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Synthesis and Identification Symmetrically Azo Dyes Derived from Sulfa Compounds and Spectrophotometric study of Nickel (II) Complexes with Prepared Dyes

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***Abstract*— Two new azo compounds are prepared, the first dye (A_1) is 4,4'- (diazene - 1, 2 - diyl) bis (N - carbamimidoyl benzene sulfonamide) and the second dye (A_3) is 4,4'- (diazene -1, 2-diyl) bis (N -(pyrimidin-2-yl)benzene sulfonamide), were synthesized and characterized by FT/IR , Elemental analysis (CHNS) and 1H-NMR spectroscopy. The complexes of these azo are prepared with the metal ions Ni (II) and were spectrally studied after fixing the optimum conditions, where these conditions can be summarized as follows: determine λmax, pH for a wide range of optimum at (pH = 0.7 – 12), effect of sequence addition on formation of complexes azo dyes, time effect, and the molar concentrations that obey Lambert – Beer's law. The mole ratios method of the Metal : Ligand (M : L) has showed (1: 2) for all the prepared complexes.**

***Index Terms*— Azo Dye, Sulfa drag, determination of metals by Spectrophotometric methods.**

I. INTRODUCTION

Azo compounds are a class of chemical compounds that are continuously receiving attention in scientific research [1]. They are usually strongly coloured compounds which can be intensily yellow, red, orange, blue or even green, depending on the exact structure of the molecule. As a result of their colour, azo compounds are tremendous importance as dyes and also as pigments for a long time [2]. The structural features in organic compounds, that usually produce colour are C = C, N = O, N=N, aromatic rings, C = O and NO_2. Most importantly, the groups that invariably confer colour are the azo (–N=N–) and nitroso (–N=O) while the other groups actually do so under certain circumstances [3]. Azo dyes contain one or more azo groups (- N =N -) which are linked to SP^2 hybridized carbon atoms, based on the number of such groups [4]. The azo dyes compounds are regarded highly active towards most of the metal ions. They have great importance in chemical analysis because these compounds contain more than one active group, which is able to formulate chelatic coordinational complexes with metal ions distinguished by their color and ability to dissolve in different solvents [5], [6], [7]. These dyes and their complexes are widely used as dyes for tissues, which increase their industrial importance [8], [9], [10].

The present paper reports on the synthesis of two new symmetrically azo compounds which are derived from Sulfa compounds. As well as the study was achieved through the complexes formed between these a new prepared symmetrically azo dyes with metal ion Ni (II).

II. EXPERIMENTAL

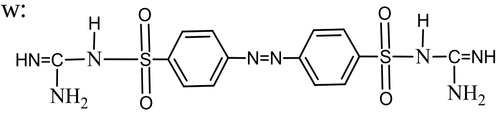
A. Materials and Instruments

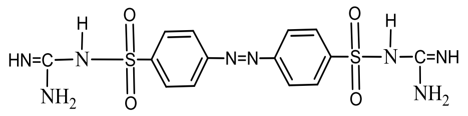
All materials and solvents used in this study were of analytical grade. All chemical reagents were purchased from commercial sources: Sulfaguanidin (99 %), Sulfanilamide (99%), (1,2-Naphthoquinone- 4- methoxy (99 %), Nickel nitrate (98%). ^{1}H NMR spectra were recorded on a Bruker Avance DRX 400 MHz spectrometer. DMSO-D6 was used as solvent and chemical shifts recorded were internally referenced to Me_4Si (0 ppm). IR spectra were obtained on a Bruker Tensor 27 FT-IR spectrophotometer. Elemental analysis was measured by Heraus CHNS Proapparatus Elemental analyzer. Absorbance readings were obtained with a PD-303 UV. VIS-Spectrophotometer (Japan) spectrophotometer.

