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RESEARCH ARTICLE

Synthesis, Analytical, Thermodynamic Studies and Uptake Behavior of: Copper and Cadmium by New Schiff-base Chelating Resins

W.S. Hanoosh, Hanaa H. Haddad, Bassim Abdul hassun

Chemistry department, College of science, University of Basra, Iraq.

Abstract

The present work carried out a study on new Schiff-bases ligand derived from (P-phenyl amine and O-amino phenol) with 3-hydroxy benzaldehyde, which has been successfully prepared in warm alcoholic medium. These ligands were characterized by FTIR spectroscopy, CHN analysis & Uv-Visible spectra. From the UV –Vis spectra show that both heavy metal [$Cu2^+$, Cd^{2+}] form complexes with both schiff-bases in the ratio (1:2) [M: L]. Thermodynamic parameters were evaluated at different temperature using vant-hoff equation. Finally polyurethane foam from these ligand were prepared through the reaction with diisocyanate compound (MDI) and thermal study of these prepared polymers were evaluated by using thermogravemetric analysis (TGA)

Keywords: *Schiff-base, Polyurethane foam, TGA analysis.*

Introduction

Schiff-bases derived from aromatic amine and aromatic aldehyde or ketone have a wide variety of applications in many field (1) schiff-base complexes have key role in catalysis of a variety of organic reaction such as metathesis process (2), reductive carbonylation(3) polymerization (4) decarboxylation (5) and industrial chemistry ligand (6) . A metal surrounded by a cluster of ions or molecule is used for preparation of complex compounds named as Schiff-based (7). A wide variety of ligand may be obtained via the Schiff-base condensation reaction which varies in identity, flexibility nature of donor atoms and electronic properties (8). The (C=N) stretching frequencies of the ligand occurs in region between (1680-1603) cm^{-1} depending upon the nature of substituent present either on nitrogen or on carbon (9).

Photochemical degradation of natural rubber yield amine (10) terminated ligand natural rubber (ATNR) when carried out in solution in presence of ethylene diamine (ATNR) on reaction with glyoxal yield poly Schiff-base which improves aging resistance. Organo-cobalt complexes with tridentate Schiff-base act as initiator of emulsion polymerization and copolymerization of dienyl and vinyl monomers (11). Schiff-base which are effective as coordinating ligands have functional group [OH, NH_2, SH] sufficiently, near the site of condensation so as to form five or six membered chelating ring on reaction with metal ions (12). Schiff-base has played an important role in the development of coordination chemistry as they form stable complexes with most of transition metal (13). Same as polymeric materials have an essential place in everyday life which has been applied wildly (14).

In these years' researchers starting focus on polymers containing conjugating structure, due to their variety of application in many field such as polymer containing conjugation chain with (CH-N) structural unit (15) which is known as polymeric Schiff-base or polyimines. The imine (-CH=N) group formed immediately after mixing and it was found cleanly during the polymerization. In this work we wish to report synthesis & characterization of Schiff-base ligand and its polymerization then to study thermodynamic behaviors toward [Cu^{+2} and Cd^{+2}] (heavy metal ions) and its loading capacity against the polymerized Schiff-base.

Experimental

2.1. All the reagents, starting materials as well as solvents were porch used commercially and used without any further purification. The partial dehydrated salts in oven for several hours at 100-110C^0

Instrumentation

- Melting point ware recorded on hot stage Galen Kamp melting point apparatus caveego, dijital vmp-D (jenway)
- The Infrared (FTER) spectra were recorded by using shimadzu FTIR-8400S-Japan.
- Elemental (CHN) analysis was carried out by perkin Elmer 2400 series (11) CHN elemental Analyzer
- UV-VIS spectra were recorded by using phonix-986 Biotcch Engineering Management Co, LTD-(UK)
- ^{1}H NMR spectra were recorded on an Avance 400 MHz NMR spectrometer (Bruker) in deterated chloroform and DMSO/CHCL$_3$ using the solvent signal as internal reference.
- Thermal stability study of polymer were evaluated using Aperkin-Elmer STA600 simultaneous thermal analyzer (TG with DSC) approximately 10 mg of each sample was added to ceramic crucible and heated from 30-700C^0 at heating rate of 10C^0/min in N$_2$ gas at a flow rate of 20 ml/min

Preparation Methods

Preparation of Schiff-base Ligand (L$_1$)

Ligand (L$_1$) was prepared through the reaction of (5.25g, 0.05 mole) (O-aminophenol) with (6.1g, 0.05 mole) (3-hydroxy-benzaldehyde in 30ml warm ethanolic solution containing 2 drops of glacial acetic acid ,at (40-45C^0) to speed up the reaction under stirring for 2hrs in an ice bath. after complete reaction precipitate was obtained after cooling, filtrate and recrystallization from ethanol to give a brown powder with m-point 118-120C^0 and yield 76.9%

Preparation of Schiff- base Ligand (L$_2$)

The same procedure above was used to prepare L$_2$ except using of P-phenylenediamine instead of O-aminophenol. The product was white in color, with melting point 231C^0 and yield 85.8%.

Preparation of Polyurethane Foam

Two polymeric foam were prepared from these two liquid, first synthesis of polyurethane terminated isocyanate by mixing polyester polyol with excess of MDI in the presence of triethyl amine as catalyst at room tempreture for one hrs.

Then appropriate quantity(30% based on polyesterpolyol) of ligands were added and mixing at 50 C^0 to get homogenous for about(3-4) hrs to complete polymerization after this, these foam were washing twice with hot water in order to remove unreacted compounds. Then filtrate and drying. Tables (1) show the quantity of reacted compounds.

Table 1: Show the weight of material

Schiff-base	Ligand (g)	Poly-ol (g)	MDI eynate (g)	Weight (g)	Color
L$_1$	0.78	1.9	2.54	5.18	Pall yellow
L$_2$	0.78	1.9	2.54	5.21	white

Result and Discussion

Physical Measurement

The physical properties of the prepared ligands were shown in Table 2. From this table the melting point of L1 was less than melting point of L2 this depends on the chemical structure of the final product.

Table 2: Physical properties of Schiff-bases

Schiff-base	Molecular formula	Molecular weight	M.p. C^0	Color	Yield
L$_1$	$C_{13}H_{11}O_2N$	213	118-120	Browen	76.9% 8.18g
L$_2$	$C_{13}H_{12}N_2O$	213	229-231	White	85.8% 9.1g

FTIR Spectra of the Prepared Ligands

Some characteristic IR peak of the two ligands have been presented in Table (3), which show the absence of band at 1735 cm^{-1} (C=O) due to carbonyl and 3315 cm^{-1} for NH$_2$, stretching vibration of strong new bond appeared at 1620.21 cm^{-1} for (L$_1$) and 1622.13

cm^{-1} for (L_2) assigned to azomethine (HC=N) which indicates the absent of (C=O) and (NH_2) of starting material and have been converted to a new Schiff-bases (16).

Table 3: IR Spectra of Schiff-bases

Ligand	CH aliphatic	CH aromatic	C=O	C=N	C-N	C=C	OH
L_1	3402.43	3047.53	-	1620.21	1585.49	1381.03	1485.19
L_2	3363.86	3035.96	-	1622.13	1593.20	1276.88	1454.33

