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ANALYTICAL STUDIES OF AZODYE 2-(SULFAPYRIDINE AZO)-4,5-DIPHENYL IMIDAZOLE AS REAGENT FOR COMPLEXES FORMATION WITH CADMIUM(II) AND MERCURY (II) IONS

Asaad A. Ali and Montha Kh. H. and Tarek A. Fahad*

Department of Chemistry, College of Education for Pure Science, Basrah University, Iraq.

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***Corresponding Author**
Dr. Tarek A. Fahad
Department of Chemistry, College of Education for Pure Science, Basrah University, Iraq.

ABSTRACT

The yellow azodye ligand 2-(Sulfapyridine azo)-4,5-Diphenyl Imidazole (L) (λ_{max} 440nm.) forms a stable orange color with each cadmium (II) (λ_{max} 490nm.) and mercury (II) (λ_{max} 490nm.), with stoichiometry of both 1:2 (M:L). The complexes were characterized by FT-IR, M.P., visible, molar conductivity and atomic absorption spectroscopic. The suitable pH values for forming complexes are 11 and ethanol respectively. With molar absorptivity coefficients 4.6 and 2.3 x 10^4 l.mole^{-1}.cm^{-1} respectively. The obeyness of Beer's law up to 4.5 ppm of Cd and 2.8 ppm of Hg. The optimum conditions of the formation of complexes were investigated and their stability formation constants were determined by using of corresponding solutions method. The chemical formula of each complex was suggested.

KEYWORDS: Sulfapyridine, Azodyes, Corresponding solutions method, Formation constant, Stoichiometery, Complexes and Spectral studies, Molar conductivity.

INTRODUCTION

Most of azodyes are weak acids or weak bases of very important class of chemical compounds containing a heterocyclic moieties which have attracted the attention of many researchers in recent years. They have high soluble in common solvents and highly colored (from yellow to blue, due to conjugated π system). Several studies have been published on the synthesis and spectral properties of azo dyes.[1-6] This reflects their widely important applications in different field. Most of azodyes have acid – base properties with presence of a fixed isobestic points (which represent the number of equilibriums in such azodye), for this

reason they are used as acid – base indicators.[7,8] New heterocyclic azo dye ligand 2-[1-(2-Hydroxy-5-methyl phenyl)azo]-4,5- diphenyl imidazole (HMAI), was prepared by reacting a diazonium salt solution of 2- amino-4-methyl phenol with 4,5-diphenyl imidazole in alkaline pyridine. The complexes with Cd and Hg were prepared and characterized using available techniques. The analytical data show that the metal to ligand ratio in two complexes is (1:2).[9] Thiazolylazo dyes and their applications in analytical chemistry were reviewed.[10] the pyridylazo and quinolylazo derivatives are suitable as chromogenic reagents, the best being 2-(quinolylazo)-4,5-diphenylimidazole (QAI), which reacts with several metal ions. The copper and mercury complexes of QAI show molar absorptivities of the order of $8x10^4$ $l.mol^{-1}$ cm^{-1}.[11] 2-[2-(5-Bromopyridyl)azol-4,5-dimethylphenol (BrPDMP) and 2-[2-benzothiazolylazo)-5-dimethylaminophenol (BTADAP) have been synthesized and compared, as reagents for cadmium, with the related dyes BrPADAP and BTDMP. They form stable highly colored 2:1 complexes with cadmium, with molar absorptivities (in *o*-xylene solution) of 3.8×10^4 $1.mole^{-1}.cm^{-1}$ at 590 nm. (BrPDMP) and 4.5×10^4 $1.mole^{-1}.cm^{-1}$ at 600 nm (BTADAP).[12] A spectrophotometric method for the determination of micro amounts of cadmium with a new and selective reagent, o-carboxybenzenediazoaminobenzene-p-azo benzene.[13] 2-(4-R-Phenylazo)-4,5-diphenylimidazole (R=H, PAI; = OH, HPAI; = COOH, CPAI) acts as a bidentate chelating ligand to form stable complexes with Cd(II) and Hg(II) ions.[14] The present work represents by formation a stable complexes of azodye 2-(Sulfapyridine azo)-4,5-Diphenyl Imidazole with Cd(II) and Hg(II) with optimum conditions.

EXPERMINTAL

Double distilled water, solvents (for spectral use) and all chemicals of highest purity were used.

Apparatus and materials

Visible absorption spectra were recorded by using PD-303 UV.,V. spectrophotometer, FT-IR-8400S spectrophotometer (Shimadzw) College of science Basrah university, pH-meter (H.Jurgons Co. Beremen, L. Puls Munchen 15), Bunchi B190K for melting point measurement, accurate balance E-Mette Weender (Land Strasse) 94-108, The molar conductivity (**Λ)** measurements were measured by (Germany condi 315i), The complexes were recorded by using and element analysis (C.H.N.), they were carried out by perkin elemer 2400-11 element analysis and AAs measurements by U.K., Pg instruments AA500.

