of (n̄) against PL (PL=-Log[L]) Figs.(9,10 and 11) show the curves for Y, Sc and La ions, respectively (n̄ =0.5 gives LogK<sub>1</sub>, n̄ =1.5

gives  $\text{Log}K_2$ ). By using Rossotti - Rossotti method  $\text{Log}\beta_1$  and  $\text{Log}\beta_2$  are obtained by plotting  $n/(1-n)[L]$  versus  $(2-n)[L]/(1-n)$ , where a straight line is obtained, the slope of which is equal to  $\text{log}\beta_2$  and intersection with  $n/(1-n)[L]$  axis gives  $\text{Log}\beta_1$

(Figs.12,13 and 14) show the straight line for Y, Sc and La ions respectively. The results obtained by different methods are listed in table (2) A, B and C Half values, Olerop and Rossoti Rossoti methode respectively

**Conclusion**

The results obtained from the present study indicate that complex formation between the ligand (L) and some group (IIIB) metal ions (Y, Sc, and La) with 1:1 and 1:2 (M:L) complexes. The stability

constant of the complexes were studied. The present methode is sensitive and accurate for the spectrophotometric determination of Y, Sc and La metal ions.

**Table (1) : Data obtained from Beer's Law for the complex at  $\lambda_{max}$**

Complex	ppm up to	$\epsilon \times 10^{-4}$ L.mol <sup>-1</sup> .cm <sup>-1</sup>	$a \times 10^{-2}$ ml.g <sup>-1</sup> .cm <sup>-1</sup>	$S \times 10^{-2}$ $\mu\text{g.cm}^{-2}$	S.D	r	D.L mg/mlx10 <sup>-3</sup>
La-L	22	0.518	0.037	0.027	0.005	0.987	~ □□
Y-L	16	0.340	0.038	0.026	0.004	0.999	~ □□
Sc-L	8	0.261	0.059	0.017	0.004	0.998	~ □□

**Table (2) :Determination of stability constant of the complexes using corresponding solutions method**

Complex	$\text{Log}\beta_1$				$\text{Log}\beta_2$			
	A	B	C	mean	A	B	C	mean
La-L	3.941	3.718	3.834	3.831	7.373	6.806	6.693	6.957
Y-L	4.150	3.910	3.989	4.016	7.742	7.045	7.530	7.439
Sc-L	4.419	4.146	4.185	4.250	8.234	7.625	7.951	7.937