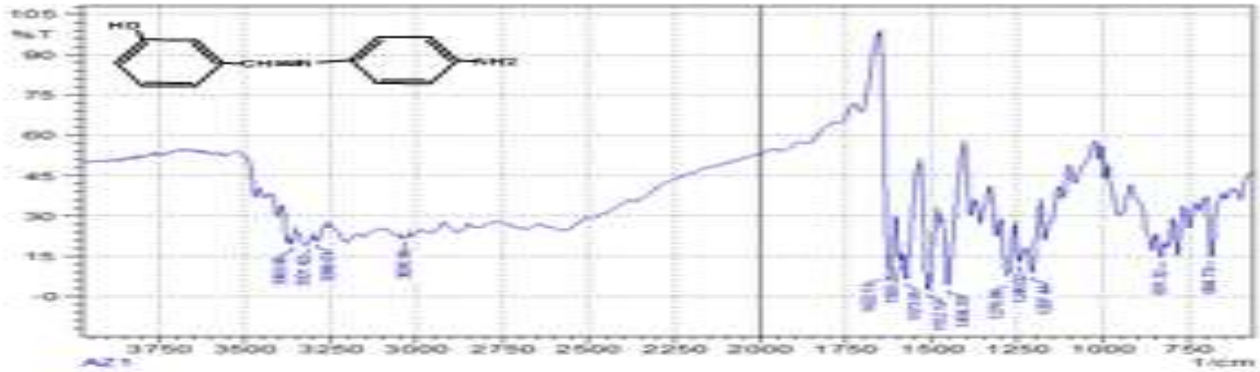


Figure 3-1: FTIR spectra for Schiff-base L_1

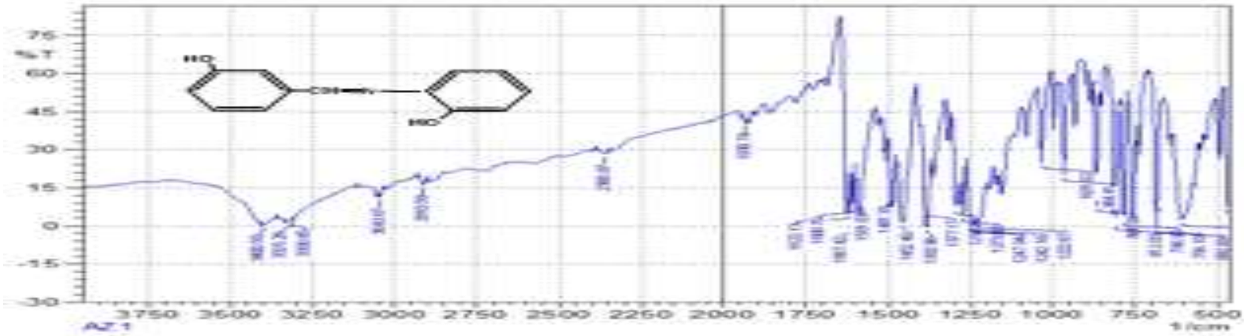


Figure 3-2: FTIR spectra for Schiff-base L_2

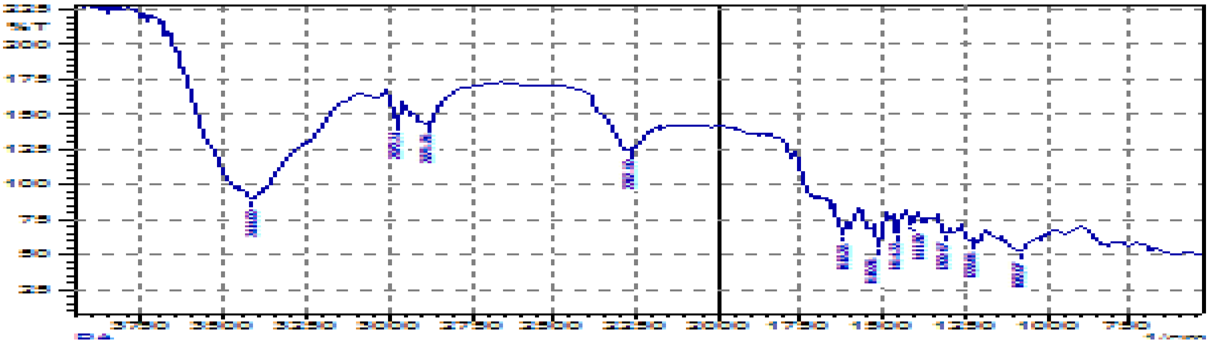


Figure 3-3: FTIR spectra for copolymer L_1

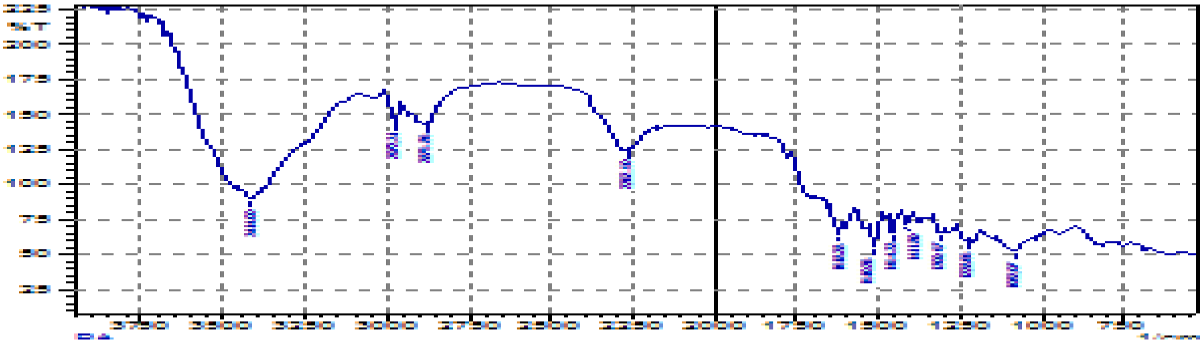


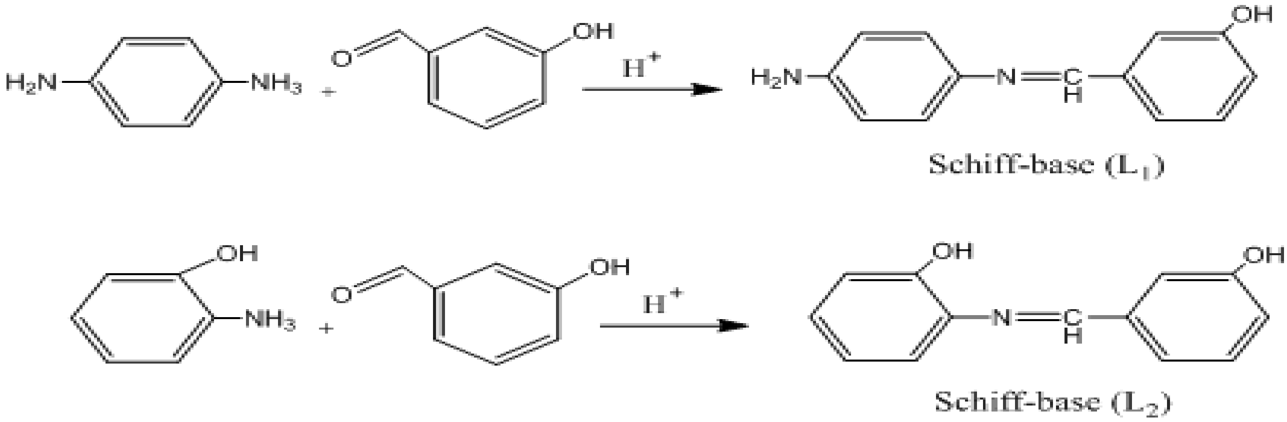
Figure 3-4: FTIR spectra for copolymer L_2

FTIR Spectra for Polymer Based on L_1 and L_2

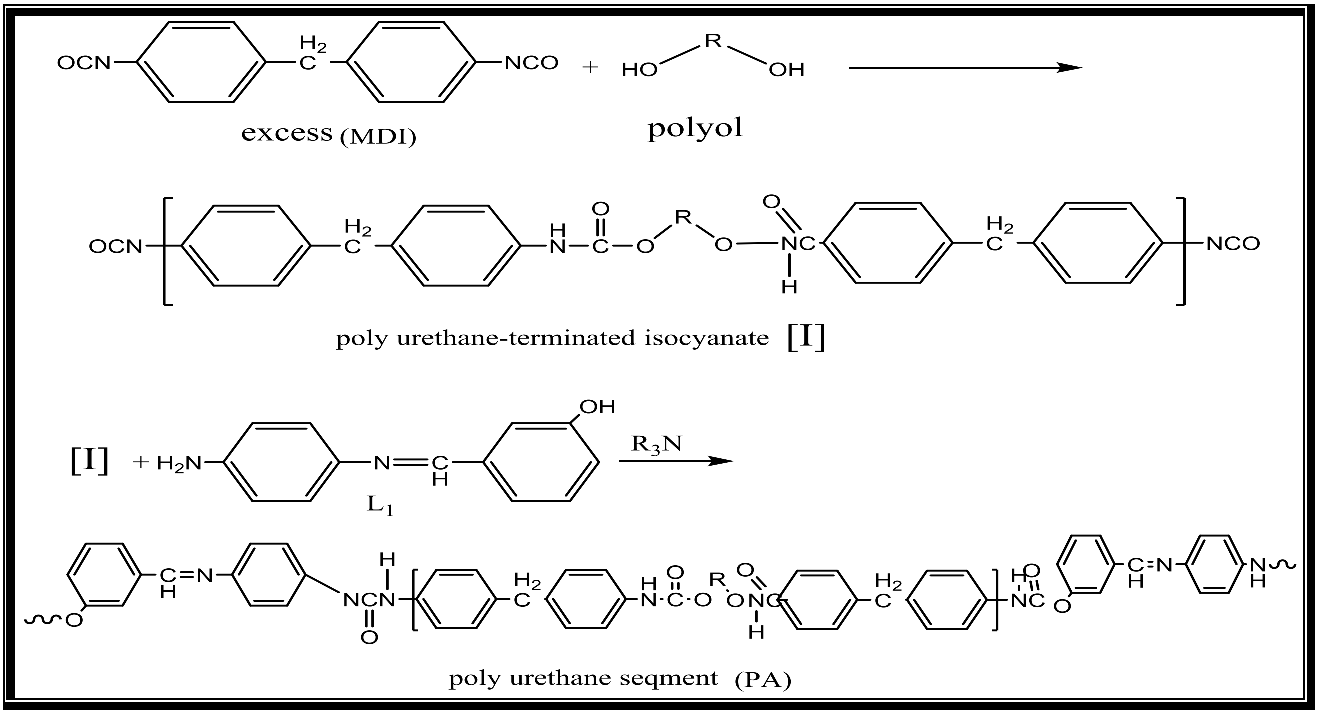
Table 4: FT-IR spectra for polymerized L_1 and L_2

Polymer	C-O-C	C=C	C=N	CH_2	C-N	OH	C-O
Poly-L_1	1082.07	1537.27	1670.35	2875.86-2968.45	2258.64	3402.43	1219.01
Poly-L_2	1082.07	1510.26	1618.28	2868.15-2972.31	2262.50	3414.00	1228.66

FTIR spectrum of polymer showed sharp characteristic absorption for (-CH=N) group at (1670.35 cm^{-1}) L_1 and (1618.28 cm^{-1}) L_2, the broad band at(3402.43 cm^{-1} 3414 cm^{-1}) for (L_1&L_2) was manly associated with water trapped in the product(19) And multiple peaks around (1537.27 cm^{-1}) represent the aromatic –C=C- stretching. The strong absorption peak at (1246 cm^{-1}) is C-O stretching absorption at (3122 cm^{-1} (20). Sometime the broad peak at(3414 cm^{-1}) could also explained as overlapping result of primary amine (NH_2) stretching and water lapping in polymer (19). The overall clean spectrum indicates that the polymerization was carried out via effective formation of –C=N- bonds.Schem.1and 2. show synthesis of these ligands and polymers.