Solutions

- $1x10^{-3}$ M of 2-(Sulfapyridine azo)-4,5-Diphenyl Imidazole (L)
- $1x10^{-3}$ M of the nitrate salts of Cd(II)and Hg(II), and standardized by recommended methods
- pH (1.4 -12) (Universal, Hexamine and acetate buffer solutions).[15]
- 1 x 10^{-2} M stock solutions of nitrate salts of Li^{+}، Na^{+}، K^{+} ، Mg^{2+} ،Mn^{2+},Ag^{+}, Ba^{2+} ،Pb^{2+} ، Ca^{2+} ، Cr^{3+} ، Zr^{4+} ، Ti^{+} ، $Fe^{3+,}$ $VO^{2+,}$$Zn^{2+}$, Sr^{2+}, $La^{3+,}$ EDTA.Na_2.$2H_2O$ and Cl^{-},SO_4^{2-},PO^{3-}.

Procedure

For complex formation, the absorbance of series solutions of 0.001M of azodye and studies ions were measured at wavelength range of 350 – 650 nm. and at for the optimum conditions, interference, determination of formation constants and Beer's law and at λ_{max} also, by using the azodye as blank.

RESULTS AND DISSCUSION

The azodye (L of m.p. 163-165 C) (Fig. 1) was prepared and described by FT- IR, NMR., CHN and Visible spectroscopic. The acid-base properties and ionization and protonation constants were studied at different pH values (2-12), then the solvents effect of different polarities was studied at previous work.[16]

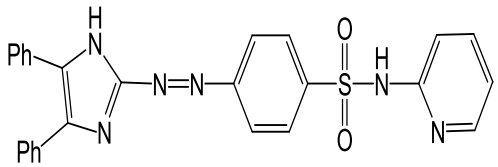

Fig.(1): 2-(Sulfapyridine azo)-4,5-Diphenyl Imidazole (L)($C_{26}H_{20}N_6O_2S$).

The studied ions complexes

The yellow color of azodye (L, λ_{max} 440 nm.) forms a stable orange (μ_{max} 490nm.) and orange (μ_{max} 490nm.) color complexes with divalent cations and cadmium and mercury respectively. The complexes were characterized by measuring of melting point which be increased due to the combination of metal ion with azodye liganad (Table 1). The complex characterized by C.H.N. technique (Table 1), which shows good agreement between calculated and found values.

Table 1: C.H.N., %M and molar conductivity of the ligand complexes.

Formula	Λ ohm^{-1} cm^{2}mol^{-1}	M.P.	% C		% H		% N		% M	
			Cal.	Fou.	Cal.	Fou.	Cal.	Fou.	Cal.	Fou.
$[Cd(L_1)_2(NO_3)_2].6H_2O$	26	>300	47.84	46.90	3.99	4.21	15.03	15.23	8.62	8.68
$Hg(L)_2(NO_3)_2$	28	269	48.58	48.32	3.11	2.97	15.26	15.41	*	*

* AAs dose not used for determination of Hg (volatile element)

IR-Studies

The complexes were also characterized by IR spectra (Fig. 2). It was found there are differences between the spectra of free ligand azodye L and their complexes (L-Cd and L-Hg) spectra. in both spectra there are bands at 3423 cm^{-1} due to stretching vibration for N - H and O-H bonds, that means this bond don't sharing with metal ions. In case of stretching vibration of C=N cm^{-1} showed lower shifts in absorption, the means the possibility of coordination between azodye and metal ion. In case of stretching vibration for N=N (azo group) bond in all complexed metal ions there are clear lower shift in frequency of azo in the range of (10 – 15 cm^{-1}), due to forming coordination bonds between metal ion and azodye.