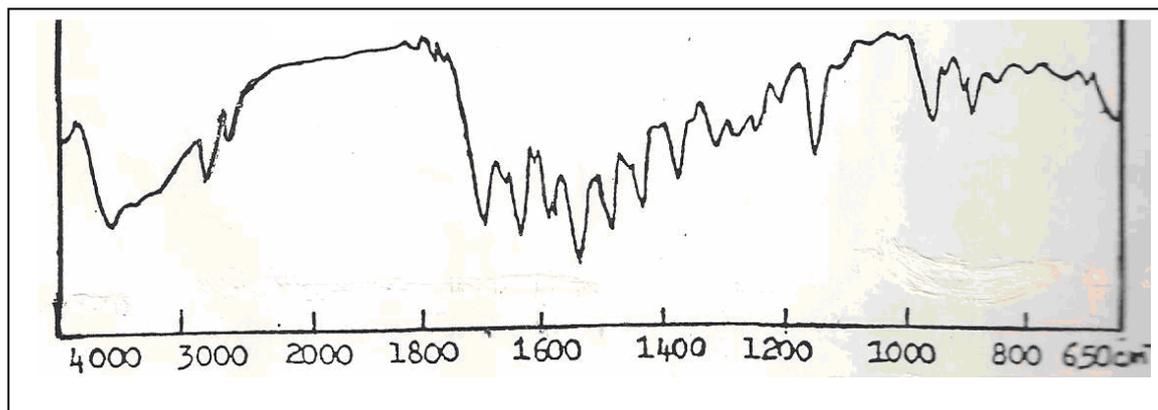


Fig.(1): I.R. spectra for ligand

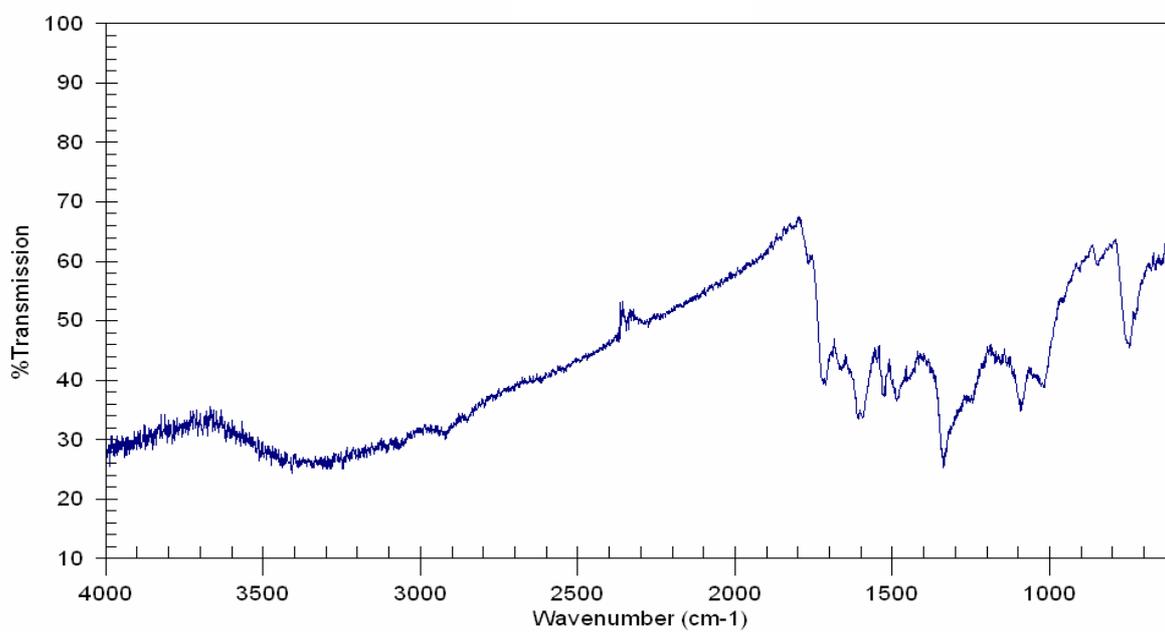


Fig.(2): I.R. spectra for complex Sc[III]-ligand

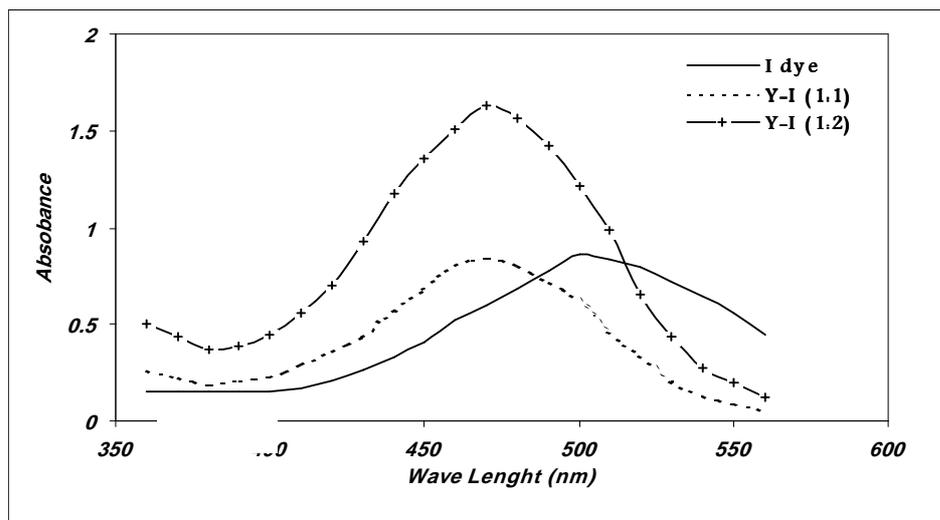


Fig.(3): Absorption spectra of the Y-Complex

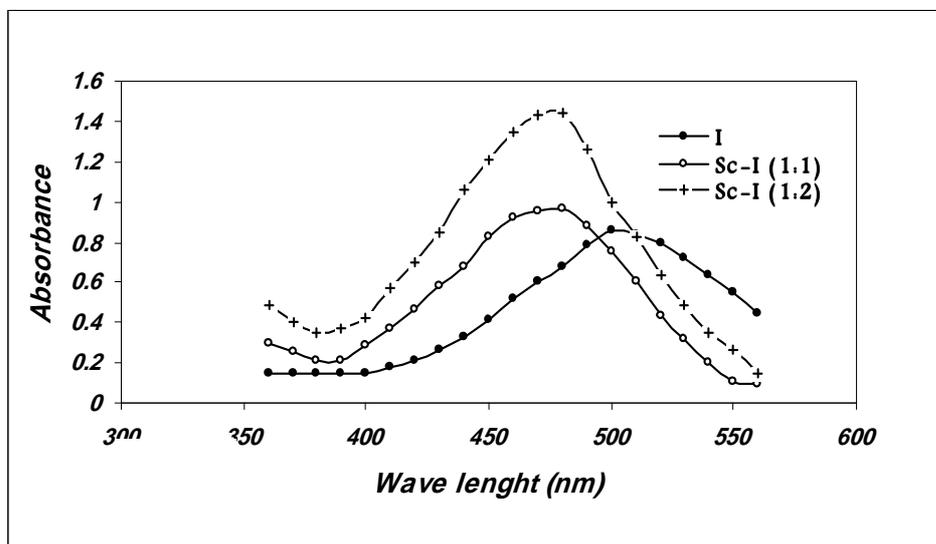