B. Synthesis of Symmetrically Azo Compounds

- ***A_1 / 4,4'-(diazene-1,2-diyl) bis (N-carbamimidoyl benzene sulfonamide)***

1,2-Naphthoquinone- 4-methoxy (0.1881 g, 0.001 mole) was mixed with small amount of water and added Sulfaguanidin (0.4248 g, 0.002 mole). The mixture was stirred for a few minutes and the resulting product was filtered, washed with water, dried and recrystallized by using H_2O:DMF (2:10) to give the titled compound as reddish solid crystals in 84.2 % yield, m.p. 257- 260 °C, ^{1}HNMR (DMSO-d6) δ = 8.05 – 8.10 (m, 4H, **CH**-N=N-), 7.37 – 7.41 (m, 4H, **CH**-SO_2), 3.37 (s, 2H, NH), 8.34 (s, 2H, NH_2), 6.75 (s, 2H, C=**NH**) ; FT-IR (KBr), 3307 cm^{-1}(v NH), 3020 cm^{-1} (v CH), 1404 cm^{-1}(v -N=N-); Elemental Analyses calculated For $C_{14}N_8H_{16}S_2O_4$: C 39.58; H 3.77; N 26.39; S 15.08; Found C 39.09; H 3.92; N 26.20; S 14.53. The structure of A_1 is shown below:





- ***A_3 / 4,4'-(diazene-1,2-diyl) bis (N-(pyrimidin-2-yl) benzene sulfonamide)***

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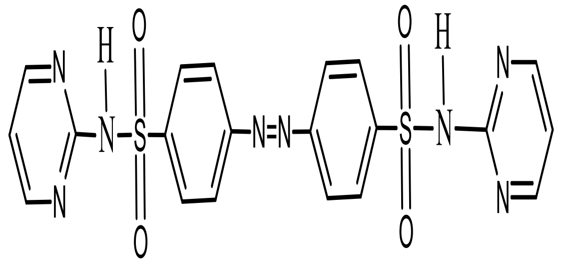
1,2-Naphthoquinone- 4-methoxy (0.1881 g, 0.001 mole) was mixed with small amount of water and added Sulfaguanidin (0.4960 g, 0.002 mole). The mixture was stirred for a few minutes and the resulting product was filtered, washed with water, dried and recrystallized by using H_2O:DMF (13.5:6.7) to give the titled compound as red blackish solid crystals in 80.9 % yield, m.p. 295-298 ºC, ^{1}HNMR (DMSO-d6) δ = 7.62 – 7.77 (m, 4H, **CH**-N=N-), 7.45 – 7.55 (m, 4H, **CH**-SO_2), 5.52 (s, 2H, NH), 7.80 – 8.10 (m, 4H, **CH**=N), 7.30 – 7.40 (d, 2H, **CH**-CH=N) ; FT-IR (KBr): 3261 cm^{-1}(v NH), 3074 cm^{-1} (v CH), 1408 cm^{-1}(v -N=N-); Elemental Analyses calculated For $C_{20}N_6H_{16}S_2O_4$: C 48.33; H 3.22; N 22.55; S 12.88; Found C 49.01; H 2.99; N 22.17; S 13.29. The structure of A_2 is shown below:



C. Preparation of Solutions

- Stock solution of (1*10^{-3}) M azo dye was prepared by dissolving accurate weight of each dye in small amount of DMSO, and completes the volume to 50 ml absolute ethanol.

- Universal buffer solutions of pH (0.7-12).

- (1*10^{-3}) M of Nickel (II) nitrate hexahydrate solution, by dissolving 0.029 g. of $Ni(NO_3)_2.6H_2O$ in dilute. Water and complete to 100 ml.