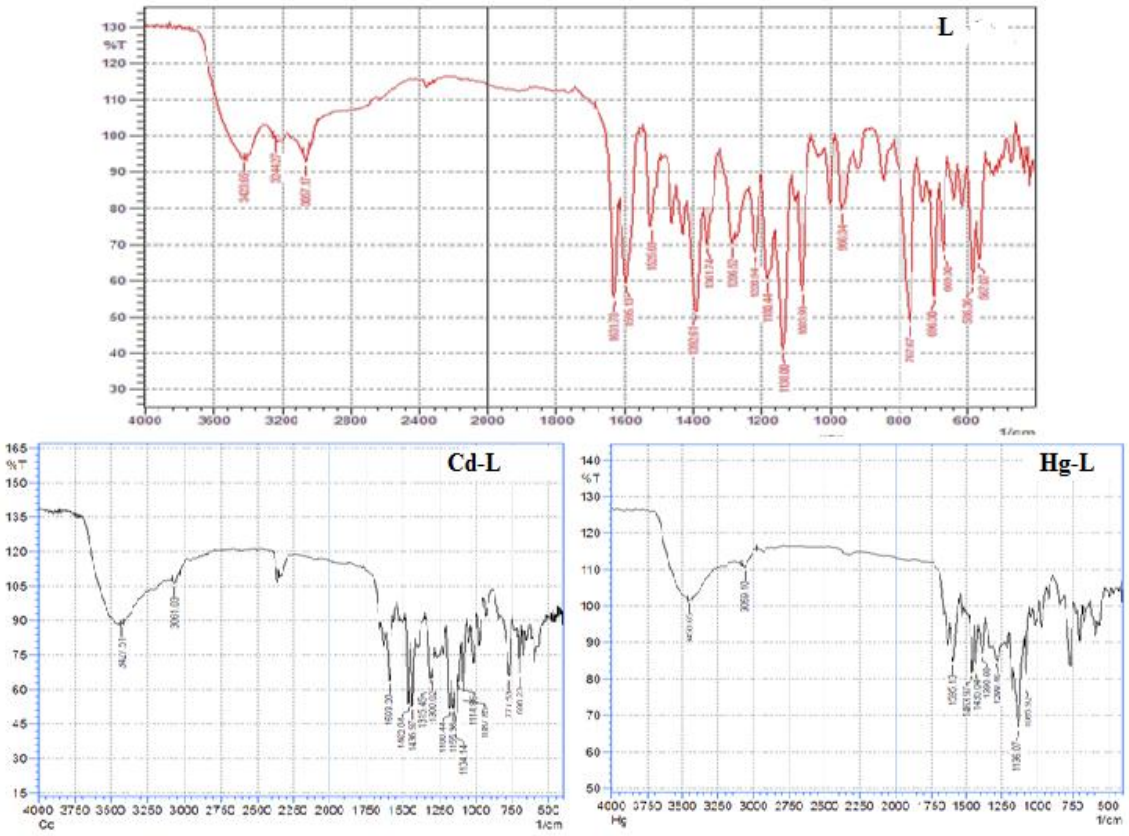

Fig. (2): IR spectrum of azodye L and its complex M-L.

Optimum conditions for forming complex

The important Optimum conditions for forming M-L complexes include.

Effect of time

The stability of complexes with time at λ_{max} was listed in Table.2, from the data obtained it was found that the absorbance of high value and be constant for a long times (over the night 1440 sec.) as shown in (Fig.3). Generally no change in absorbance with time so the complex will be stable.

Table (2): Time effect on the absorbance of M-L complexes.

Time mn.		1	5	10	20	40	60	90	180	1440
A	Cd-L $\lambda_{max\ 500}$	1.143	1.48	1.151	1.156	1.169	1.155	1.142	1.140	1.037
	Hg-L $\lambda_{max\ 500}$	0.810	0.806	0.801	0.792	0.782	0.779	0.771	0.769	0.755

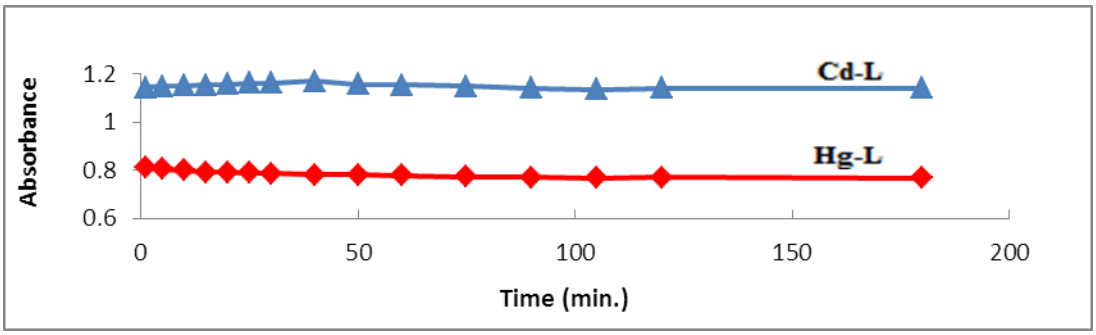

Fig.(3): Time effect on the absorbance of M-L complexes.

pH effect

In the visible region (350 – 650 nm.) the absorbance of a complexes were measured by using universal and acetate buffer solutions of pH range (1.4-12) by using a buffer solution as blank. From Fig.4, it was found that the pH of 11 the best value for giving highest absorbance at $\lambda_{max\ 500}$ and for Cd-L complex ethanol medium at $\lambda_{max\ 500}$ for Hg-L is used.

Kinds of best buffer solution

Two kinds of buffer solutions were used, for knowing the best one which gives highest absorbance. It was found that the universal buffer solution (in case of Cd-L) is the best and gives highest absorbance but in case of Hg-L the best one is ethanol medium as shown in Fig. 5.

Sequence of edition

The study of three probability sequence of additions are listed in Table 3.

Table (3): The different sequence of editions for forming complex.

No.	Sequence of edition	Absorbance	
		Cd-L	Hg-L
1	L + M + pH	1.162	0.820
2	L + pH + M	0.984	0.618
3	M + pH + L	0.98	0.654

[M] = [L] = $4x10^{-5}$ M

So, it was found the sequence L + Cd + pH_{11} and L + Hg + ethanol is the best sequence for Cd and Hg respectively.