Schem-1: Synthesis of Schiff-base compounds



Schem-2: Synthesis route of polymer (A) (polyurethane based on Schiff-base L_1)

The Elemental Analysis (CHN) of Ligands

The data of element analysis have shown that the result obtained is in good agreement with those calculated for suggested formula in Table (5).

Table 5: Elemental analysis data for ligands

Schiff-base	%C Founded (Calculated)	%H Founded (Calculated)	%N Founded (Calculated)
L_1	73.223 (73.171)	5.162 (5.106)	6.309 (6.202)
L_2	73.256 (73.311)	5.694 (5.872)	6.163 (6.202)

UV-Visible Spectrum of Ligands

From a wide studied range of molar concentration (10^{-3}-10^{-5}) M of mixed solution, only concentration ($0.5x10^{-4}$) M obeys Beer-lambert low and showed intense color. A calibration curve was plotted on absorbance (10^{-3}-10^{-4}) M, best fits straight line were obtained. The composition of complexes formed in solution has been established by mole ration and continuous variation methods. In both cases the result reveals (1:2) (M: L) ratio.

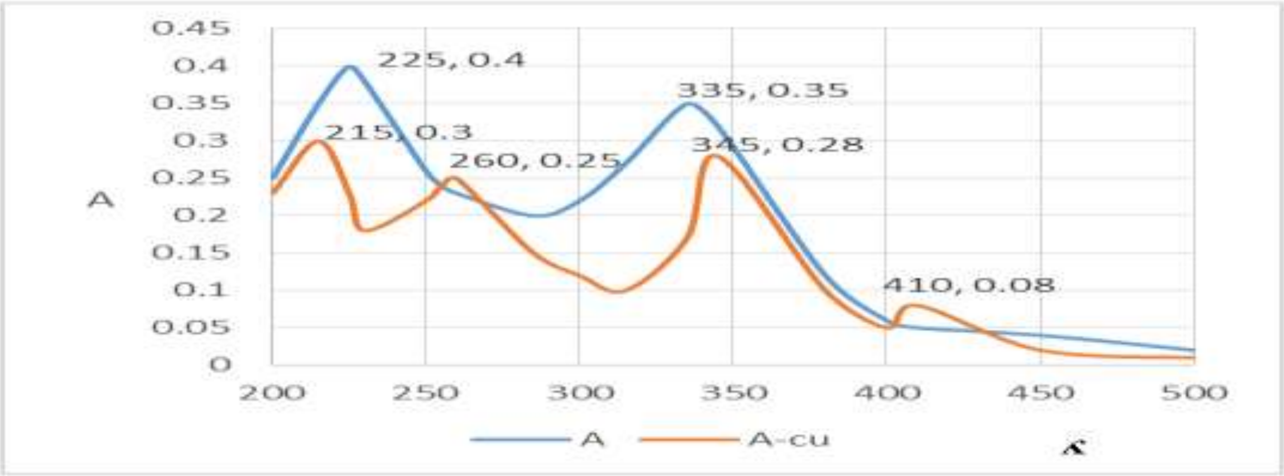


Fig. 3-5: Uv-Vis spectra for copper with L_1

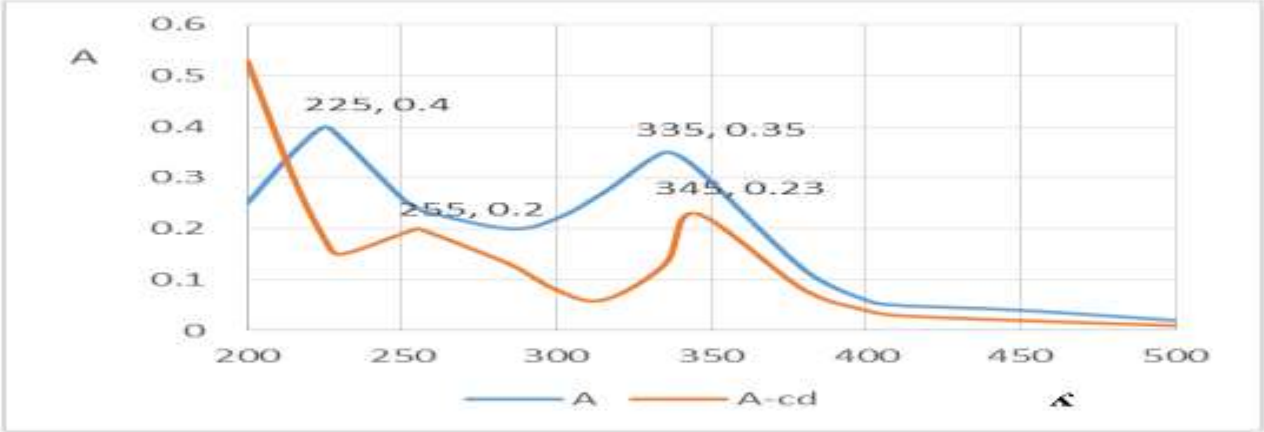


Fig. 3-6: Uv-Vis spectra for cadmium with L_1

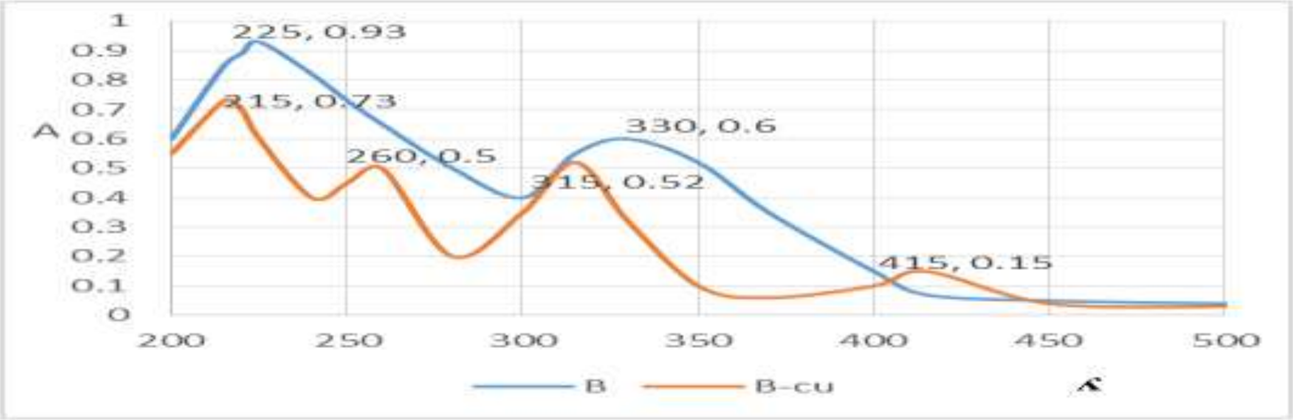


Fig. 3-7: Uv-Vis spectra for copper with L_2