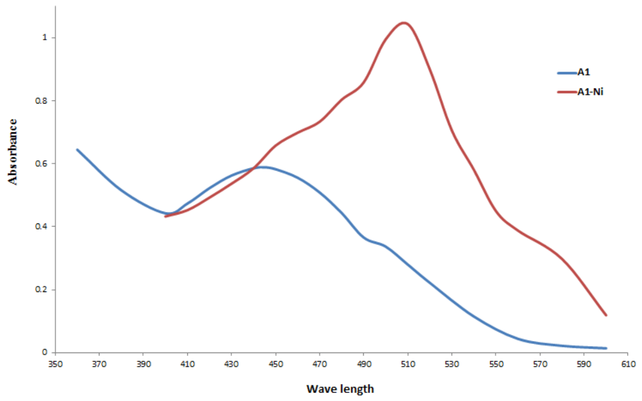
III. RESULTS AND DISCUSSION

A. Fixing the Optimum Conditions

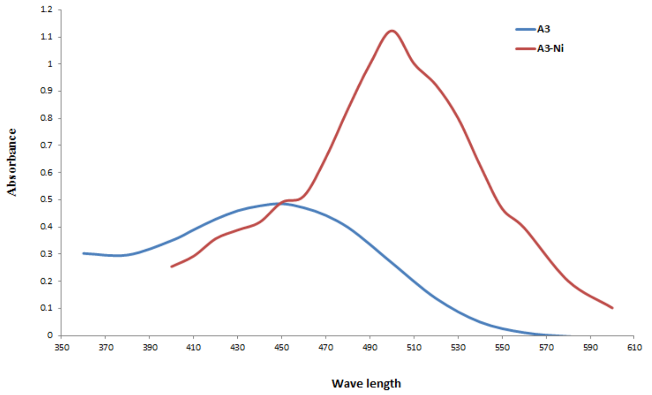
The following are some of the optimum conditions for the formation of the metal ion Ni(II) complexes with prepared azo dyes A_1 and A_3, which color turns from orange to dark red is considered evidence of formation the complexes. These conditions are mainly in the work to conduct applied studies on the azo dyes and these conditions can be summarized as follows:

- **The wavelength of maxima absorbance (λ_{max})**

The choice of (λ_{max}) is one of the important things that must be taken into consideration in study of the optimum conditions for the formation of any complex. Absorption spectra were recorded in the visible region at range (360-600) nm to studied dyes and their complexes, as shown in Figures (1) and (2), and found that the wavelengths of maximum absorbance (λ_{max}) for azo dyes (A_1, A_3) are 455 and 450 nm, respectively. While the Ni (II) complexes with prepared azo dyes (A_1, A_3) are 510 and 500 nm by using ethanol as a reference solution.



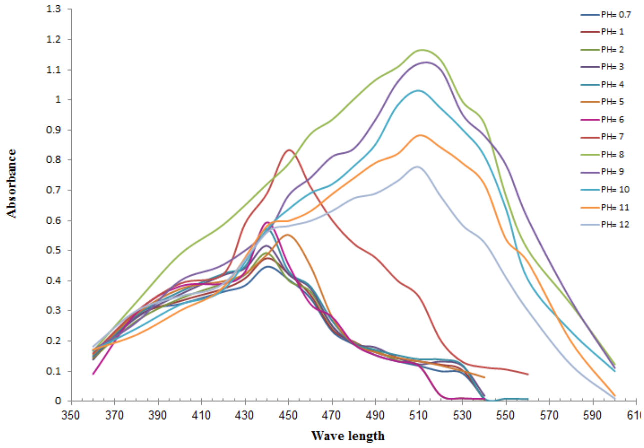
Fig(1): Absorbance spectra of azo dye A_1 and its complex with Ni(II) at 5X10^{-5} M in ethanolic solution



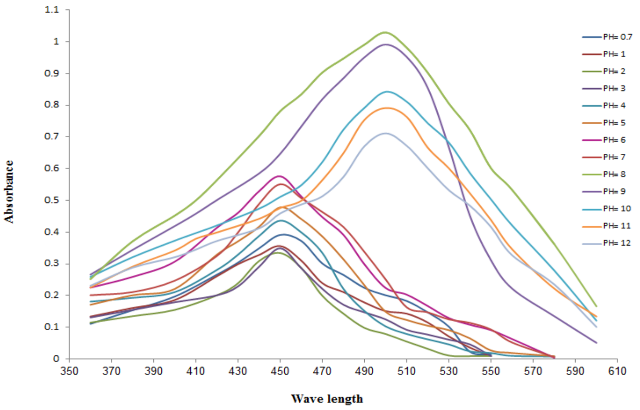
Fig(2): Absorbance spectra of azo dye A_3 and its complex with Ni (II) at 5X10^{-5} M in ethanolic solution