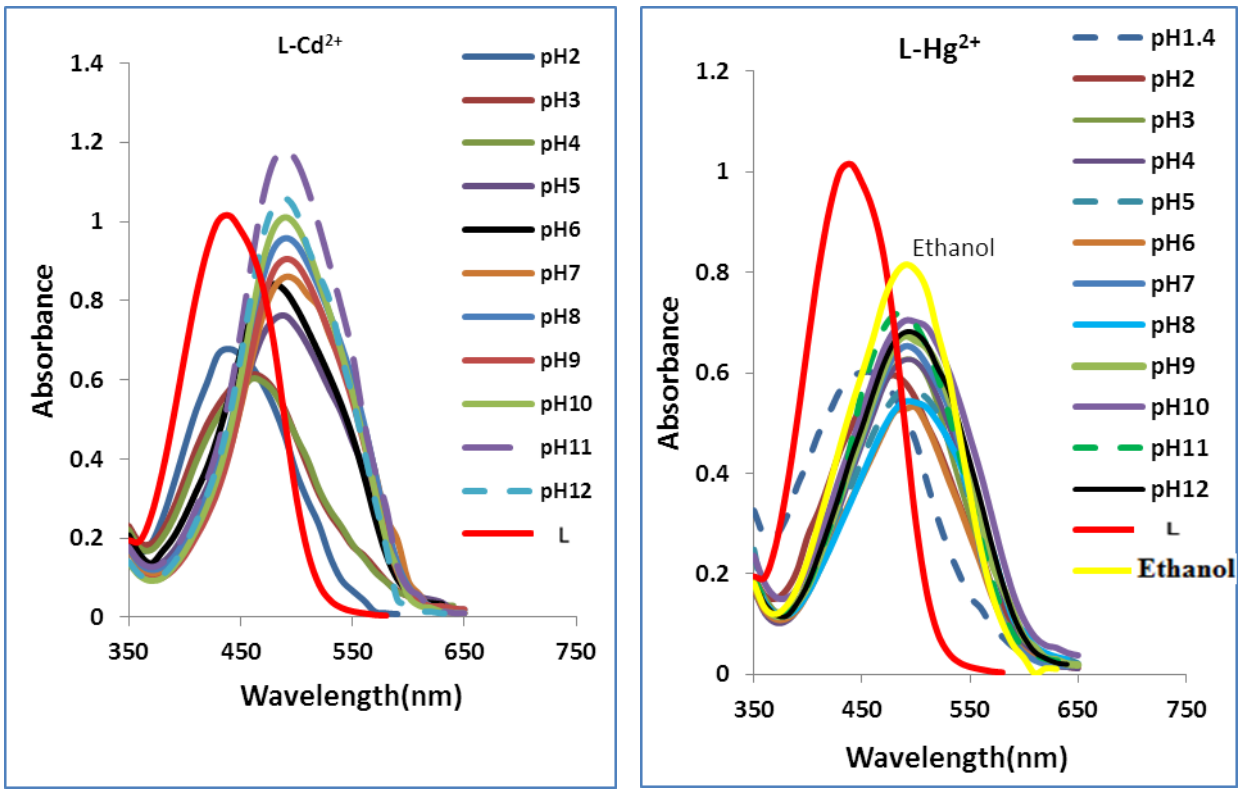

Fig.(4): Spectra of M-L complexes ([M]=[L]= 4 x 10^{-5} M)

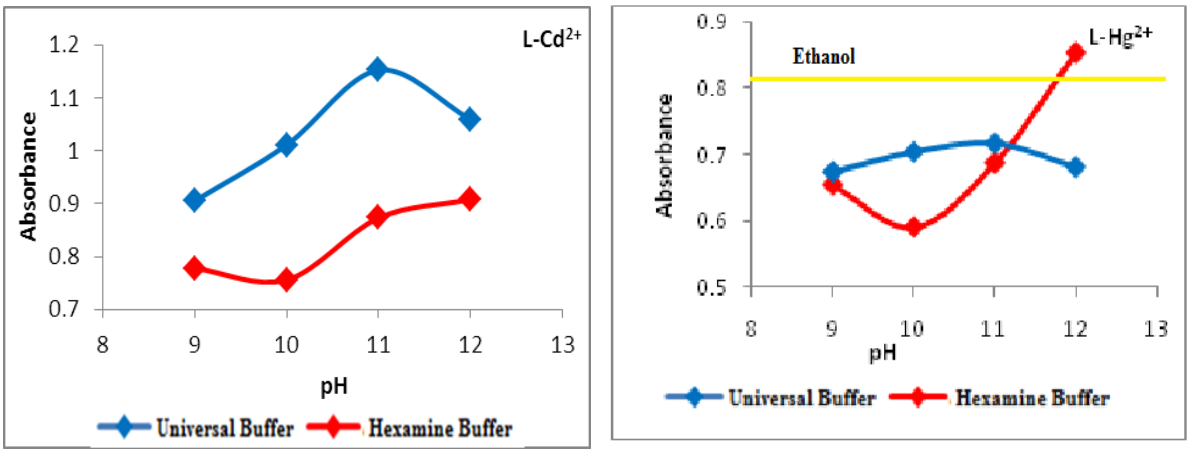

Fig.(5): Kinds of buffer solutions at different pH values and ethanol medium.

