Spectrophotometric Determination of Silver by New Azodyes Deriven From 2-Thiobarbituric Acid Partll: Silver Complexes

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Abstract:

This study describe the use of new azodyes reagents 5-(2,3- dihydro-1,4-phathalezindion- azo) -2-thiobarbituric acid (L_1) and 5-(2-thiobarbituric acid azo)-phenyl-4-acetic acid (L_2) as sensitive and selective analytical reagents for the determination of Ag(I) spectrophotometrically. L_1 and L_2 react with Ag^+ at pH (9 and 10) respectively
to form colored complexes of 1 :2 stoichiometry which show a maximum absorbance of 540 and 425 nm. of molar ratio absorbitivity 0.59 $X10^4$ and 1.63 $X10^4$ $l.mol^{-1}.cm^{-1}$ respectively. fixed optimum conditions were constructed, precision , accuracy, R.S.D.and correlation factors. The Beers law was obeyed up to 25 and 7.56 ppm. respectively.The stability constants of complexes were determined.

Keywords: –*spectrophotometric ,azodyes,2-Thiobarbituric acid,Silver complexes*

Introduction :

Azo compounds are very important class of chemical compounds containing a hetro cyclic moiety which have attracted the attention of many researchers in the recent years [1] .They are highly colored and have been used as dyes and pigments for long years [2] furthermore they have been studied widely because of their excellent thermal and optical properties in applications . Recently azo metal chelate have also attracted increasing attention due to their interesting electronic and geometrical features [3-4].They were used as good reagents for the extraction and spectrophotometric determination of metal ions [5-9]. Many studies used azo dyes as analytical reagents for the spectrophotometric determinatin of sliver [5] , 4-(2-qunolinolazo)phenol [10]at pH (8.1- 11.2) with molar absorbtivity (ε) = 8.3 $x10^4$ $l.mol^{-1}cm^{-1}$, 7-(4-chloro-2-nitrophenylazo)-8-qunolinol [11] at pH (4.0-4.5) with ε = 3.2 $x10^4$ $l.mol^{-1}cm^{-1}$, 3-(4-amino-1,2,4-triazo)-4-hydroxy-nephthaline-1-sodium sulphate [12] ,at pH 9.11 and also with some pyridyl derivativs like 4-(5-chloropyridylazo)-3-phenelenediamine [13] with ε = $1.7x10^4$ $l.mol^{-1}$ cm^{-1}. and 4-(3,5-bromo-2-pyridyl -N-ethyl-3-sulphopropyl [14] . This work aims to study the complexsation and spectrophotometric determination of silver ion with new ligands 5-(2,3- dihydro-1,4-phathalezindion- azo) -2-thiobarbituric acid (L_1) and 5-(2-thiobarbituric acid azo)-phenyl-4-acetic acid (L_2) . The overall stability constants of complexes were also determined by using the corresponding solutions method [15] .

Experimental :

Double distilled water and all chemicals of highest purity were used in this work which supplied by Fluka and BDH