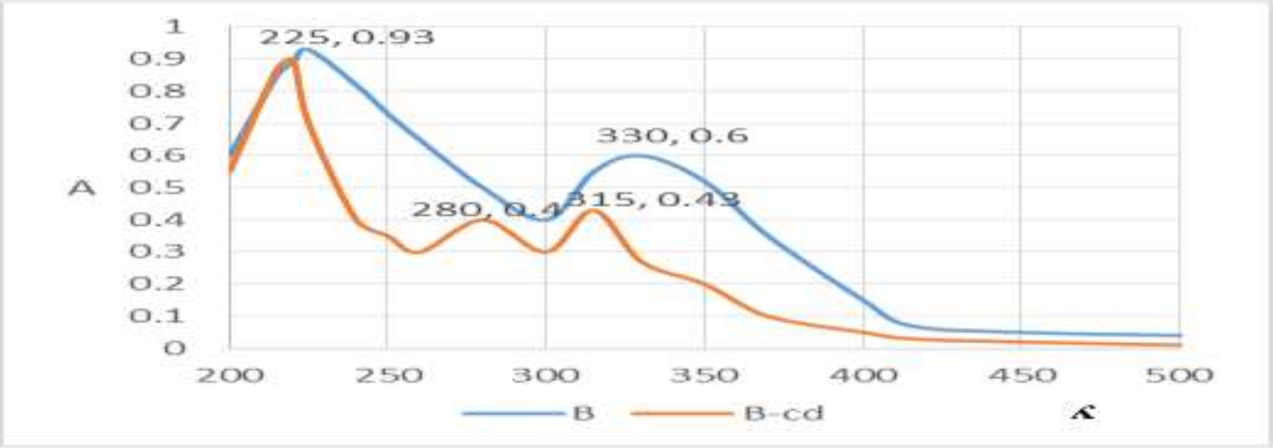


Fig. 3-8: Uv-Vis spectra for cadmium with L_2

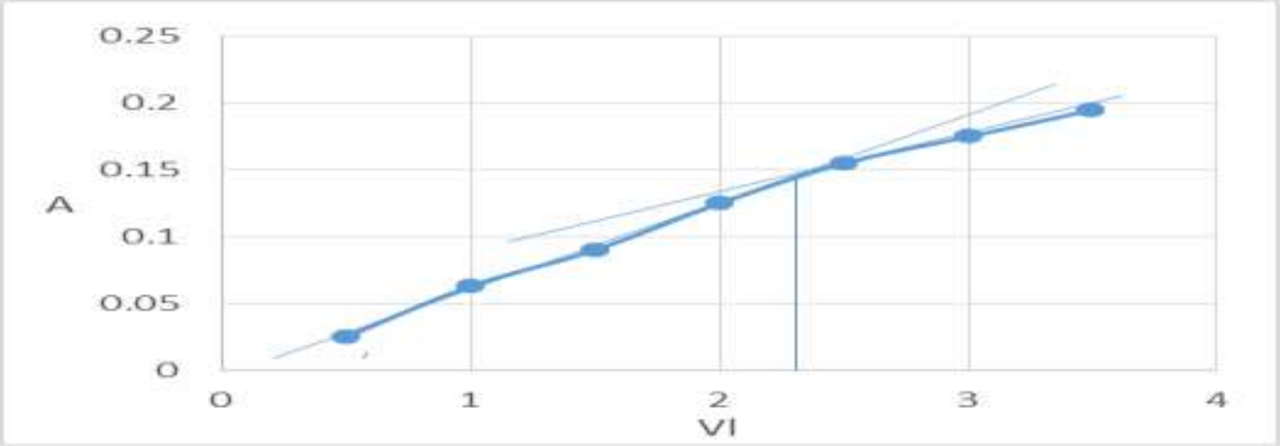


Fig.3-9: Mole ratio for copper with L_1

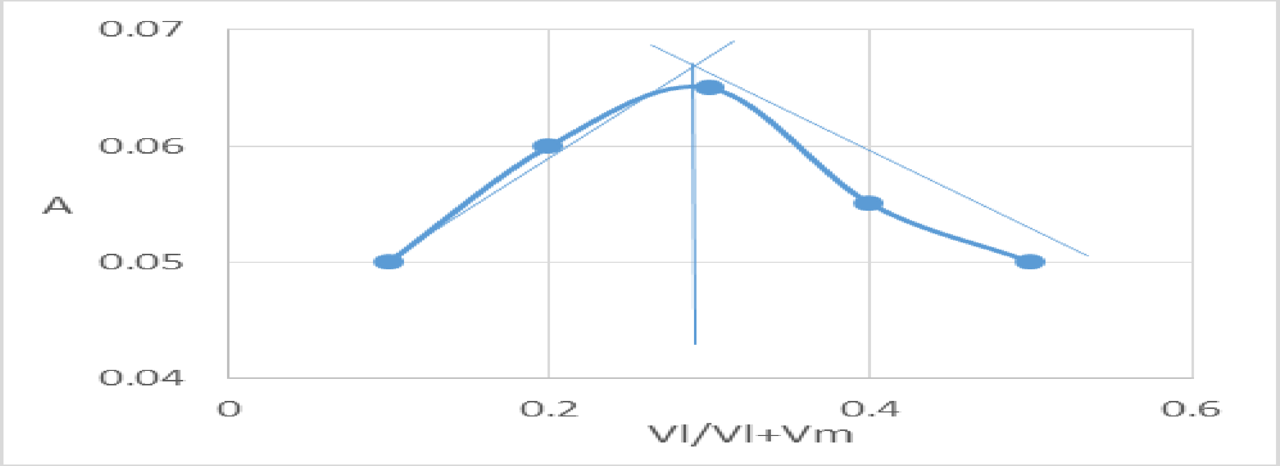


Fig. 3-10: Continues variation for copper with L_1

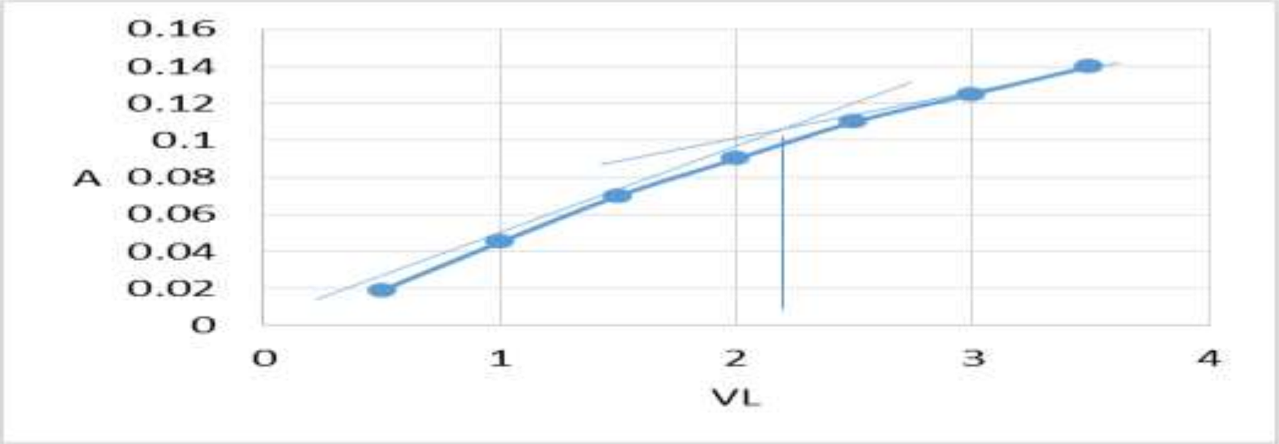


Fig.3-11: Mole ratio for cadmium with

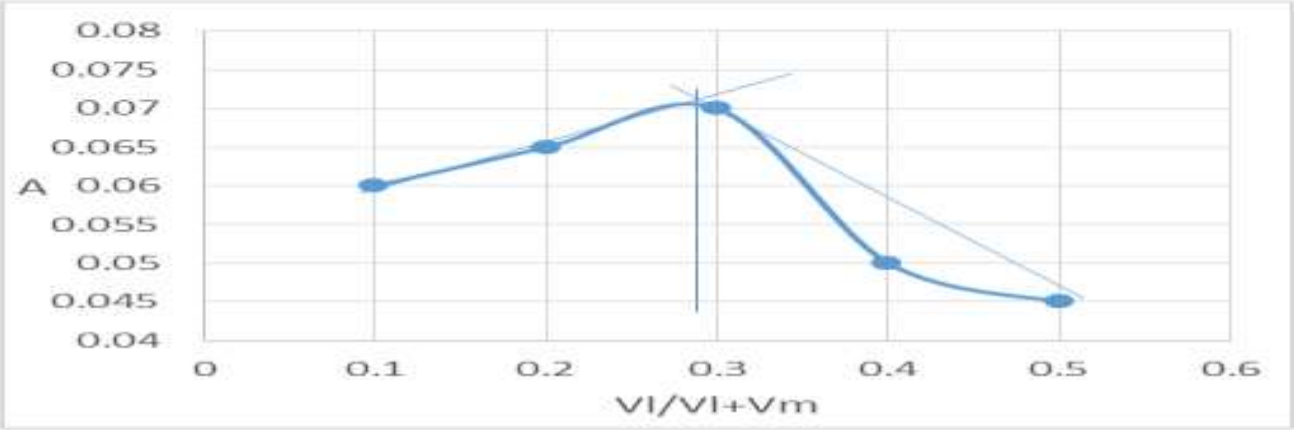


Fig.3-12: Continues variation for cadmium with L_1

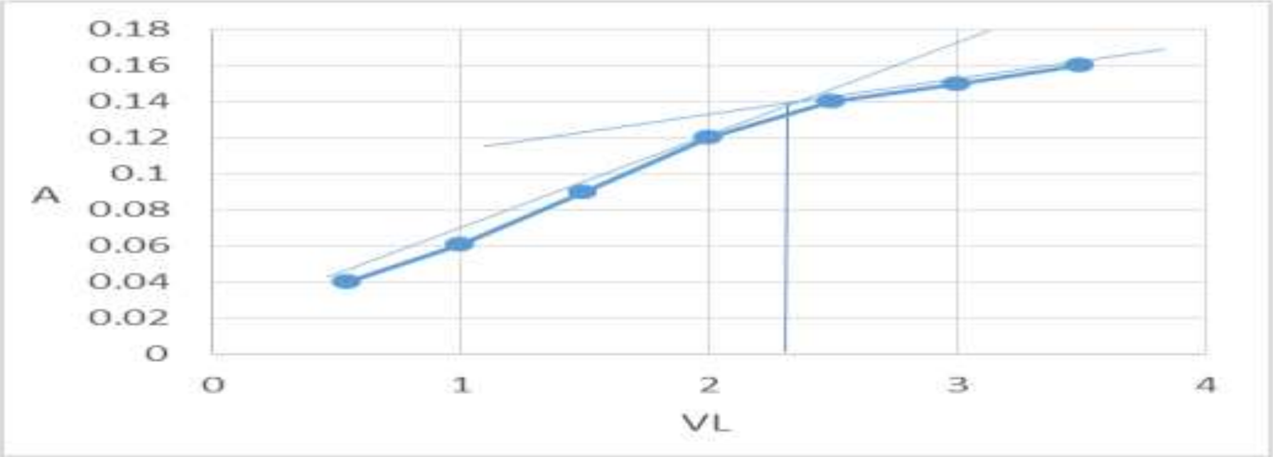


Fig. 3-13: Mole ratio for copper with L2

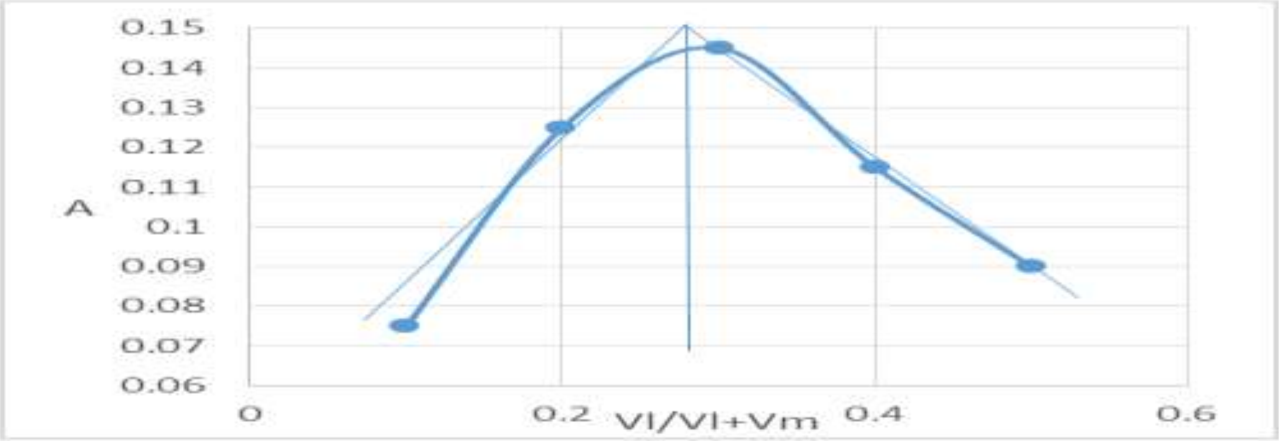


Fig.3-14: Continues variation for copper with L_2

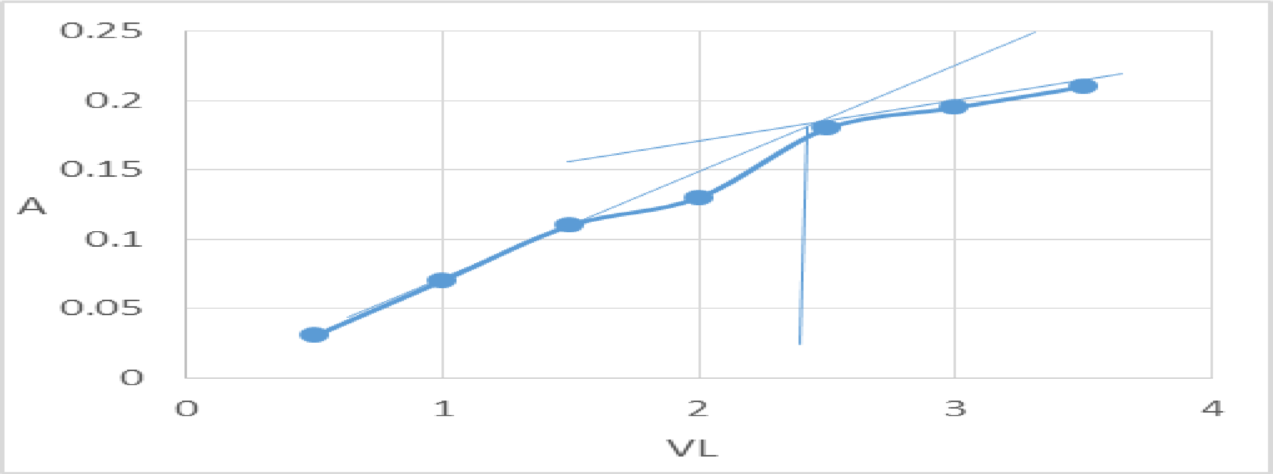


Fig.3-15: Mole ratio for cadmium with L_2

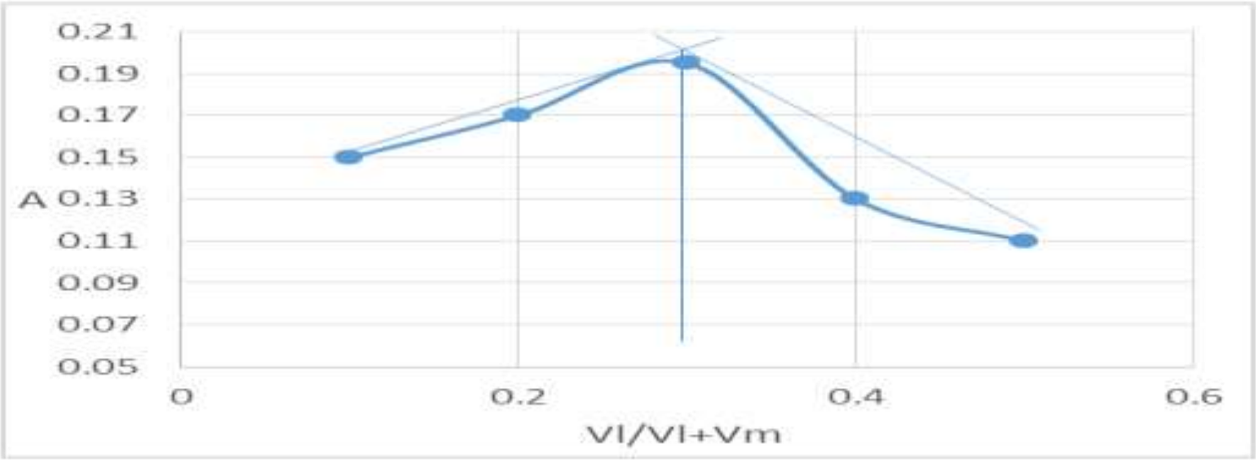


Fig.3-16: Continues variation for cadmium with L_2

Determination of Stability Constant for Complexes

$$\propto = A_m - A_s / A_m \text{ ---------- (1)}$$

$$\kappa = 1 - \alpha / 4d^3 C^2 \text{ ---------- (2)}$$

α: Degree of analysis

A_m: Absorbance of equivalent amount of L: M

A_s: Absorbance of excess amount volume of metal [17].

C: concentration of ligand which equal to the concentration of metal

Table 6: A_s, A_m, α and κ parameter for Schiff-base ion-complexes

complex	298K				283K			