Study stoichiometry of M-L complexes and mole ratio method

By using of the mole ratio method for knowing chemical composition (Stoichiometery) of a complex, A serious of solutions prepared by keeping concentration of metal ion constant (2 $x10^{-5}$ M) with varying concentration of azodye (0.4 – 6 $x10^{-5}$ M). Then the absorbances were measured at λ_{max} by using of azodye as blank solution. From Fig.6, it was shown the ratio M: L is 1 : 2.

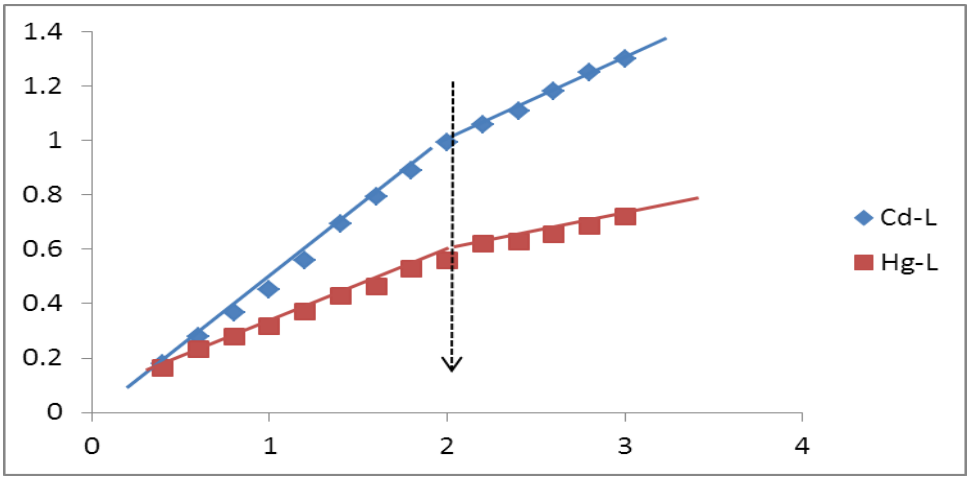

Fig. (6): The mole ratio method for M-L complexes.

Molar Conductometry

In order to get more identifications on prepared complexes with respect of ionic character of complexes, it was necessary to measure the molar conductivity of complexes solutions using DMF as solvent. The results show molar conductivity of 26 and 28 cm^2. $mole^{-1}$. ohm^{-1} for Cd-L and Hg-L complexes respectively. The low values of molar conductivity of Cd-L and Hg-L complexes mean that the complexes not having any ionic character.

By the aid of, I.R. spectra, the stoichiometry studies and molar conductivity, the chemical structures of complexes were suggested (Fig. 7).

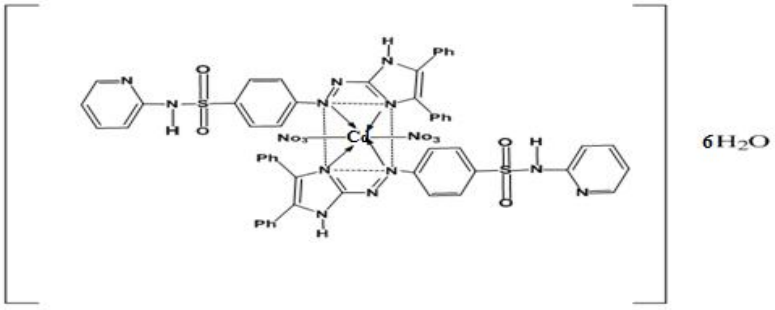

Fig.(7): The Suggested chemical structures of Cd-L complex.

Sensitivity and Beer's law

A serious solutions mixture of variable concentrations of metal ions with excess constant concentration, the absorbances were measured at λ_{max}. Beer's law was obeyed to the complexes under investigation for the spectrophotometric determination of metal, with linear calibration curves passing through the origin were obtained (Fig. 8). Better results were obtained by applying the optimum blank composition technique.[17] i.e using the amount of the unreacted azodye as the blank from knowledge of the stoichiometry of complexes.Table (4) shows the high sensitivity, which is represented by the values of specific absorptivity (a), the molar absorpitivity coeff. (ε) and sensitivity index (S) for complexes M-L with high precision that represented by the values of standard deviation (S.D.), and high linearity of Beer's law which represent by the correlation coeff. (r) which is nearly to unity.

Table (4): Data obtained from Beer's law for M-L complexes.