Fig.( 4): Absorption spectra of the Sc-Complex

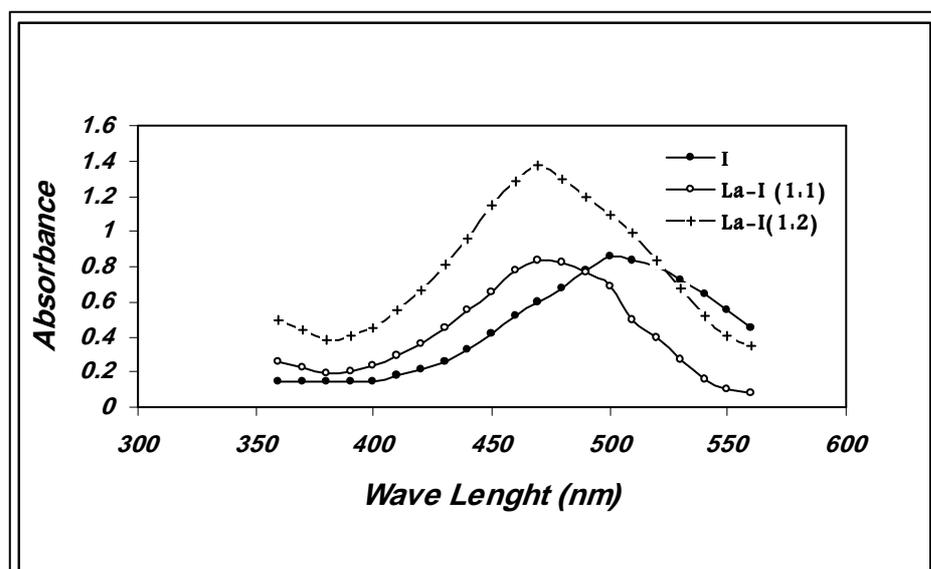


Fig.(5): Absorption spectra of the La-Complex

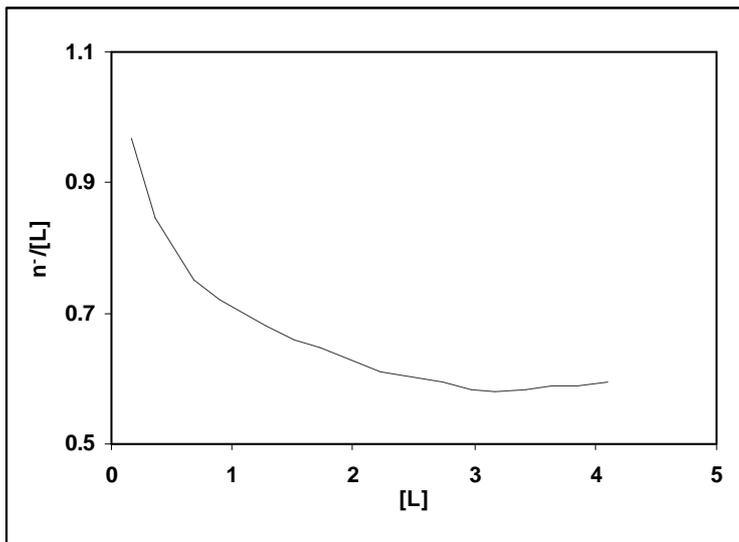


Fig.(6): Olerup method for the calculation of the formation constant of the Y-Complex