- **Effect of pH**

The effect of pH on the absorbance of the metal chelate solutions were studied by using Universal solution at pH range (0.7 – 12), and measured the absorbance at range of wavelengths (360 – 600) nm by using buffer solution and alcohol as reference solutions at concentration 5X10^{-5} M for each of metal and dyes, as shown in Figures (3) and (4), where the figures are illustrating that buffer solution at pH (8-9) for two complexes is very suitable to formation the complexes because they gave the highest absorption[11]. Since pH of the complexes when mixing is (7) so was not added buffer solution to the mixture of the complexes.



Fig(3): Visible absorption spectra to the complex of A_1 with Ni (II) in the buffer solutions which are have different pH at concentration 5X10^{-5} M for each of dye and metal



Fig(4): Visible absorption spectra to the complex of A_3 with Ni (II) in the buffer solutions which are have different pH at concentration $5X10^{-5}$ M for each of dye and metal

It should be noted that the two complexes of dyes with Ni (II) can be used as indicator of acid – base, as shown in the Figures (3) and (4), which shows deviation toward the shorter wavelength in the case of acidic solutions.

- **Effect of Sequence Addition**

The sequence addition is studied on formation of dyes complexes with Ni (II), and three different possibilities succession add were found as the following: (dye + metal +alcohol), (dye + alcohol + metal) are the beast studied sequence, which give the highest absorption. While the third sequence has the lowest adsorption due to precipitate portion of metal then decrease the concentration of complex, table (1) shows the effect of sequence addition on adsorption values to complexes Ni II with dyes A_1 and A_3.

Table (1). The effect of sequence addition on absorption values to complexes Ni (II) with dyes A_1 and A_3

№	Addition	Adsorption at 510 nm	Adsorption at 510 nm
		A_1 + Ni $^{+2}$	A_3 + Ni $^{+2}$
1	dye + metal +alcohol	1.029	1.123
2	dye + alcohol + metal	1.032	1.119
3	metal + alcohol + dye	0.987	1.016

$5x10^{-5}$ M =[Ni^{+2}]=[L]

- **Effect of Time**

The effect of time was studied on the absorption spectra of azo dyes complexes to periods of time ranging from 1 to 1440 minutes. The results of this study showed that all complexes formed temporary and need a period ranging between (10 – 15) minutes to settle down and remain stable more than 24 hours, as shown in Figure (5).

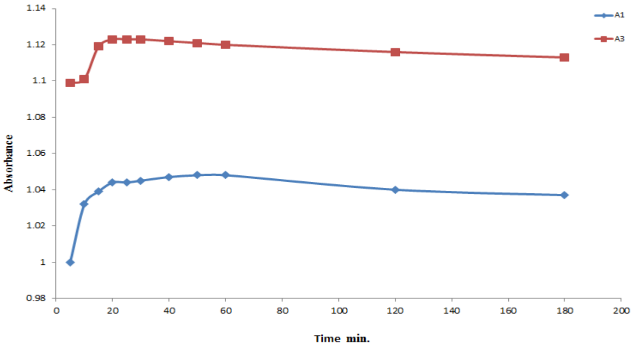


Fig (5). The effect of time on absorption of the complexes prepared dyes

- **Stoichiometry**

The results of spectrophotometric studies are showed the molecular proportions (2:1) , (M:L) by using the method of molar ratios, as shown in Table (2), Figures (6) and (7).