Complex	max λ nm	DL $\mu g.ml^{-1}$	S.D	$S\times10^{-3}$ $\mu g.cm^{-2}$	r	aml.g-1.cm-1	ε $L.mol^{-1}.cm^{-1} \times 10^{4}$	Beer's law up to
Cd-L	490	0.1200	0.0520	2.56	0.969	0.4050	4.6	4.5
Hg-L	490	0.0197	0.0073	8.65	0.988	0.1155	2.3	2.8

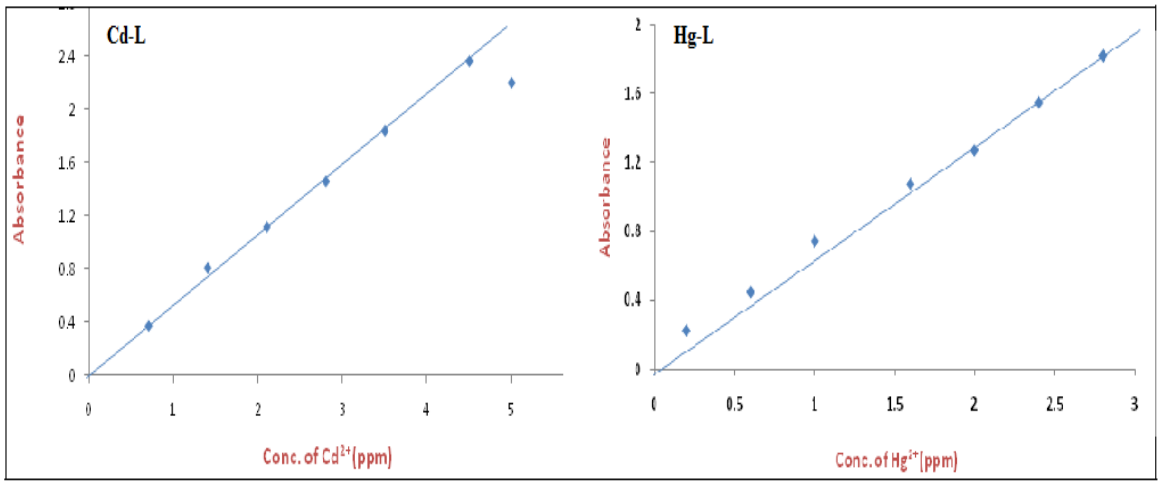

Fig (8): Beer's law for M-L complexes.

Interferences of foreign ions

It is important to study the effects of foreign ions on the absorbance of M-L complexes. So that happened by using (1 fold, 5 folds & 10 folds) of foreign ions concentrations. The Absorbance will be compared with that in absent of foreign ions. (The formed complexes Cd-L and Hg-L will give absorbance of 1.105 and 0.838 respectively in absent of foreign ions).

For interferences with Cd-L, it was found that the ions (Li^{+}، Na^{+}، K^{+} ، Mg^{2+} ،VO^{2+} ، Mn^{2+} ، Ni^{2+}، Sr^{2+}،Cu^{2+}، Hg^{2+}،Ba^{2++} ،Pb^{2} ، Ca^{2+} ، Cr^{3+} ،Fe^{3++} ، La^{3+} ،Zr^{4}، Cl^{-}،SO_4^{2} ،PO_4^{3-}) don't interfering, but the ions (Ag^{+} ، Cu^{2+}، Zn^{2+} and EDTA.Na_2.2H_2O) will do (Table 5).

For interferences with Hg-L, it was found that the ions (Li^{+}، Na^{+}، K^{+}، Mg^{2+} ،VO^{2+} ، Mn^{2+} ، Co^{2+} ، Ni^{2+}، Sr^{2+}، Cd^{2+}، Ba^{2+} ،Pb^{2+} ، Ca^{2+} ، Cr^{3+} ، Fe^{3+} ، La^{3+} ،Zr^{4+}، Cl^{-} ،SO_4^{2-} ،PO_4^{3-}) don't interfering but the ions (Ag^{+} ، Cu^{2+} ،$Zn^{2+}$and EDTA.Na_2.2H_2O) will do (Table 5).

Table (5): Interferences of foreign ions the absorbance of ([Cd] =[Hg]= [L] = 4 x 10^{-5} M The complexes Cd-L and Hg-L will give absorbance of 1.105 and 0.838 respectively in absent of foreign ions.

ion	Absorbance of Cd-L			Absorbance of Hg-L		
	1-fold	5-fold	10-fold	1-fold	5-fold	10-fold
Li^{+}	1.109	1.119	1.081	0.846	0.823	0.823
Na^{+}	1.011	1.113	1.107	0.821	0.835	0.823
K^{+}	1.027	1.063	1.001	0.831	0.820	0.819
Ag^{+}	0.986	0.994	0.984	0.791	0.851	0.799
Mg^{2+}	1.055	1.062	1.093	0.810	0.815	0.809
VO^{2+}	1.166	1.129	1.104	0.827	0.830	0.833
Mn^{2+}	1.355	1.317	1.365	0.821	0.838	0.831
Ni^{2+}	1.563	1.503	1.474	0.825	0.820	0.824
Cu^{2+}	1.092	1.099	1.098	0.826	0.838	0.818
Zn^{2+}	1.170	1.175	1.158	0.770	0.818	0.742
Sr^{2+}	0.946	0.989	0.972	0.777	0.778	0.717
Cd^{2+}	1.063	1.231	1.088	0.822	0.837	0.821
Hg^{2+}	1.064	1.123	1.091	0.789	0.795	0.783
Ba^{2+}	1.027	1.021	0.994	0.819	0.828	0.833
Pb^{2+}	1.070	1.074	1.069	0.836	0.845	0.826
Ca^{2+}	1.080	1.099	1.076	0.812	0.822	0.834
Cr^{3+}	1.047	1.089	0.976	0.814	0.816	0.819
Fe^{3+}	1.026	1.029	0.978	0.816	0.815	0.821
La^{3+}	1.100	1.125	1.111	0.817	0.826	0.823
Zr^{4+}	1.071	1.110	1.082	0.827	0.844	0.822
Cl^{-}	1.111	1.119	1.101	0.829	0.835	0.843
SO_4^{2-}	0.997	1.109	1.000	0.841	0.834	0.844
PO_4^{3-}	1.098	0.999	1.121	0.831	0.837	0.830