	A_s	A_m	α	Kx10^8	A_s	A_m	α	Kx10^8
A-Cu	0.063	0.09	0.3	26	0.057	0.08	0.28	33
A-Cl	0.047	0.07	0.328	19	0.042	0.06	0.3	25
B-Cu	0.061	0.09	0.32	20	0.055	0.08	0.31	23
B-CCl	0.072	0.11	0.34	16	0.06	0.09	0.33	18

The Thermodynamic Parameters

The thermodynamic parameters (ΔG, ΔH and ΔS) were calculated from their stability constant at different temperatures from the flowing equations [18]. As shown in Table (7)

$$\Delta G = -RT \ln K \text{ ------------ (3)}$$

$$\ln \frac{K_2}{K_2} = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \text{ --------- (4)}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \text{ -------------- (5)}$$

Where ΔG: Free Energy, ΔH: Enthalpy ΔS: Entropy

Table 7: shows the difference in constant stability and their thermodynamic parameters at different temperatures

complex	298K			283K		
	ΔG-(KJ)	ΔH-(KJ)	ΔS+(J)	ΔG-(KJ)	ΔH-(KJ)	ΔS+(J)
A-Cu	-53.6	10.6	0.144	50.6	10.6	0.141
A-Cd	52.8	12.4	0.135	50.8	12.4	0.135
B-Cu	53	6.4	0.155	50.6	6.4	0.156
B-Cd	52.4	5.2	0.158	50	5.2	0.158

Analytical Studies of Polymerized Ligand

Total capacity of resin in the maximum theoretical quantity of ions that the resin can load operating capacity (useful capacity) it is the number of ions exchange sites where exchange has really taken place during the loading run.