Table (2). The absorption values to complexes Ni (II) with dyes A_1 and A_3 at (λ_{max})

Adsorption at 500 nm	Adsorption at 510 nm	[Dye]/[Metal]	[Dye]×10^{-5} M
A_3 + Ni^{+2}	A_1 + Ni^{+2}		
0.201	0.112	0.166	0.5
0.298	0.189	0.33	1
0.374	0.274	0.5	1.5
0.455	0.354	0.66	2
0.532	0.444	0.83	2.5
0.599	0.499	1	3
0.667	0.576	1.16	3.5
0.753	0.649	1.33	4
0.834	0.733	1.5	4.5
0.897	0.839	1.66	5
0.956	0.898	1.83	5.5
1.001	0.994	2	6
1.098	1.086	2.16	6.5
1.152	1.089	2.33	7
1.217	1.153	2.5	7.5
1.256	1.224	2.66	8
1.278	1.263	2.83	8.5
1.311	1.301	3	9

3×10^{-5}M =[Metal]

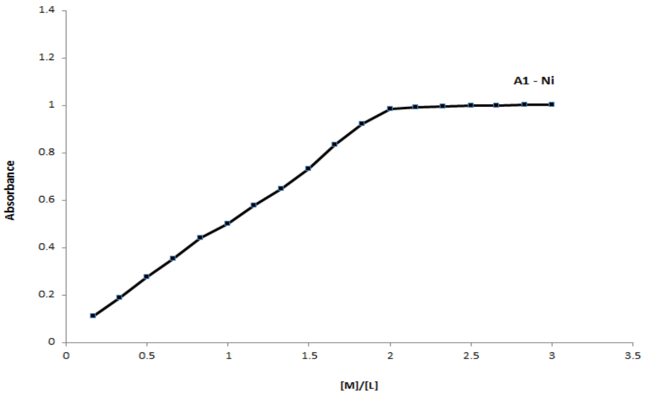


Fig (6). Spectral method to calculate the molar ratios to Ni (II) with A_1 dye complex

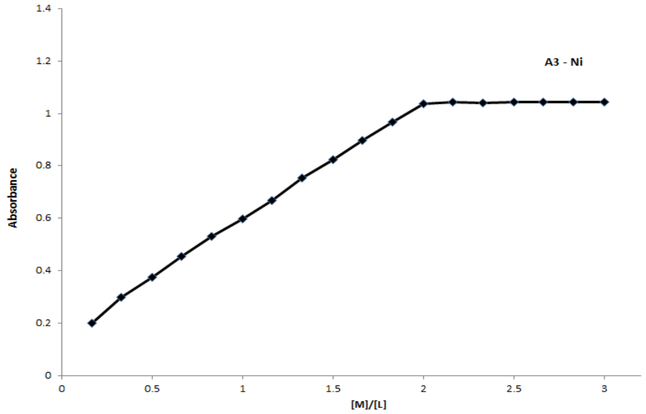


Fig (7). Spectral method to calculate the molar ratios to Ni (II) with A_3 dye complex

B. *Beer Law and the Sensitivity of Method*

The applicability of Beer Law was studied on complexes solutions by Calibration Curve, Which represents the relation between absorbance and concentration in ppm, as shown in Figure (8). In order to approaching the calibration curve of idealism and high accuracy it was necessary to use Optimum Blank Compensation [12]. Generally, represent the sensitivity of method through the slop of calibration curve which is equal to the molar absorptivity (ε), this term is often used for indicating a less quantity or concentration to substance. Table (3) shows the Specification Absorbitivity (a), which represents the absorption solution (1 Micro Gram.ml $^{-1}$) in a cell that optical path length (11 cm). It is one of the important things that can know the sensitivity of the method.