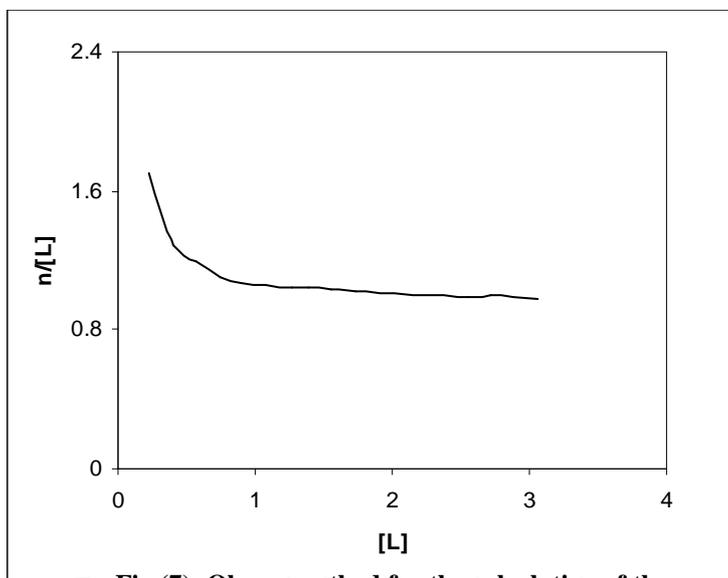


Fig.(7): Olerup method for the calculation of the formation constant of the Sc-Complex

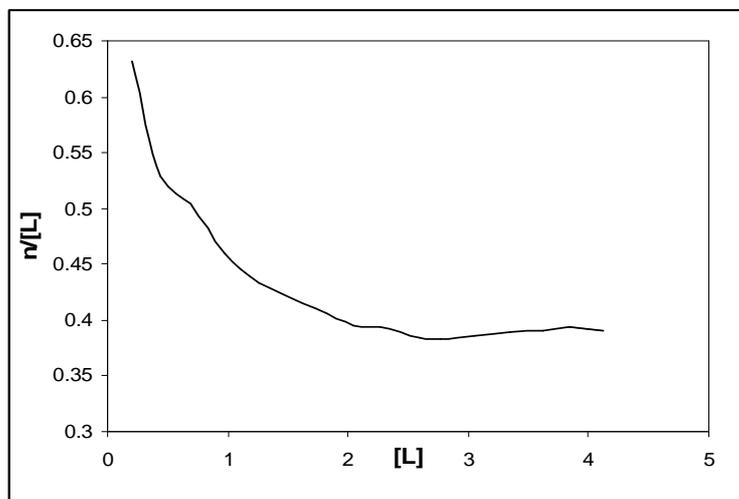


Fig.(8): Olerup method for the calculation of the formation constant of the La-Complex

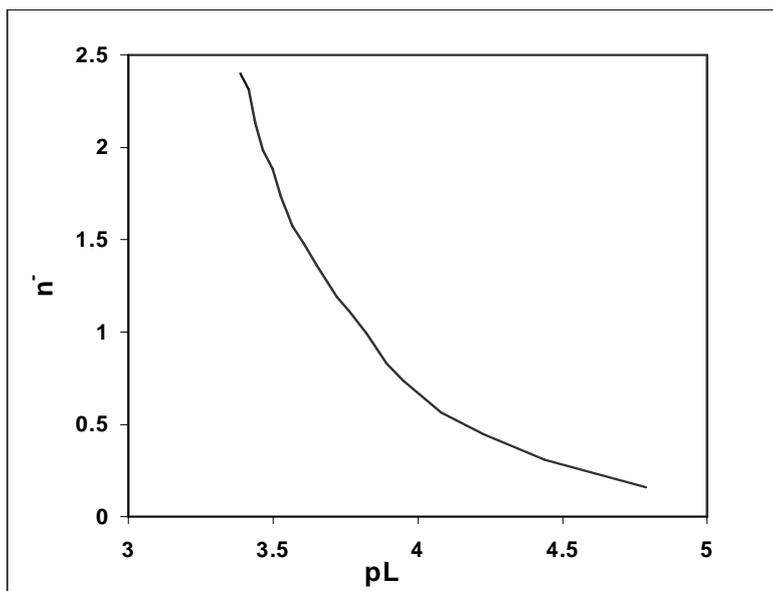


Fig.(9): Half values method for the calculation of the formation constant of the Y-Complex