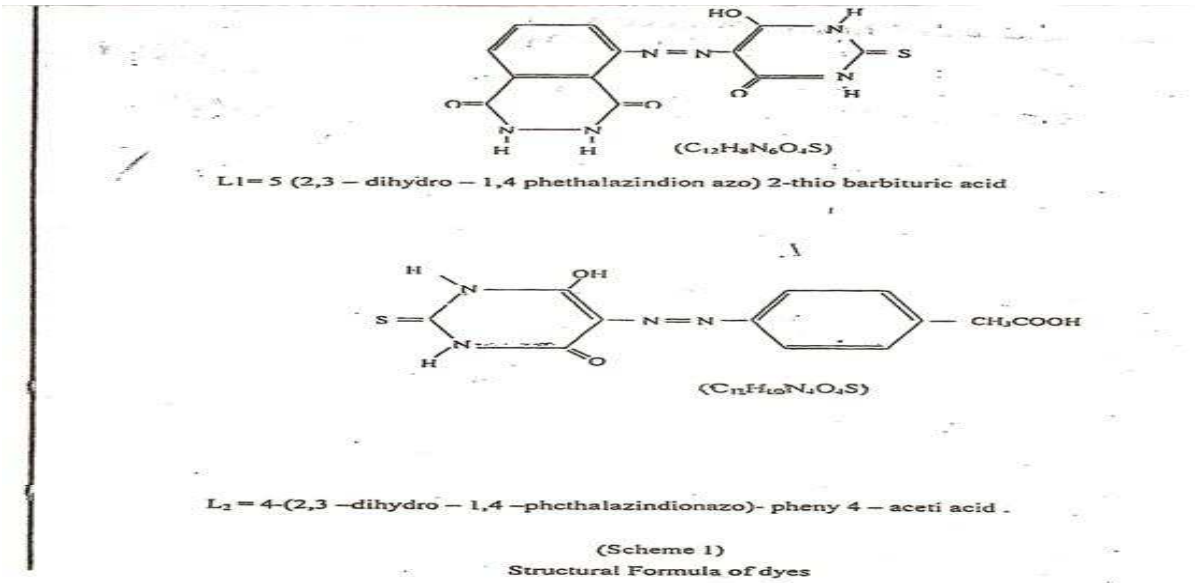
Apparatus and Metrials :

Visible absorption spectra were recoreded by using LKB(Biochrom ultra space II-4050 UV./V.) spectrophotometer, IR spectra were recorded by using of IR – spectrophotometer (Shimadzw 470), pH measurements were made with pH-Meter (H.Jurgons Co. Bremen, L. Pusl Munchen 15)

Synthesis of Azodyes Reagents :

The azodyes reagents L_1 (M.Wt.= 332) and L_2 (M.Wt.=306) were prepared and

characterized as mentioned in part (I) [16] . According to the data obtained from IR spectra and C.H.N elemental analysis , schem 1 shwos the chemical structures of L1 and L2 .



Solutions :

- A stock standard silver solution (1 x 10^{-3}M) was prepared by dissolving 0.017 g. of silver nitrate , the volum was completed to 100 ml with distled . water and the solution was standardized by recomended procedure [17] .
- Solutions of azodyes reageants L_1 and L_2 (1 x 10^{-3} M) were prepared by disolving (0.0332 g . and 0.0306 g. respevtively) and complete the volum to 100 with absolute ethanol .
- Universal buffer solutions [18] of pH range (2-12) were prepared

Procedure :

To get highest absorbance of complexe formed , it is necessary to get optimum conditions of forming such complex , which include , the selection of the suitable wavelenth (λ_{max}) , effect of time , effect of pH values , effect of sequence of additions , stoichiometry and effect of interferences of strange ions.

The general procedure was summerizied by taking (0.05 – 2 ml) of 1 x 10^{-3} M solution of siver ions with (0.05 – 2 ml) of 1 x 10^{-3} M of each azodye reagent L_1 ana L_2 , then the volum was completed to 5 ml with a buffer solution of pH 9 in case of L_1 and with pH 10 in case of L_2 . Then after 15 min. the absorbance of formed complexes Ag-L_1 (C_1) and Ag-L_2 (C_2) were at λ_{max} of 540 nm. and 425nm. Respectively .

Reslts and Discussion:

Absorption Spectra :

The electronic spectra of L_1 and L_2 and their complexes with silver ion, C_1 and C_2 complexesare at max wavelenths were fixed. Fig.(1) shows the absorbance max. of azodyes reagents L_1 and its comples C_1 are (440 & 540nm.) respectively , and for reagent L_2 and its complex C_2 of (450 & 425 nm.) respectively . It is clear that according to the shift that happened in λ_{max} show the stable complexes are formed immeditaly . π-----> π^* transition within the azo group and hetrocyclic moieties,

involving the whole π electronic system of the compound influenced by inter-molcular charge transfere character [19]. I.R. spectra of L_1 and L_2 show the appearance of the bands ν_{O-H} (3350 & 3400 cm^{-1}), ν_{N-H} (3300–3200 cm^{-1}) , $\nu_{C=O}$ (1700 cm-1) and $\nu_{C=S}$ (1210 cm^{-1}) [15], but in their complexes C_1 and C_2,it was found that the disappearance of O-H frencuency (Tabel 1) .