It is also the number of resin charges. Not the number of ions because some ions have more than one charge picked up by the resin in one cycle. In other words, the operating capacity is the actual quantity of ions loaded on the resin between regeneration. Capacity is expressed as (eplr) (equivalent per liter of resin).

The operating capacity is always smaller than total capacity to deterrmined the capacity of the polymerized diagonal (0.1g) resin mixed with 10ml (100ppmCu^{2+}) at different time and PH to determined the best time and PH for each ligand as showen in the following figures

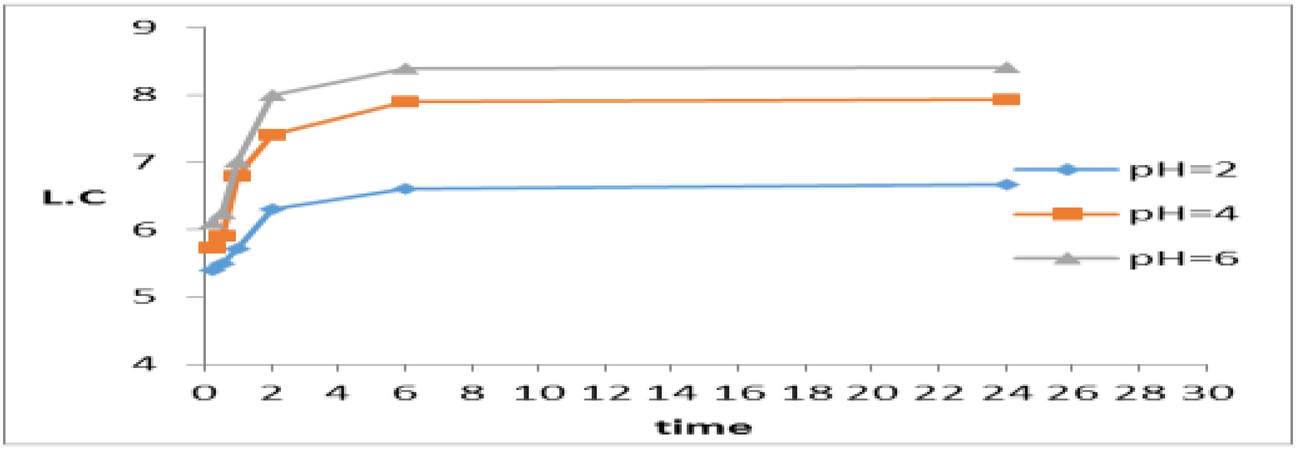


Fig. 3-17: Loading capacity vs. time for Cd^{2+} + PA

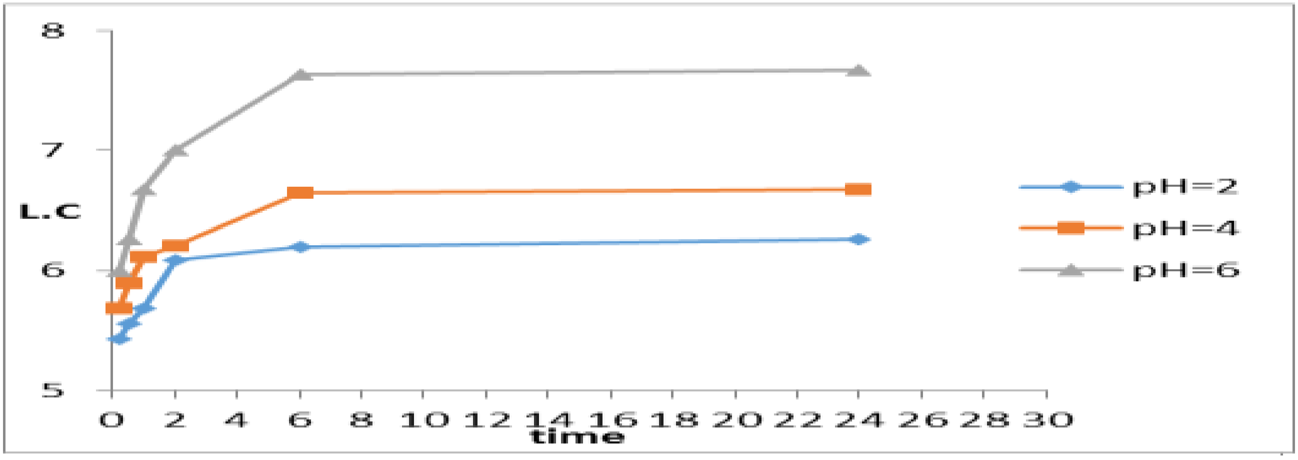


Fig.3-18: Loading capacity vs. PH for Cd^{2+} + PB

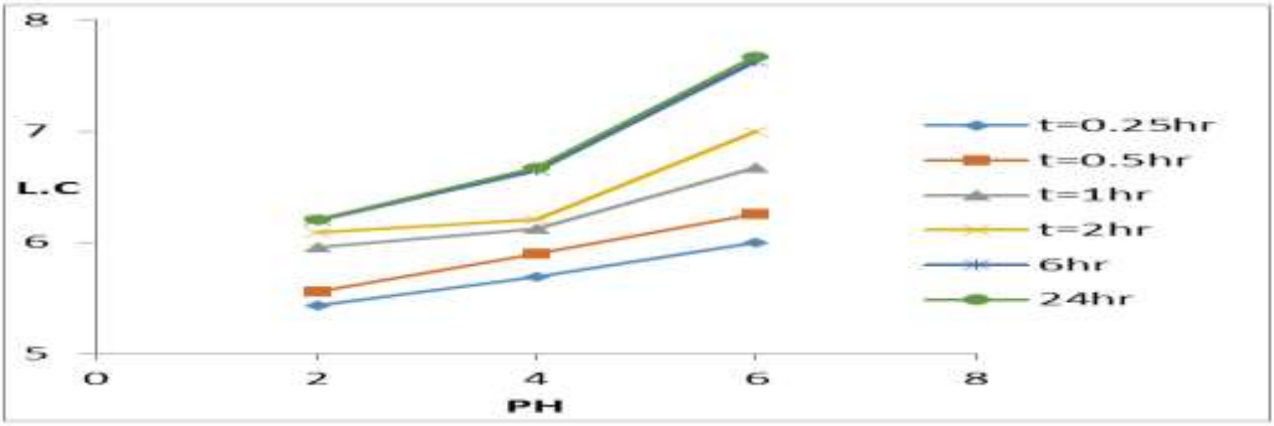


Fig.3-19: Loading capacity vs. PH for Cd^{2+} + PA

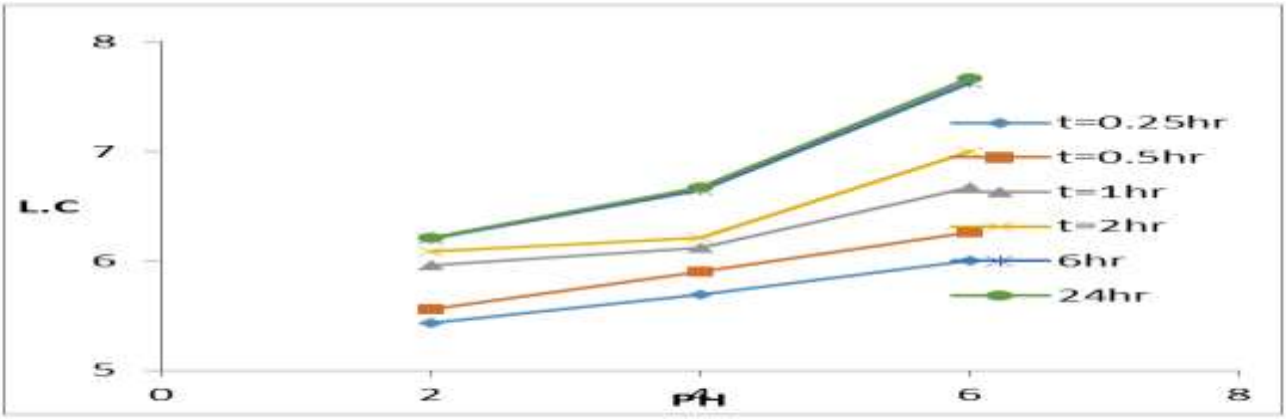


Fig. 3-20: Loading capacity vs. PH for Cd^{2+} + PB

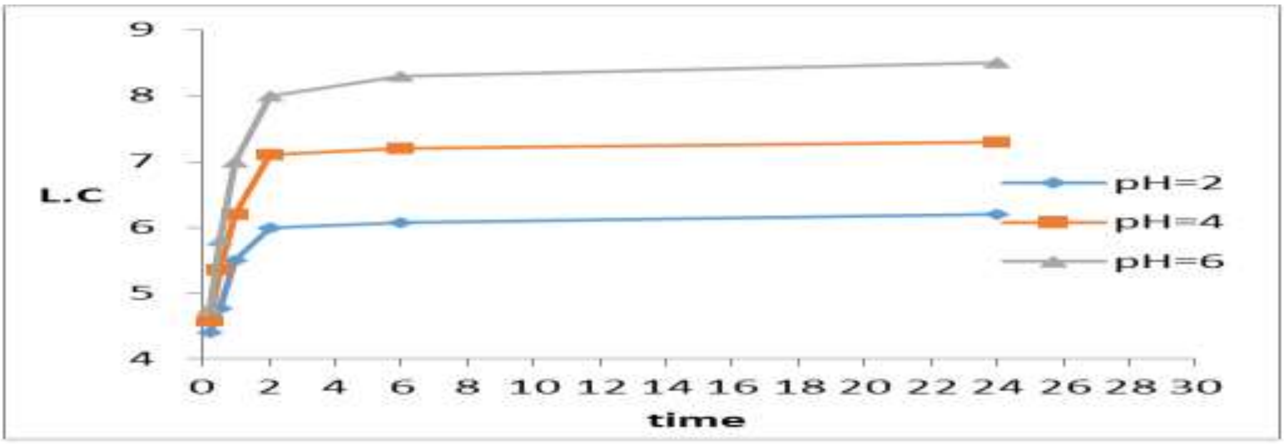


Fig. 3-21: Loading capacity vs. time for Cu^{2+} + PA

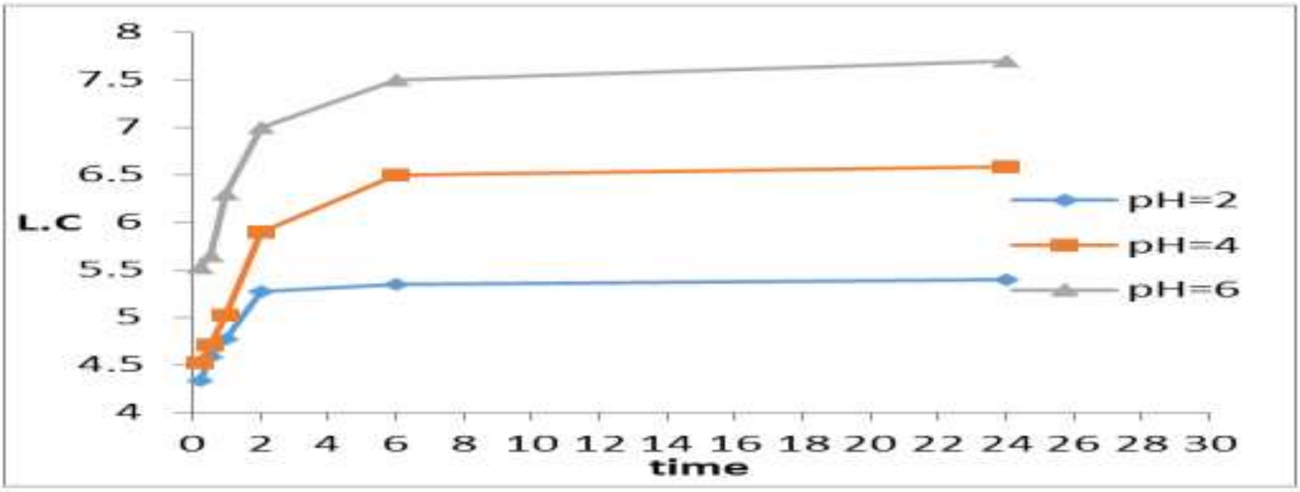


Fig. 3-22: Loading capacity vs. time for Cu^{2+} + PB

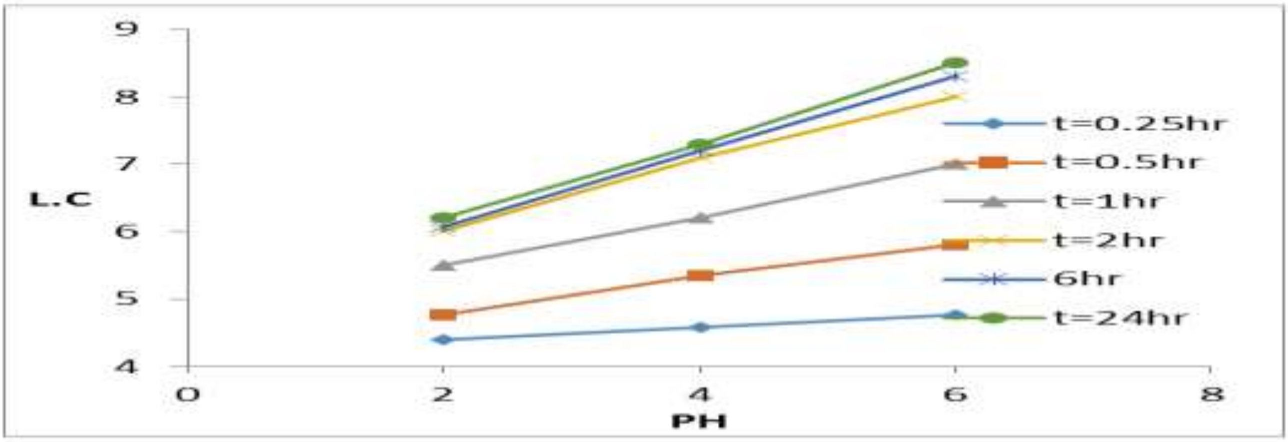


Fig.3-23: Loading capacity vs. PH for Cu^{2+} + PA

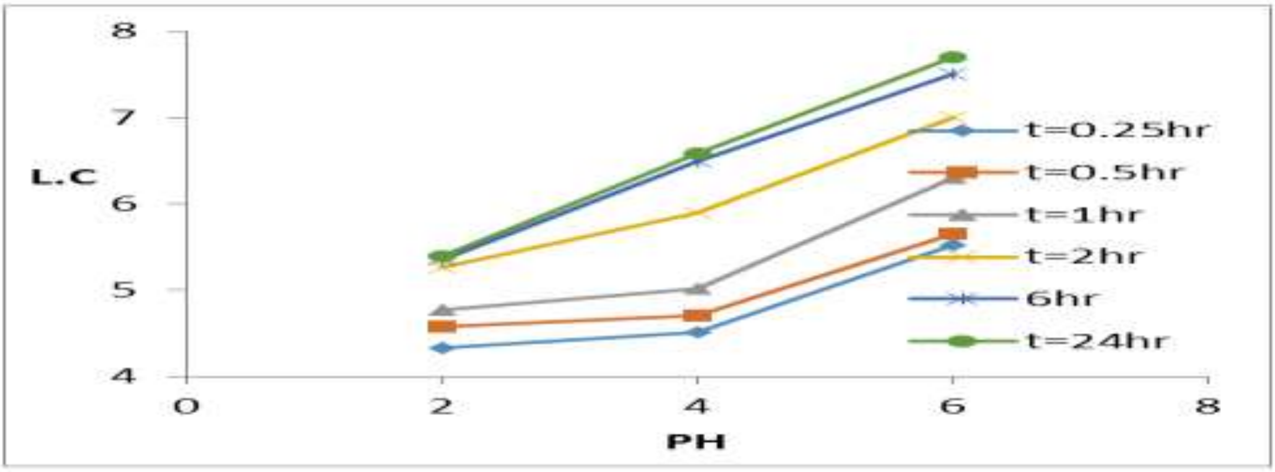


Fig.3-24: Loading capacity vs. PH for Cu^{2+} + PB

Thermal Stability Study

