Using Sulfadiazine Derivatives as a New Azodyes Reagents for the Complexation and Determination of Aluminum

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Abstract:

This study involves the study of the complexation of three azodyes sulfadiazine derivatives, with aluminum. The characterizations of complexes were studied, which confirming of forming stable azo dyes complexes. The formation and stabilization of these complexes were studied by the optimum conditions, like time effect, pH effect at different values of pH (2-12) and sequence of additions. The stoichiometry was found that the aluminium complexes form 1:2 (M:L) at pH value of 12. The molar absorptivity coefficients, sensitivity and obeys of Beer's law were established .The interferences of others ions were also studied. The stability (formation) constants of the complexes were determined by use of corresponding solutions method by aid of half-height method. This method was found of good selectivity and high sensitivity for the determination of aluminum ions.

Key Words: Azodyes complexes, stability constants, spectral studies, corresponding solution method, stoichiometry

Introduction

Aluminum occurs in solution in the 3+ oxidation state .Between pH 4 & 9, the hydroxide is precipitated. Above pH 9, it is converted into the soluble tetrahydroxoaluminate anion (Marczenko, 1976). The aluminium is important for manufacturing antiacid drugs ., as inhibiters for corrosion [Hart ,2011 ; Abdallah *et al*.,2008], some of azo dyes were used as inhibiters and analytical reagent specially for aluminium (Jassim, 2007) Al-Juaid, 2007] and in the medicine field [Mkpenie *et al*.,2008 ; Baroliya *et al*.,2011].The azo reagents are used as analytical reagents for the determination of aluminium ion such as ,Stilbazo is an important azo reagent for aluminium ,of molar absorptivity coefficient of complex is 1.8 x 10^4 $l.mol^{-1}.cm^{-1}$ at 496 nm (Marczenko, 1976). A number of other azo dyes have been reviewed as spectrophotometric reagents for aluminium (e.g. Aluminon, Arsenazo, Alizarine S, Chromotrope 2C, SPANNS, Calcichrome, Stilbazo-chrome, Stilbazogoll I, Calmagite. Sulphochlorophenol S and Chlorocya-noformazan (Marczenko, 1976). Until recently, aluminon was an important colorimetric reagent for aluminium (Lurie, 1975). And also reviewed as analytical reagent for specrophoto-metric determination of aluminium like PAN,5-Sulpho-4-diethylamino-2,2-dihydroxyazobenzen, (E)-5-((4-hydroxyphenyl)diazenyl)quinolin-8-hudroxyquinoline and Eriochrom-Black3-hyrroxy-4-((8-hydroxynaphthalen-2-yl)diazenyl)-7-nitronaphthalene-1-sulfonate [Lurie,1975].5- (p-Hydroxyphenylazo)-8- hydroxyquninoline is also a

good azo dye reagent for the determination of aluminium , of molar absorptivity coefficient of the aluminium complex is 2780 $l.mol^{-1}.cm^{-1}$ at 390 nm. at suitable pH value of in the range of 6.5-7.5 [Ali ; Issa,1994]. THSA (2,3,4,6-tetrahydroxy -3- sulfoazo (Tufan *et*

al.,2009) and Sodium (E)-2-hydroxy-5-((4-nitrophenyl)diazenyl)benzonate (Seleim *et al.,* 2009) were also used for the determination of aluminium.

The present work involves the spectrophotometric studies of complexation of sulfadiazine derivatives (sulfadizine, sulfamerazine and sulfmethazine) azo dyes (Ali and Alyousife, 2013) with aluminium (III). The studies include, optimum conditions for forming the stable complexes such as**,** time effect, pH effect at different values, sequence of additions, interferences of others ions and the stoichiometry. The molar absorptivity coefficients, sensitivity and obeys of Beer's law were established. The stability (formation) constants of the complexes were determined by use of corresponding solutions method by aid of half-height method. The aims of this work constructing on determination of aluminum ions, by using of sulfadiazine derivatives.

Experimental:

Distilled water and all the reagents and solvents were of reagent-grad quality. Melting point were determined on melting point apparatus (Bunchi B190K). UV & Vis. absorption were recorded by using LKB (Biochrom ultra space II-4050 UV/Vis.) spectrophotometer .The pH measurements were made with pH-Meter (H. Jurgons Co. Bremen,L.Puls Munchen15) **.**The pure chemical drugs (sulfadizine,sulfamerazine and sulfmethazine) were of highest purity from Merck.