The shift of $\nu_{N=N}$ streching of complexes to relatively lower energy ≈ 10 cm^{-1} compared to that dyes, indicats coordination via the N=N group.

Table (1) : IR spectral properties of dyes [16] and their complexes

Comp.			ν (cm^{-1})			
	OH	C=O	O-C	N=N	C=N	C=S
L_1	3350	1700	1460	1410	1600	1210
C_1	---	1720	1465	1403	1602	1213
L_2	3400	1700	1610	1500	1600	1150
C_2	----	1705	1605	1492	1605	1155

Effect of pH :

The influence of pH value on the absorbance of comlexes C_1 & C_2 was studied at different pH (Fig . 2) by using of buffer solutions (pH 5-12) . It was found that the hightest absorbance at pH 9 and 10 for C_1 and C_2 respectively , becaused of the formation of the anionic form of the reagent , which can easily react with silver ions to form complexes.

Effect of time:

The stability of complexes with time was listed in table (2), from the data obtained it was found that the highest absorbance reached at 15 min. for both complexes,and remains constant up to 2 hrs.and to 24 hrs with respect to C_1 and C_2 respectively

Table (2): Effect of time on the absorbance of two complexes (C1&C2) at λ_{max}

Time (min.)	Absorbance of C_1	Absorbance of C_2
3	0.430	0.466
5	0.438	0.478
10	0.440	0.479
15	0.455	0.483
20	0.458	0.485
30	0.453	0.485
40	0.448	0.485
60	0.442	0.485
120	0.435	0.484
180	0.429	0.485
1440	0.412	0.488
2880	0.408	0.478
4320	0.400	0.470

[Ag] = [L] = 1 X10^{-4} M

Sequence of Eddition :

It is important to study the sequence of the addition of specieses which are : Ag +L + B (buffer) , Ag + B + L and L + B + Ag . It is found that the last one gives more absor- bance for both complexes because of anionic form of ligand due to the action of buffer soulion and easy attact of silver ions .

Composition of the complexes (Stoichiometery) :

The empirical formula of the complexes was evaluated by using continous variation method (Jop method). It was found that both complexes form 1 : 1 and 1 : 2 (M : L) (Fig. 3 for C_1) .

Beer s Law and Sensitivity :

Beer s law was obeyed to the complexes under investigation for the spectrophoto-metric determination of sliver , with linear calibration curves through the origin wereobtained in the range of (0 - 25 ppm) and (0 – 7.56 ppm) for C_1 and C_2 respectively.Better results were obtained by applying the optimum blank compostion technique [20] i.e using the amount of the unreacted ligand as the blank from knowledge of the stoichiometry of complexes .Table (3) shows the high sensitivity,which is represented by the values of specific absorbtivity (a) , the molar absorbtivity coeff. (ε) and sensitivity index (S) for complexes C_1 and C_2. with high precision that represented by the values of standarad deviation (S.D.), and high linearity of Beer s law which represent by the correlation coeff. (r) which is nearly to unity

Table (3) : Data obtained from Beer s Law for the complexes

Complex	a $ml.g^{-1}.cm^{-1}$	ε x10^4 $l.mol^{-1}cm^{-1}$	S $\mu g.cm^{-2}$	S.D	r	DL $\mu g. ml^{-1}$	Beer s obyed ppm.
C_1	0.055	0.594	0.018	0.018	0.997	0.664	0 - 25
C_2	0.151	1.63	0.007	0.131	0.994	0.088	0 - 7.56