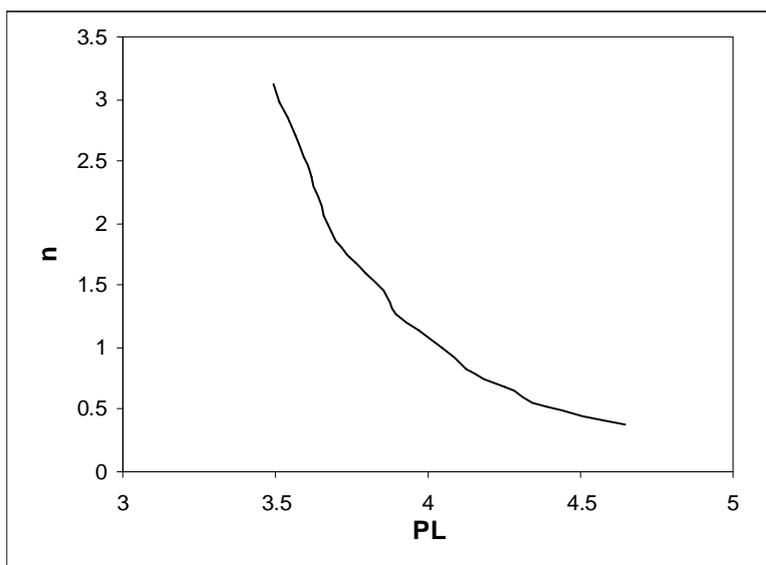


Fig.(10): Half values method for the calculation of the formation constant of the Sc-Complex

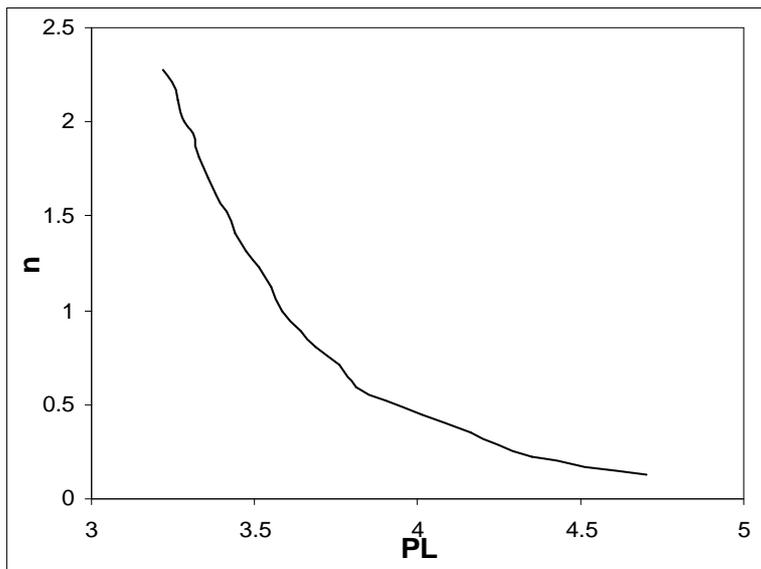


Fig.(11): Half values method for the calculation of the formation constant of the La-Complex

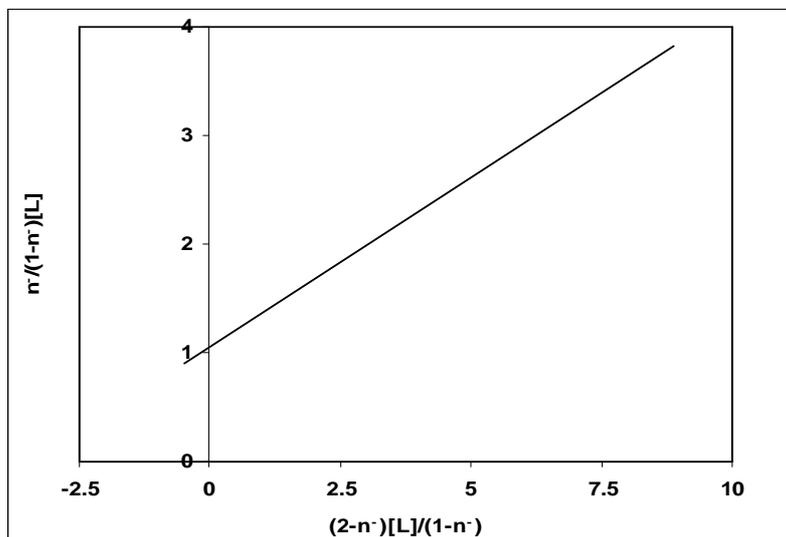


Fig.(12): Rossotti-Rossotti method for the calculation of the formation constant of the Y-Complex