Determination of stability constant of M-L

By the aid of the corresponding solutions method[18] the stability constants of M-L complexes were calculated using Half-value method.[19-20] This method requires two series of solutions of total metal ion concentration C1M (concentrated series) and C2M (diluted series) (where C1M>C2M) and varying azodye ligand concentrations C1L and C2L. The absorbencies were

measured at λ_{max} (Table 6).The corresponding solutions are those which have the same absorbance at different ligand concentrations. Then the diluted series was multiplied by the factor (C1M /C2M). From the absorbance - CL plot (Fig.9). Many pairs of C1L and C2L, consequently, **ñ** (Complex formation function) and [L] **(**free ligand concentration) can be determined (Table 6).

ñ = (C1L – C2L) / (C1M – C2M) and [**L**] = (C1M x C2L – C2M x C1L) / (C1M – C2M) By using the half value method log K (stability constant) was obtained from a plot of **ñ** against **pL** (Table 7), at **ñ** = 0.5 and 1.5 the log K_1 and log K_2 were determined (Fig. 10).

Table (6): The absorbance of dil. serious and concn. Seriouses.

Concn. series x 10^{-5} M(C1L)	Concn. series (C1M=8x10^{-5}M)		Dil. series x 10^{-5} M (C2L)	Dil. Series (C2M=4x10^{-5}M)	
	Absorbance at λ_{max}			Absorbance at λ_{max}	
	Cd-L	Cu-L		Cd-L	Cu-L
1.6	0.385	0.385	0.8	0.412	0.358
2.4	0.582	0.582	1.2	0.604	0.51
3.2	0.854	0.824	1.6	0.776	0.578
4	1.108	1.08	2	0.964	872
4.8	1.342	1.342	2.4	1.128	1.036
5.6	1.622	1.622	2.8	1.414	1.152
6.4	1.9	1.9	3.2	1.55	1.19

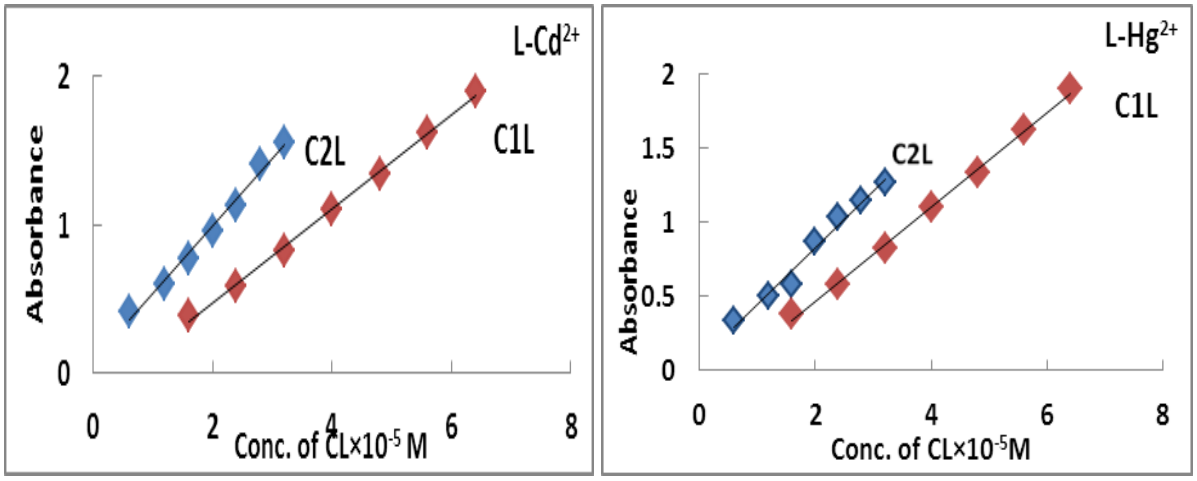

Fig.(9): The absorbance – Cl curve or the M-L complexes.

Table (7): Pairs of same absorbance C_{1L} and C_{2L} and getting ñ & pL values.