DL is the detection limit

Interferences of Foreign Ions :

A systematic suddy of the foreign ions led to the conclusion that the presence of the following ions in 1 , 5 and10- fold excess relative to Ag don't interfere : Na^+, K^+ , Li^+ , NH_4^+, Cu^{2+}, Ca^{2+}, Be^{2+} , Mg^{2+}, Sr^{2+}, Cd^{2+}, Cr^{3+},Ru^{3+},In^{3+} ,Br^-,Cl^-, I^-, F^-, $SO_4^{2-,}$ and CO_3^{2-} .

On the other hand, the following ions should not be present : Ni^{2+}, Fe^{3+}, Nd^{3+}, Cr^{3+} Eu^{3+}, and EDTA

Stability Constants of Complexes :

By the aid of the corresponding solutions method [15] the stability constants of complexes of silver with azodyes ligands were calculated using Half-value [21] method. This method requreds two series of solutions of total metal ion concentrations C_{1M} (concentrated series) and C_{2M} (diluted series) (where $C_{M1} > C_{M2}$) and varying ligand concentrations C_{1L} and C_{2L} , then the diluted series was multiplied by the factor (C_{1M} / C_{2M}) .The corresponding solutions are those which have the same absorbance at different ligand concen trations. From the absorbance - C_L plots (Fig.4 for C_2). Many pairs of C_{1L} and C_{2L}, consequently , **n** (complex formation function) and **[L] (** free ligand concentration) can be determined .

$$n = (C_{1L} - C_{2L}) / (C_{1M} - C_{2M}) \text{ and}$$
$$[L] = (C_{1M} \times C_{2L} - C_{2M} \times C_{1L}) / (C_{1M} - C_{2M})$$

By using the half value method $\log \beta_1$ and $\log \beta_2$ are obtained from a plot of n against pL (Fig. 5 for C_1) , n = 0.5 gives $\log K_1$, n =1.5 gives $\log K_2$. (Table 4) .

$\log \beta_1 = \log K_1$ and $\log \beta_2 = \log K_1 + \log K_2$

Table (4) : The stability constants $\log \beta_1$ and $\log \beta_2$ by use of half value method.

Complex	$\log \beta_1$	$\log \beta_2$
C_1	4.74	8.80
C_2	5.90	10.82

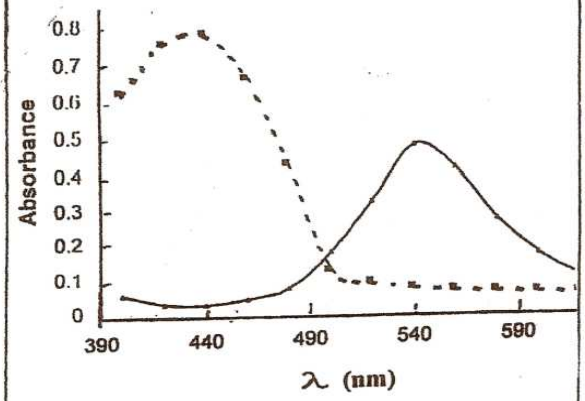


Fig.(1): Electronic spectra of L_1 (—) and C_1 (——) .[Ag]=[L_1]=1x10^{-4}M

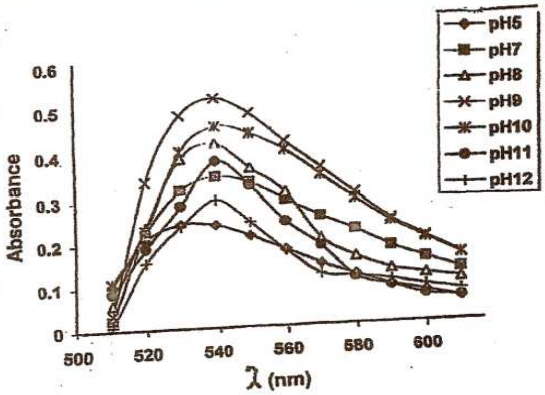


Fig.(2): Electronic spectra of C_1 at diffrent pH Value. [Ag]=[L_1]=1x10^{-4}M and λ_{540} nm.