Solutions

- A stock solution of (1 x 10^{-3} M) of each dye F_1, F_2 and F_3 (Scheme 1) were prepared by dissolving an accurately weighed amount of the compounds in the required volume of ethanol, more dilute solution were obtained by accurate dilution.

- A stock solution of (1 x 10^{-3} M) of $Al(NO_3)_3.9H_2O$ was prepared by dissolving 0.0938 g. in 250 ml of dil. Water then, more dilute solution were obtained by accurate dilution.

- A stock solutions of (1 x 10^{-3} M) on nitrate salts of interfering metals for interferences study

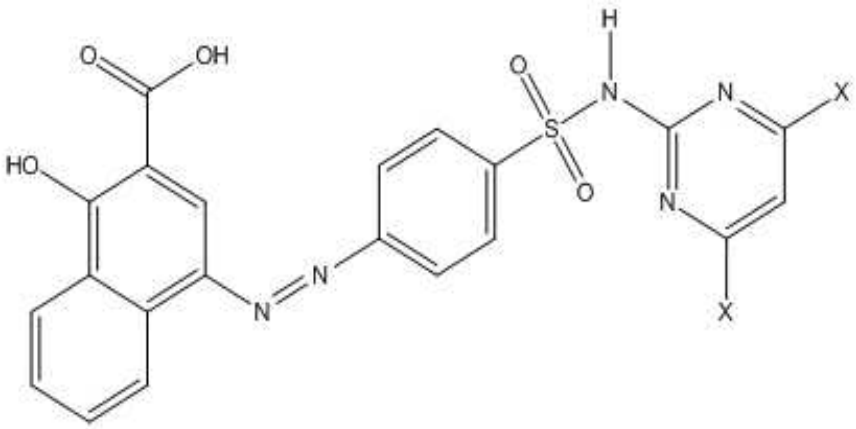
- Universal (pH of 2-12) and Acetate (pH of 1-2) buffer solutions [Dean,1999] were prepared .

Procedure

The general procedure for the complex formation and other studies include , the measuring of the absorbance of suitable concentrations of each aluminum solution and dyes solution together in the range of wavelength (350-600 nm), using the suitable blank solution.

Results and Discussion

The general chemical structure of dyes are:



X = H,H for F_1 , X= H,CH_3 for F_2 and X= CH_3,CH_3 for F_3

Scheme 1: molecular structure of dyes of F_1,F_2 and F_3.

The absorption spectra of the complexes of azodyes (F_1, F_2 and F_3) with aluminum were recorded within wavelength range 360-600 nm.**Optimum Conditions for Complexes Formation**

- pH effect

The electronic spectra of azodyes (F_1, F_2 and F_3) and their complexes with aluminum were studied within wavelength 360-600 nm. at different pH values 2-12,using universal buffer solutions (Figs. 1-3). It was found that the complexes were formed at alkaline

medium (more than pH 10) especially of pH 12 ,which gives more intense band (e.g. more stability of complex formation). Because of formed anionic form that which is east to interact with aluminium ion .From Figs. 1,2 and 3 ,It was found a large red-shift between λ_{max} of dyes and of their complexes in the range of 120 -130 nm. , that is due to the less energy $\pi \rightarrow \pi^*$ transition of the complex formed compared that energy of ligand , becausr of rigidity of the formed complex that is a good proof of formation of stable complexes .