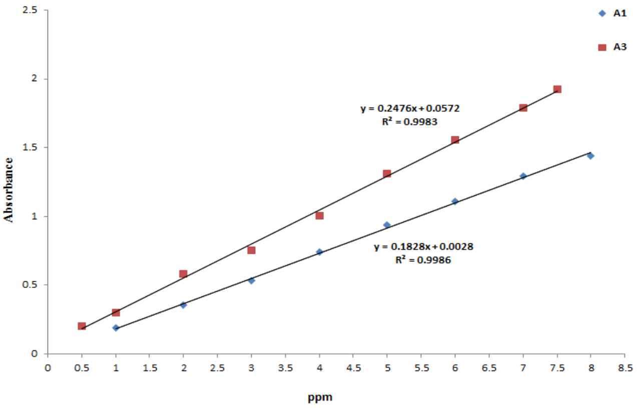


Fig (8). Calibration Curve to complexes between Ni(II) and dyes A_1 and A_3

Table (3). Results which obtained from Beer's Law

Complexes	λ max nm	The maximum applicability of Beer Law ppm	ε x 10^{-4} L.mol^{-1}.cm^{-1}	a ml.g^{-1}.cm^{-1}	S ×10^{-3} µg.cm^{-2}	r	S.D	D.L µg. ml^{-1}
A_1+Ni^{+2}	510	01-Aug	1.828	0.3114	3.2113	0.9986	0.0044	0.074
A_3+Ni^{+2}	500	0.5-7.5	2.476	0.4218	2.3701	0.9983	0.0053	0.087

A. *Formation Constant of Complexes*

In this method are used symmetric solutions in calculation of formation constant to complexes, where is prepared two series of solutions with a fixed concentration from Ni(II) (C_{1M} ‘ C_{2M}) so that it is C_{1M} greater than C_{2M} at a variable concentrations of ligand in each series of C_{1L} and C_{2L}. From the relationship between the absorption values for solutions to each series and the concentration of variable ligand in these solutions and from figures (9), (10), (11) and (12) can determine formation constant and concentration of free ligand. Table (4) shows the concentration of symmetric solutions C_{1L} and C_{2L} at different absorption values to complexes.

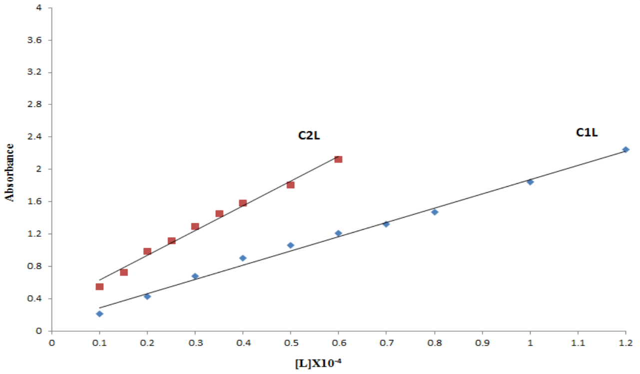


Fig (10). Half Value of formation function method to calculate formation constant for complex of Ni (II) with A_3

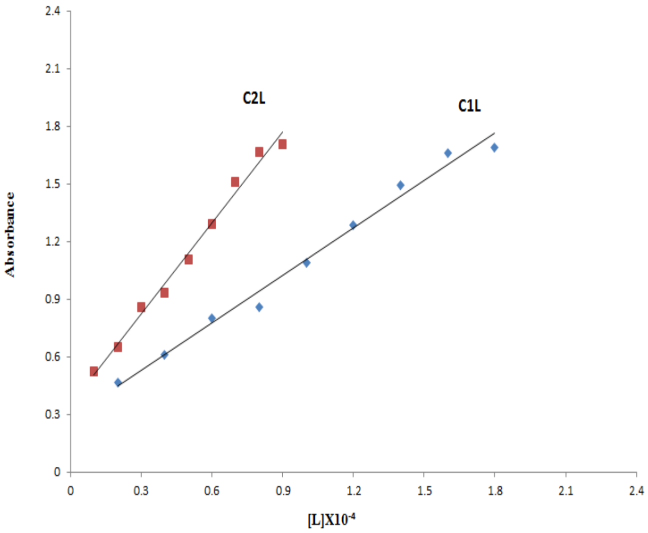


Fig (9). Half Value of formation function method to calculate formation constant for complex of Ni (II) with A_1

Table (4). The concentration of symmetric solutions C_{1L} and C_{2L} at different absorption values to complexes.