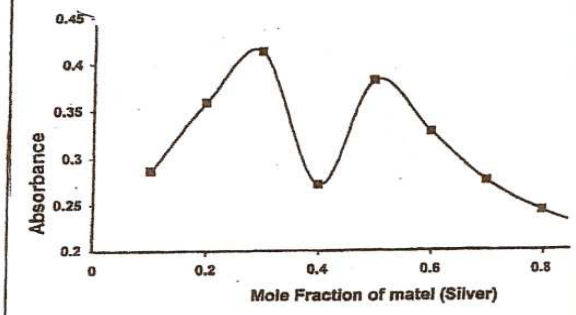


Fig.(3): Continous variation method of C_1 [Ag]=[L_1]=1x10^{-4}M and λ_{540} nm.

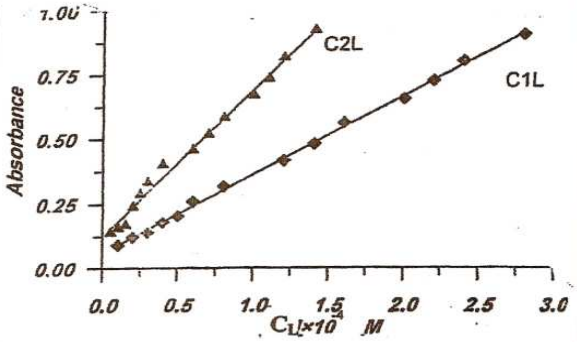
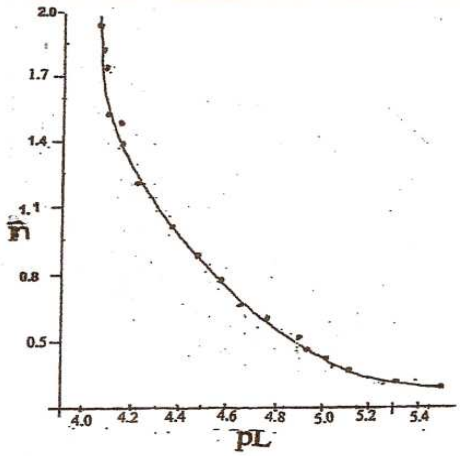


Fig.(4):Absrbance - C_L plot of C_2 at λ_{425} nm.



ig.(5):Half-valu method of C_1 at λ_{540} nm.

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الخلاصة

في هذه الدراسه تم استخدام الصبغتين الازوويتين الجديدتين 5-(2,2-ثنائيهايدرو-1,4-فيثالازينـــدايون ازو)-2-حـــامض الثايوباربيتيوريك (L1) و 5-(2- حامض الثايوباربيتيوريك ازو) -فينيل-4—حامض الاستيك (L2) ككواشف تحليليه ذات حساسيه وانتقائيه للتقدير الطيفي للفضه. حيث L1 وL2 تتحد مك ايون الفضه عند اس هيدروجيني 9 و 10 على التوالي لتكوين معقدين C1 وC2 اللذان يعطيان امتصاص اقصى عند 450 و425 نانوميترعلى التوالي. وتم حـــساب معـــاملي الامتـــصاص المولاري لهما وكانا $0.59\ X10^4$ & $1.63\ X10^4$ لتر.مول$^{-1}$ سم$^{-1}$ على التوالي. وتم تحديد الظروف المثلى لتكـــوين هـــذاين المعقدين والتي تشمل الدقه و التوافق و الانحراف المعياري ومعامل الارتباط . ووجد حدود خضوع قانون بير وكان 25 & 7.56 جزء بالمليون على التوالي وكذالك تم حساب ثوابت الاستقرايه للمعقدين.