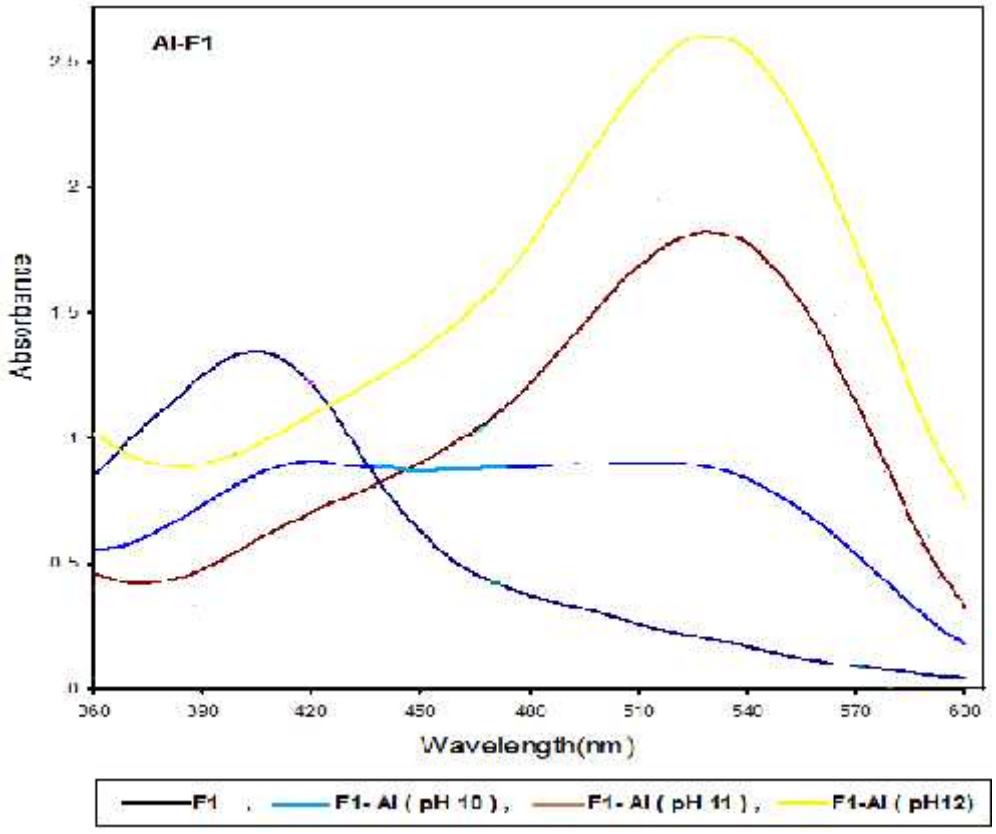


Fig. (1): Absorption spectra of Al-F_1 complex at pH (10-12)

[Dye] = [Al^{+3}]=4x10^{-5}M

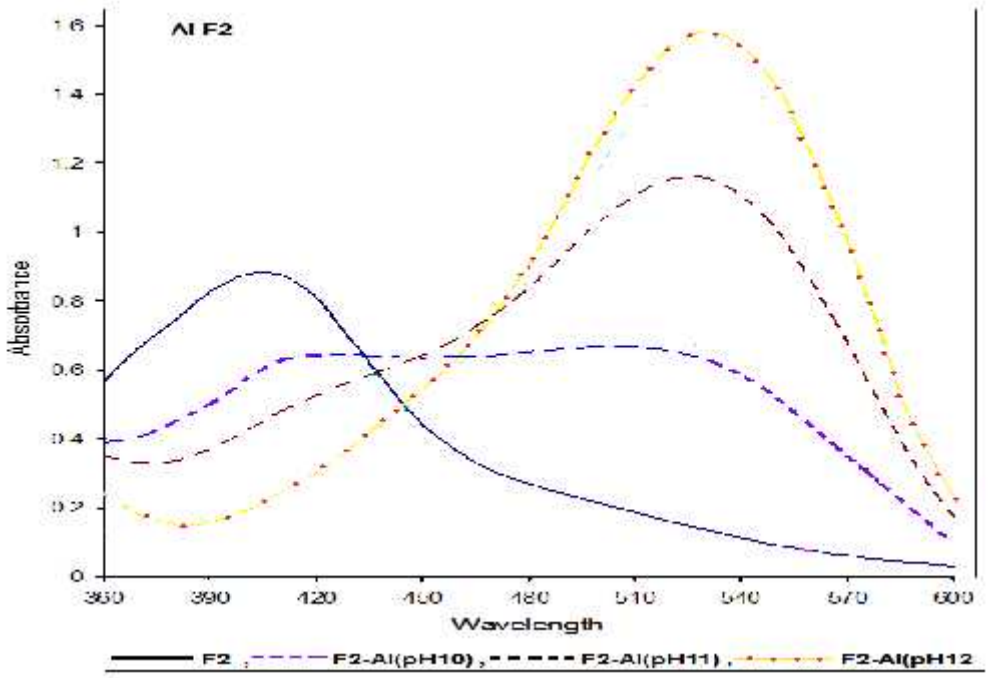


Fig. (2): Absorption spectra of Al-F_2 complex at pH (10-12)