The thermal stability of polymers is defined as the resistance of polymers towards thermal or thermo chemical degradation (21). The thermal stability of any material can be expressed either as a function of temperature or as a temperature time limit. In this study, the thermal stability of the prepared polymers was evaluated by (TGA and DSC) technique. In the TGA analysis measuring the change in weight of sample at programmed heating rate as function of temperature. The TGA DSC thermo grams in Figure (25&3-26) were analyzed and the thermal parameters were determined and shown in Table (8).

Table 8: thermal parameters of prepared polymer

Polymer NO.	D.T (C^0)	Temp. Of 50%. Wt. loss. (C^0)	ΔE (KJ/mole)	Char % residue at 500C^0
PA	253	344	55.21	23%
PB	220	341	47.72	21%

Where D.T is optimum decomposition temperature

Temp. Of 50%.weight loss which represented the temperature at which the simple loses half of its total weight. And ΔE is the activation energy of decomposition which determined from Arrhenius equation. The thermal degradation of these polymers took place through random chain scission and radical chain mechanisms also from the result polymer A(PA) has higher decomposition temperature and activation energy than polymer B, this mean that polymer A is more stable than polymer B (PB). On the other hand the DSC thermo grams represented in Figure (3-25& 3-26) shown that the two polymers have an exothermic peak around 120C^0 which due to curing reaction of remaining functional group presented in the polymer chains which react together under heating.