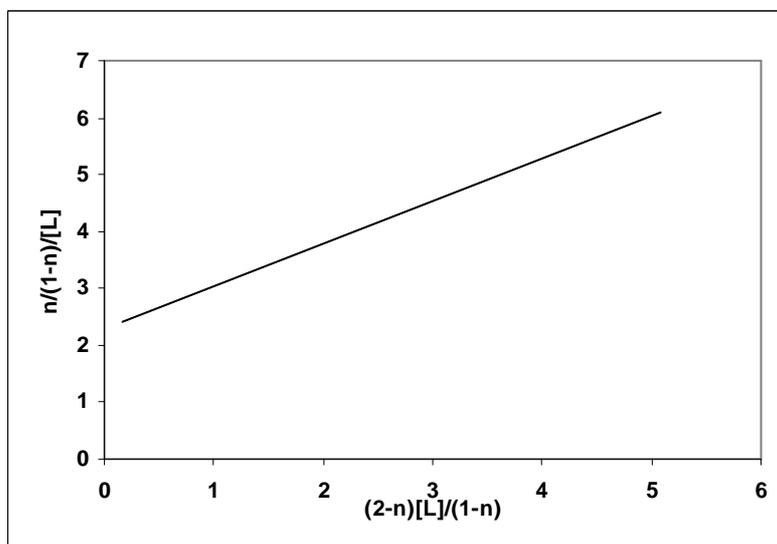


Fig.(13): Rossotti-Rossotti method for the calculation of the formation constant of the Sc-Complex

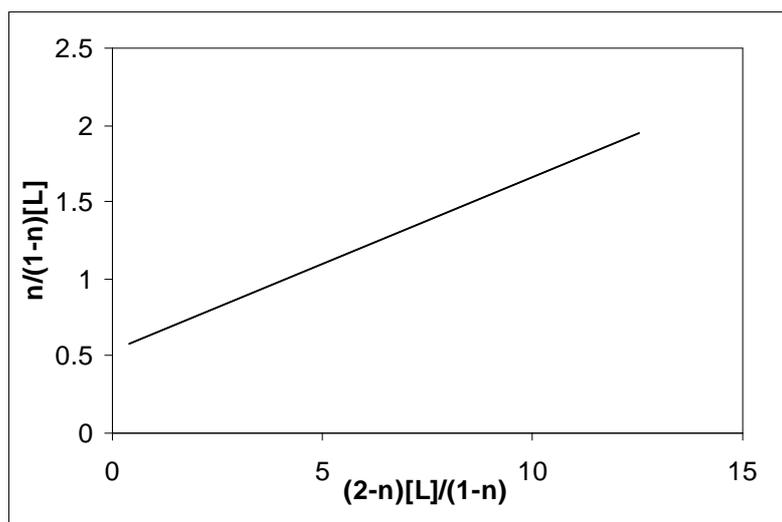


Fig.(14): Rossotti-Rossotti method for the calculation of the formation constant of the La-Complex

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دراسة طيفية لمعقدات 5(2,3-dihydro-1,4-phthalazindionazol)8-hydroxyquinolin  
مع بعض ايونات عناصر المجموعة [IIIB]

خولة سلمان عبد الرسول  
كلية الصيدلة - قسم الكيمياء الصيدلانية والعقاقير والنباتات الطبية  
جامعة البصرة-البصرة-العراق

الملخص

ان تفاعل 5(2,3-dihydro-1,4-phthalazindionazol)8-hydroxyquinolin مع ايونات Y, Sc و La اظهرت تكون معقدات بنسبة ارتباط 1:1 و 1:2 في محاليلها اظهرت الدراسة بان هذه المعقدات هي كواشف مناسبة للتقدير الطيفي المباشر لهذه الايونات ,وقد درست ثوابت الاستقرار للمعقدات المتكونة بتطبيق طريقة الارتباط بالمحاليل.