[Dye] = $[Al^{+3}]=4x10^{-5}M$

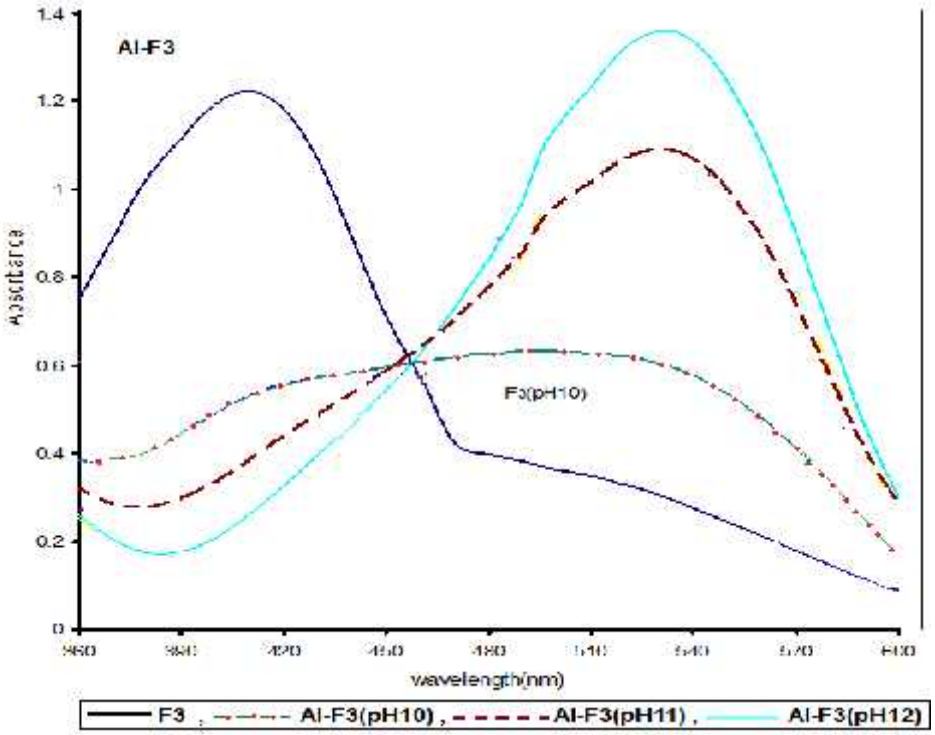


Fig. (3): Absorption spectra of Al-F_3 complex at pH (10-12)

[Dye] = $[Al^{+3}]=4x10^{-5}M$

-Time effect

It was found from Fig.-4, the absorbance of the aluminum complexes at λ_{max} vs. time. All absorbances of azodyes complexes be constant with time from beginning to the overnight. That means these complexes of high stability .

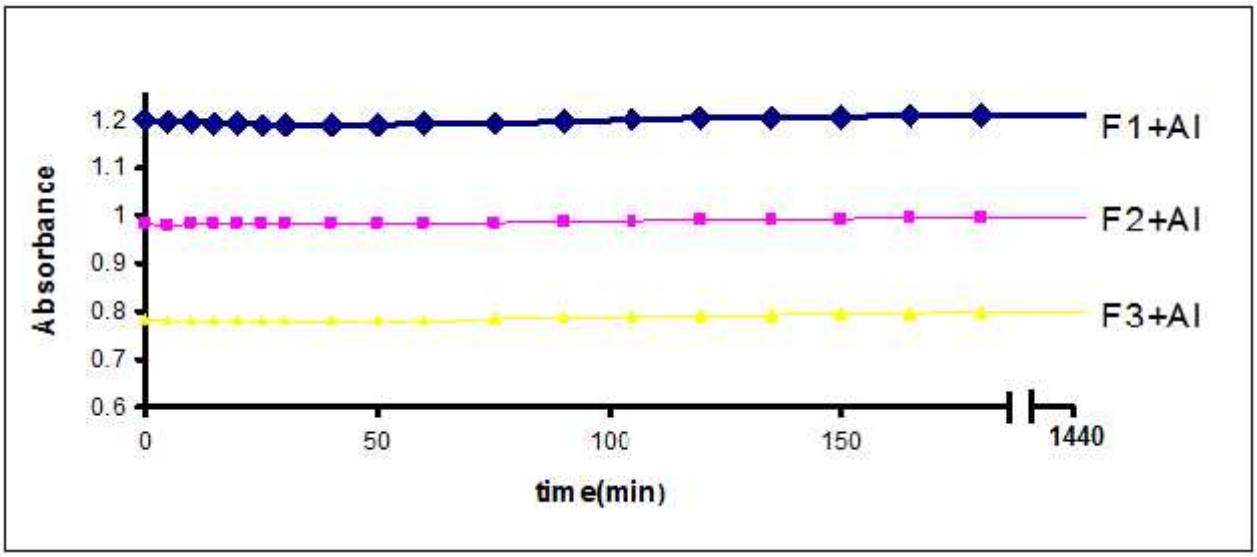


Fig.-4 : Time effect on λ_{max} of Al-azodyes complexes, [Dye] = $[Al^{+3}]$=4x10^{-5}M

- Sequence of additions

From table-1 was found that the first two sequence (Dye + Metal + Buffer and Dye + Buffer + Metal) are the propel sequence (higher absorbance). The last sequence is not preferred, because of less absorbance, this because of the precipitation of aluminum in alkaline medium (pH 12) before of adding the dye.