Diluted Series C_2M = (0.5x10^{-4}M)		Concentration of Diluted Series (10^{-4}M)	Concentrated Series C_2M = (1x10^{-4}M)		Concentration of Concentrated Series (10^{-4}M)
A_3	A_1		A_3	A_1	
0.216	0.524	0.1	0.285	0.465	0.2
0.516	0.651	0.2	0.580	0.614	0.4
0.837	0.861	0.3	0.85	0.8	0.6
1.123	0.932	0.4	1.107	0.86	0.8
1.435	1.109	0.5	1.353	1.09	1
1.741	1.294	0.6	1.571	1.286	1.2
1.945	1.509	0.7	1.733	1.497	1.4
2.29	1.670	0.8	1.883	1.661	1.6
2.54	1.71	0.9	2.009	1.693	1.8

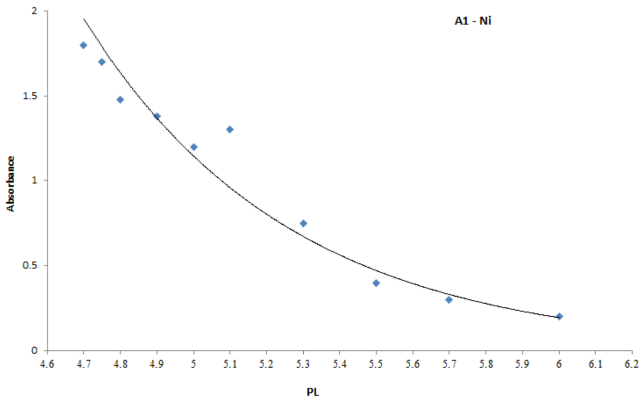


Fig (11). Method of symmetric solutions in calculation of stability constant to complex of Ni (II) with A_1 dye

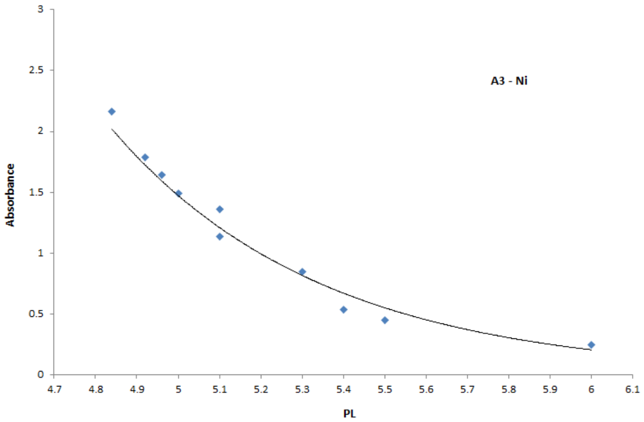


Fig (12). Method of symmetric solutions in calculation of stability constant to complex of Ni (II) with A_3 dye

B. *Half Value of Formation Function*

From Figures (9) and (10) can calculate formation constant of complexes of Ni(II) with dyes A_1 and A_3 [L] and can calculate $\log K_1$ and $\log K_2$, respectively as following:

$$\text{at } \tilde{n} = 0.5 \qquad pL = \log k_1$$

$$\text{at } \tilde{n} = 1.5 \qquad pL = \log k_2$$

$$\log \beta_1 = \log k_1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$\log \beta_2 = \log k_1 + \log k_2 \ldots\ldots\ldots\ldots (2)$$

Table (5) was showed values of $\log \beta_1$ and $\log \beta_2$ to complexes of Ni(II) with dyes A_1 and A_3.

Table (5). $\log \beta_1$ and $\log \beta_2$ to complexes of Ni(II) with dyes A_1 and A_3

A_3-Ni	A_1-Ni	Formation constant
5.6	5.55	$\log \beta_1$
10.68	10.43	$\log \beta_2$

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