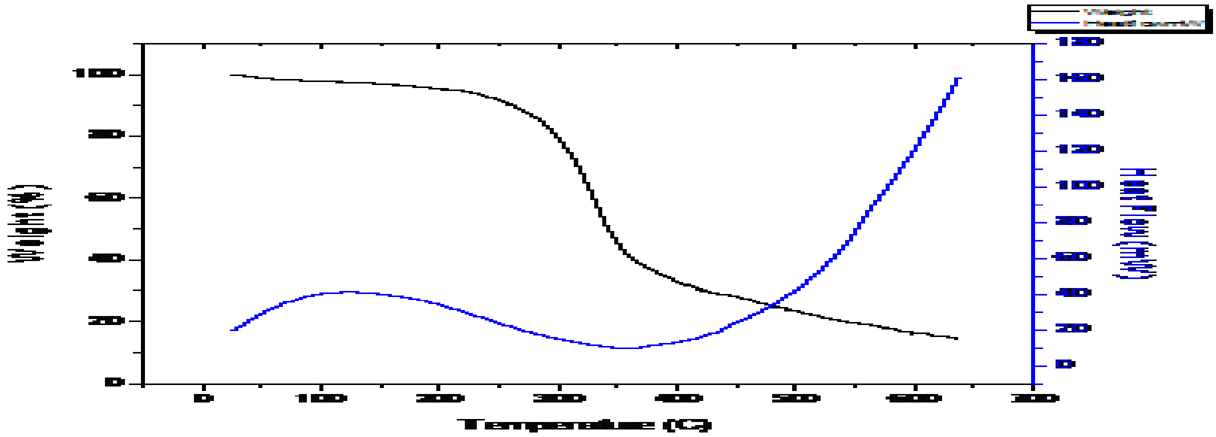


Fig.3-25: TGA and DSC thermogram of Polymer A

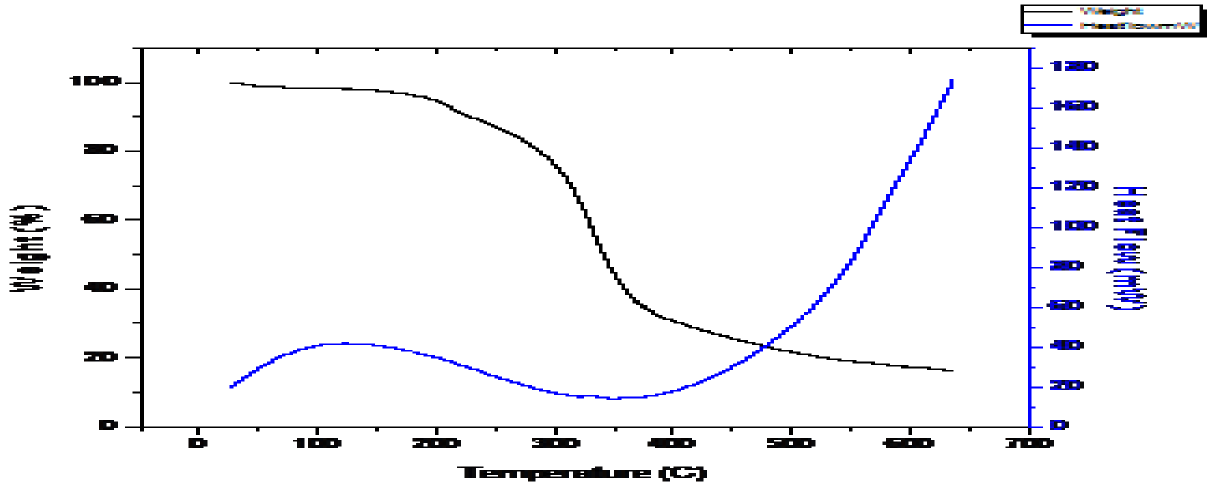


Fig.3-26: TGA and DSC thermogram of polymer B

H NMR Spectrum Studies

The newly synthesized Schiff-base ligands gave satisfactory spectral data and the molecular structure was assigned on the basic of^1 H NMR chemical shift. ^{1}H NMR spectra were determined in solution of DMSO with tetramethylsilane as an internal reference. The ^{1}H NMR spectrum of these ligands showed clear signal around (8.4-8.6) ppm for azomethane linkage N=CH- , also peak around 10 ppm for alkyl –OH.Also multiples signals at (6.6-7.4) ppm which were assigned to aromatic proton of phenyl ring.For ligand A multiples signal at (9.7-9.9) ppm which belong to amine group in the para position of phenyl ring.

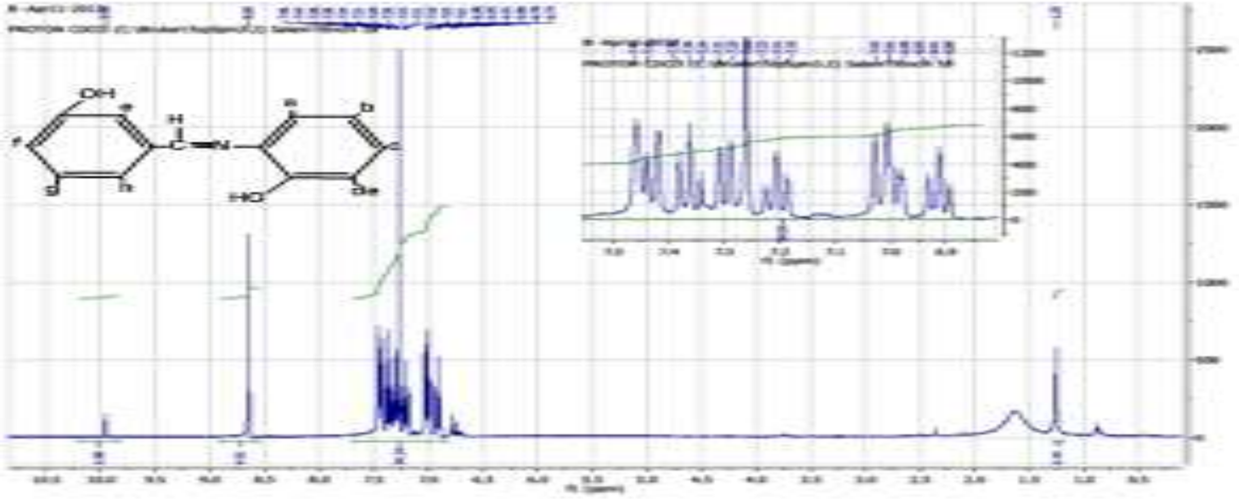


Fig. 3-27: NMR Spectrum for L_2

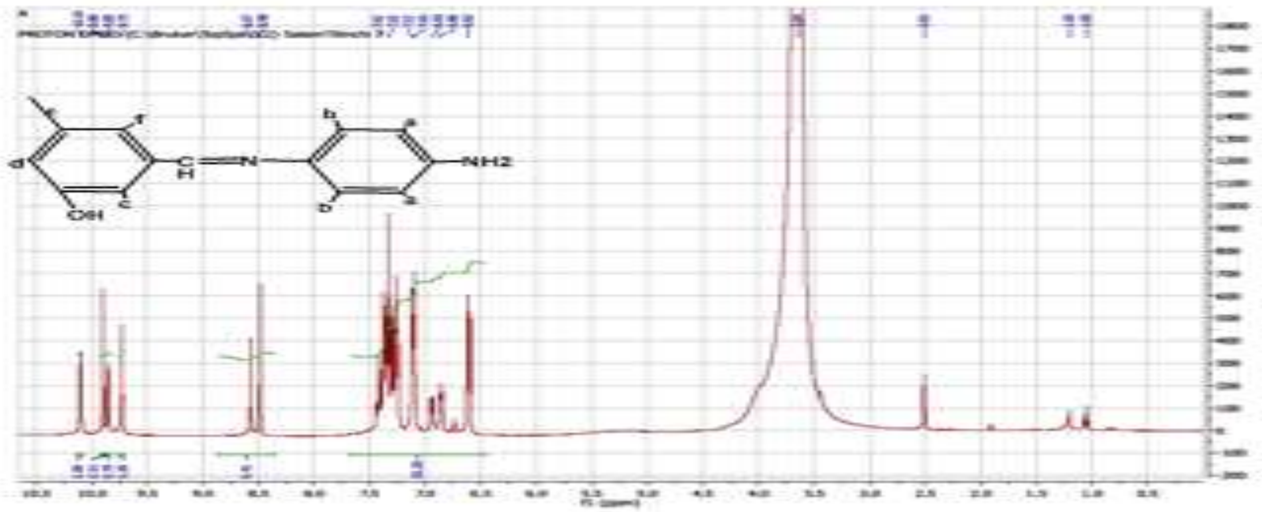


Fig.3-28: NMR Spectrum for L_1

Conclusion

Two of new Schiff-base compound were prepared from meta-hydroxy bbenzaldehyde and aromatic amine, these compound were characterized by using different technic like FTIR, CHN analysis and 1H NMR .complexion of this ligand was carried out with some metals ions (Cu^{11}, Cd^{11}) and several thermodynamic parameter were determined and the structure of complexation was proposed using UV-Visible spectroscopy. Finally polyurethane copolymers were prepared from this ligand and thermal stability was evaluated by using TGA and DSC technic.

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