Table-1 : The sequence of addition, for forming the aluminum complexes

Sequence of addition	**Absorbance**		
	F_1+Al^{+3} λ_{max}=540 nm.	**F_2+Al^{3+} λ_{max}=540 nm.**	**F_3+Al^{3+} λ_{max}=550 nm.**
Dye + Metal + Buffer	0.860	1.420	0.955
Dye + Buffer + Metal	0.850	1.426	1.018
Metal + Buffer + Dye	0.777	1.000	0.761

[Dye] = $[Al^{+3}]=4x10^{-5}M$

- Interference effect

A systematic study of the foreign ion (at same optimum condition) led to the conclusion that the presence of the following ions in 1-fold excess relative to aluminium ion don't interfere : Li^{+}، Na^{+}، K^{+}، Ag^{+}، Mg^{+2}، Mn^{+2}، Co^{+2}، Ni^{+2}، Zn^{+2}، Cd^{+2}، Ba^{+2}، Hg^{+2}، Pb^{+2}، Ca^{+2}، La^{+3}، Zr^{+4}، Cl^{-}، NO_3^{-}، $SO_4^{=}$ and PO_4^{-3}.On other hand, the following ions will interfere at 5-fold and 10-fold: Ag^{+}، Hg^{+2}، Pb^{+2}، $Zn^{+2}$and Ni^{+2}. But the following ions will interfere in all concentrations (1,5 & 10-fold) Cu^{+2}، Sr^{+2}، Cr^{+3}، UO^{+2}، $EDTA.Na_2.2H_2O$ and VO^{+2} .

The composition of the complexes(stoichiometry)

The stoichiometry of the aluminum was determined by using of continuous variation method (Job method). In this method the sum of the molar concentrations of aluminum and azodye is kept constant as their ratio is varied. Then the absorbance of solutions were measured at λ_{max} of each complex. The abscissa of the

extrapolated peak (Absorbance vs. mole fraction of aluminum in its complex peak) will corresponding to the ratio present in the complex which found to be 0.5 and 0.33 ,that means 1:1 and 1:2 complexes respectively (Fig. 5).