0.4	Cd-L					Hg-L				
	$C_{1L} \times 10^{-5}$	$C_{2L} \times 10^{-5}$	ñ	$[L] \times 10^{-5}$	pL	$C_{1L} \times 10^{-5}$	$C_{2L} \times 10^{-5}$	ñ	$[L] \times 10^{-5}$	pL
0.4						1.8	0.92	0.22	0.04	6.4
0.5	1.9	0.98	0.23	2.82	4.55	2.2	1.2	0.25	0.2	5.7
0.6	2.3	1.2	0.28	3.4	4.46	2.5	1.38	0.28	0.26	5.59
0.7	2.6	1.38	0.3	3.82	4.4	2.8	1.6	0.3	0.4	5.4
0.8	2.98	1.6	0.35	4.36	4.36	3.18	1.86	0.33	0.54	5.27
0.9	3.3	1.8	0.38	4.8	4.32	3.5	2.1	0.35	0.7	5.15
1	3.68	2.08	0.4	5.28	4.37	3.8	2.28	0.38	0.76	5.12
1.1	4	2.3	0.43	5.7	4.24	4.1	2.42	0.42	0.74	5.13
1.2	4.3	2.5	0.45	6.1	4.21	4.5	2.7	0.45	0.9	5.05
1.3	4.6	2.7	0.48	6.5	4.19	4.7	2.8	0.48	0.9	5.05
1.4	4.82	2.8	0.5	6.84	4.17	5.3	3.13	0.54	0.96	5.02
1.5	5.2	3.1	0.53	7.3	4.14	5.84	3.4	0.61	0.96	5.02
1.6	6.2	3.2	0.75	9.2	4.04					
1.7	6.5	3.4	0.78	9.6	4.02	6.5	3.74	0.69	0.98	5.01
1.8	6.8	3.64	0.79	9.96	4	6.8	3.9	0.73	1	5
1.9	7.2	3.95	0.81	10.45	3.98	7.8	4.5	0.83	1.2	4.92
2	7.44	4.1	084	10.78	3.97	8.2	4.7	0.88	1.2	4.92
2.1	7.78	4.25	0.88	11.31	3.95	8.6	5	0.9	1.4	4.85
2.2	8.12	4.5	0.91	11.74	3.93	8.9	5.16	0.94	1.42	4.85
2.3	8.4	4.64	0.94	12.16	3.92	9.2	5.34	0.97	1.48	4.83
2.4	8.76	4.8	0.99	12.72	3.9	9.58	5.58	1	1.58	4.8
2.5	9	4.9	1.03	13.1	3.88	9.9	5.74	1.04	1.58	4.8
2.6	9.5	5.1	1.1	13.9	3.87	10.54	6.1	1.11	1.66	4.78
2.7	9.8	5.22	1.15	14.38	3.84	11.35	6.54	1.20	1.73	4.76
2.8	10.75	5.4	1.34	16.1	3.79	12.12	7	1.28	1.88	4.73
2.9	11.66	5.64	1.51	17.68	3.75	12.9	7.4	1.38	1.9	4.72
3.1						13.76	7.86	1.48	1.96	4.71

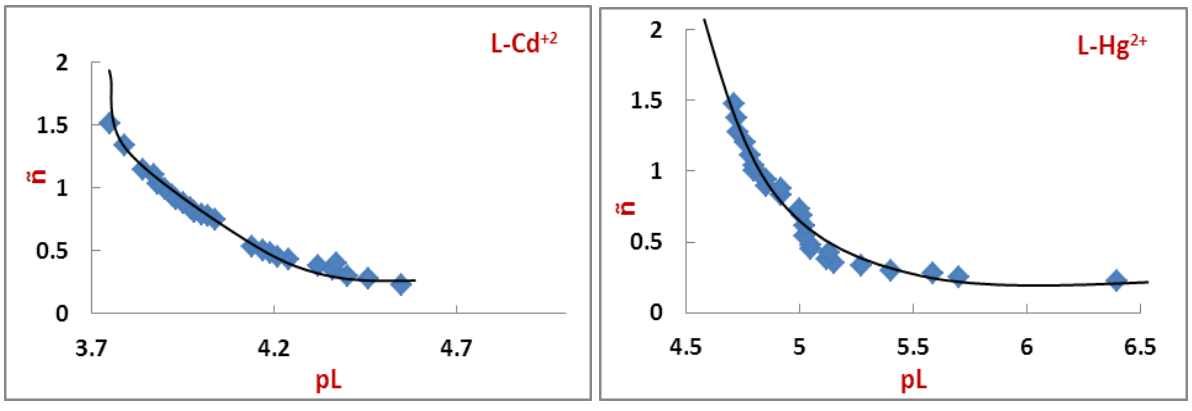

Fig.(10): Half-height method (ñ - pL curves)

Table (8) lists the values of $Log\beta_1$ and $Log\beta_2$ for complexes Cd-L and Hg-L. From the table it was found that the most stable complex is Hg-L, then Cd-L.

Table(8): $Log\beta_1$ and $Log\beta_2$ for complexes.

Log β	Cd-L	Hg-L
$Log\beta_1$	4.17	5.05
$Log\beta_2$	7.92	9.76

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