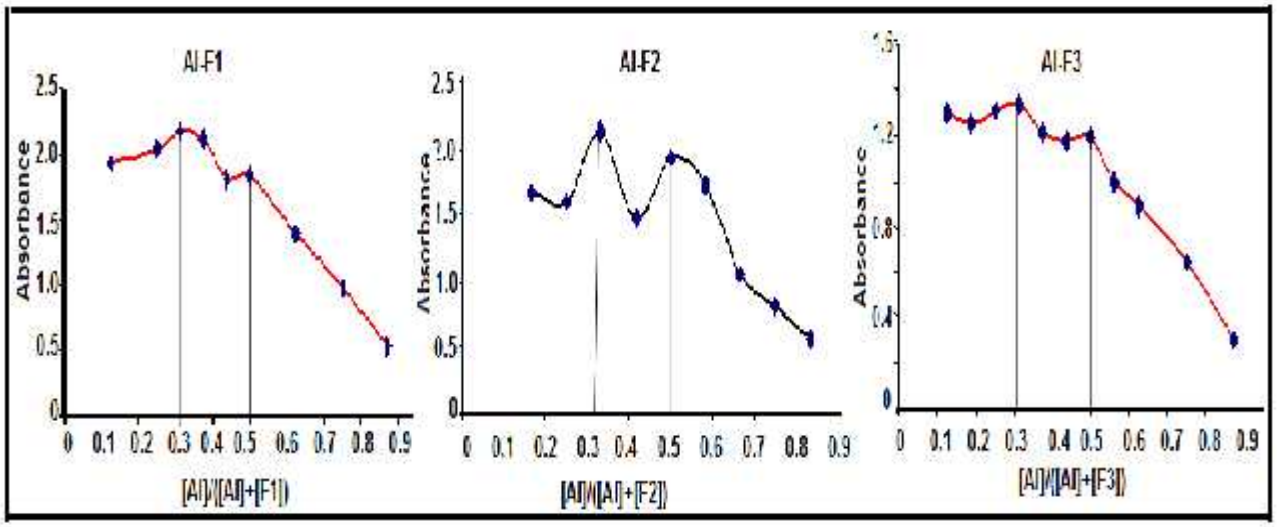


Fig.-5 : The composition of the complexes, continuous variation method

Linearity and sensitivity

Beer's law was obeyed to the aluminum-azodyes complexes under investigation for the determination of aluminum. A linear calibration curves through the origin were obtained at λ_{max} of each complex. Better results were obtained by applying the Optimum Blank Compensation technique (Issa, 1972), i.e. using the amount of the unreacted (uncomplexed) azodye reagent as the blank solution from knowledge of the stoichiometry of complexes. Table-2 shows that high sensitivity, which is represented by the values of specific absorptivity (a) (a = ε/(1000 x At.Wt.)) , molar absorptivity coefficient (ε) and sensitivity index (S) (S = 10^{-3} / a) [1]of the complexes. High linearity of Beer's law which represented by correlation coefficient (r) that nearly to the one.

Table 2: Results obtained from Beer's law

Validity of Beer's law up to (ppm)	**r**	**S $\times 10^{-3}$ $\mu g.cm^{-2}$**	**a $ml.g^{-1}.cm^{-1}$**	**$\varepsilon \times 10^4$ $L.mol^{-1}.cm^{-1}$**	**Complexes**
2.15	0.9976	1	1	2.7	**F_1+Al^{+3}**
2.15	0.9997	0.77	1.296	3.5	**F_2+Al^{+3}**
5.1	0.9986	2.5	0.39	1.05	**F_3+Al^{+3}**

The precision and statistical treatments

The high precision that represented by standard deviations (S.D*) of present method is compared with recommended method (Marczenko, 1976), the F-value at confidence level of 95% is 5.05 (from F-value table).This value is much than that calculated (Table 3), that means the present method is very suitable for calculation of aluminum

.

Table-3 : The precision and Statistical treatments

F-value	Recommended method		Present method			Complexes
	variance	S.D	Variance *	D.L	S.D*	
0.97	$0.86X10^{-4}$	0.0093	$0.83X10^{-4}$	0.022	0.0091	**F1+Al^{+3}**
0.081	$0.86X10^{-4}$	0.0093	$0.07X10^{-4}$	0.0093	0.0027	**F2+Al^{+3}**
1.97	$0.86X10^{-4}$	0.0093	$1.7X10^{-4}$	0.019	0.0131	**F3+Al^{+3}**

Where Variance = $(S.D)^2$, F-value = Variance* / Variance and D.L is detection limit

Stability constants of complexes

By aid of the corresponding solutions method (Irrving; Meller, 1955), the stability (formation) constants of the complexes of aluminium with azodyes ligands were calculated, using half-value method (Beak, 1970). This requires two series of solutions of total metal ion concentrations C_{1M} (called concentrated series) and C_{2M} (called diluted series),where $C_{1M} > C_{2M}$ and varying ligand concentrations C_{1L} and C_{2L} .The absorbance of two series were measured at λ_{max}. The absorbance of diluted series was multiplied by factor (C_{1M}/C_{2M}). The corresponding solutions are those which have the same absorbance at different ligand concentrations. From the absorbance-C_L plot (Fig. 6), many pairs of C_{1L} and C_{2L} consequently, **ñ** (complex formation function) and **[L]** (free ligand concentration) can be determined (Table 4), where: **ñ** = (C_{1L}-C_{2L})/(C_{1M}-C_{2M}) and **[L]** = (C_{1M} x C_{2L} – C_{2M} x C_{1L}) /(C_{1M} – C_{2M})

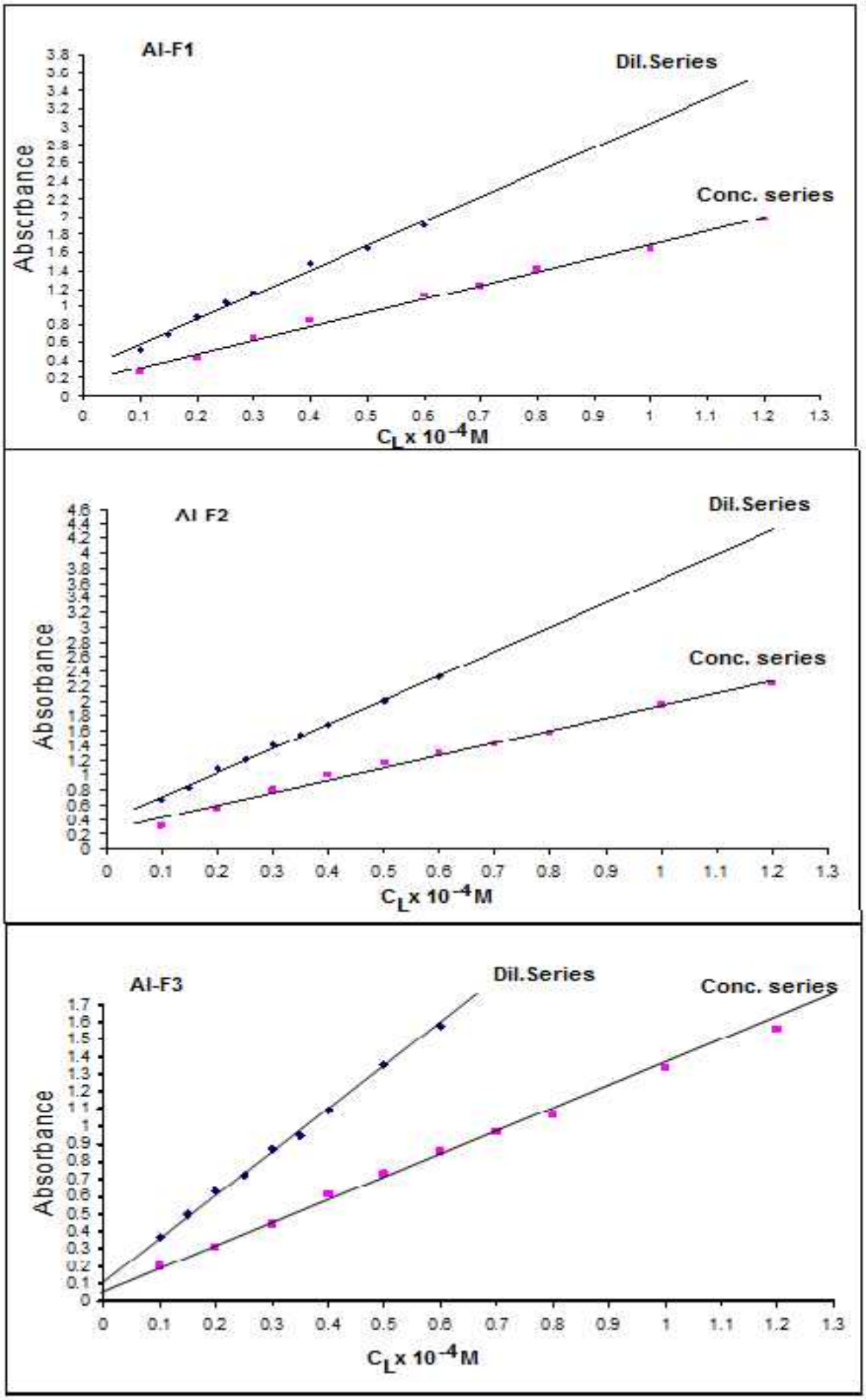


Fig. 6: Absorbance-C_L curve of the Al-azodye complexes

Table 4: C_{1L} , C_{2L} , ñ and pL values (pL = - log [L]), C_{1M} =1x10^{-5} M & C_{2M}=0.5x10^{-5} M

Abs. at λ_{max}	**Al- F_1**				**Al-F_2**				**Al-F_3**			
	C_{1L} x 10^{-4} M	**C_{2L} x 10^{-4} M**	**ñ**	**pL**	**C_{1L} x 10^{-4} M**	**C_{2L} x 10^{-4} M**	**ñ**	**pL**	**C_{1L} x 10^{-4} M**	**C_{2L} x 10^{-4} M**	**ñ**	**pL**
0.2	----	-----	-----	-----	-----	-----	-----	-----	0.1	0.04	0.30	6.70
0.3	0.080	0.030	0.25	6.69	0.06	0.02	0.20	6.69	0.19	0.08	0.55	6.52
0.4	0.150	0.060	0.45	6.52	0.13	0.05	0.40	6.52	0.28	0.12	0.80	6.40
0.5	0.210	0.085	0.63	6.39	0.18	0.07	0.55	6.39	0.35	0.15	1.00	6.30
0.6	0.280	0.115	0.83	6.3	0.24	0.095	0.73	6.30	0.45	0.20	1.28	6.30
0.7	0.355	0.150	1.03	6.25	0.29	0.115	0.88	6.22	0.52	0.23	1.45	6.22
0.8	0.410	0.175	1.18	6.22	0.35	0.14	1.03	6.18	0.59	0.26	1.65	6.22
0.9	0.485	0.210	1.38	6.18	0.41	0.17	1.20	6.15	0.68	0.3	1.90	6.18
1.0	0.560	0.245	1.58	6.15	0.47	0.195	1.38	6.09	0.77	0.34	2.13	6.15
1.1	0.625	0.275	1.75	6.12	0.53	0.22	1.53	6.07	0.84	0.38	2.33	6.15
1.2	0.680	0.300	1.90	6.09	0.59	0.25	1.70	6.04	0.92	0.41	2.53	6.09
1.3	0.760	0.335	2.13	6.04	0.63	0.27	1.80	6.04	0.98	0.44	2.70	6.04

0.5 gives **log K_1** and **ñ = 1.5** gives **log K_2** ,log β_1= log K_1 and log β_2 = log K_1 + logK_2

By using the half- height value method **log β_1** and **log β_2** were obtained from a plot of **ñ** against **pL** (Fig. 7). When **ñ =**

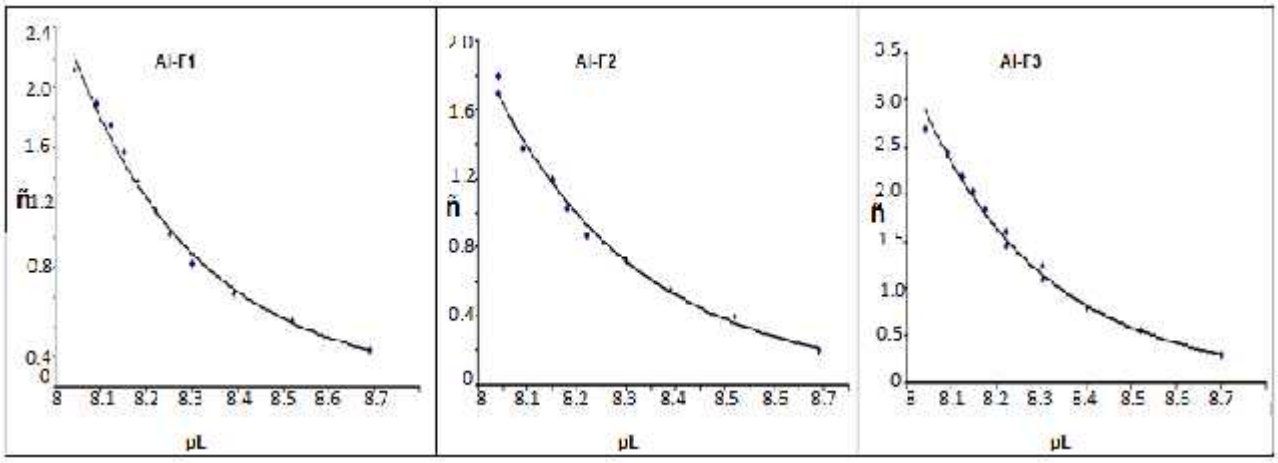


Fig. 7: ñ – pL curve for determination of log K_1 & log K_2 for aluminium complexes

From ñ – pL curve (Fig.-7) and log β_1 and log β_2 values were calculated (Table-5)

Table- : log β_1 and log β_2 values

	VALUE OF STABILITY CONSTANTS OF ALUMINIUM COMPLEXES		
	Al-F1	**Al-F2**	**Al-F3**
Log β_1	5.48	5.41	5.55
Log β_2	10.64	10.48	10.80

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استخدام مشتقات السلفادايزين ككواشف صبغية ازويه جديدة في تكوين المعقدات وتقدير الالمنيوم

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الملخص

شملت هذه الدراسه لعملية تعقيدية لثلاث من مشتقات السلفادايزين الازويه مه الالمنيوم .ودرست سلوكية المعقدات مما تؤكد تكون معقدات ازويه مستقره . ودرست الظروف المثلى لتكوين هذه المقدات مثل تأثير الزمن وتاثير الداله الحامضيه عند قيم مخلفة من الاس الهيدروجيني (2-12) و تاثير تعاقبات الاضافه . ووجد ان التركيب الجزيئي للمعقدات 1 : 2 (فلز : ليكند) عند اس هيدروجيني 12 . وتم تعيين معامل الامتصاص المولاري والامتصاصيه والحساسية ومدى انطباق قانو بير . ودرست تأثير المتداخلات من الايونات الدخيله . وحسب ثوابن الاستقراريه (التكوين) باستخدام طريقة المحاليل المتناظره مستخدمين فيها طريقة نصف الارتفاع.