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Thermodynamic and Synergistic effect on the extraction of Cu(II) & Ag(I) by use ligand 2-[α-Naphthyl azo]-4,5-diphenyl imidazole

دراسة ثرموديناميكية وبعض العوامل المؤثرة على استخلاص Ag(I) و Cu(II) بواسطة الليكاند ٢-[α-نفثايل ازو] -٤,٥ - ثنائي فنيل اميدازول

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Abstract:

2-[2-[α-Naphthyl azo]-4,5-diphenyl imidazole (α-NADPI) synthesized as new ligand and used for extraction Cu^{+2} ions Ag^{+1} ions and demonstrated the thermodynamic of reaction metal ions with ligand, as well as the effect of salting out, anion types and synergism effect on the extraction method ,the results shows thermodynamically the reaction between metal ions and ligand (α-NADPI) was exothermic for both metal ions ,salting out effect shows $MgSO_4$ was the best electrolyte salt which is giving higher distribution ratio(D), and shows the effect of electrolyte salt increase with increase the concentration of electrolyte salt solution ,anion effect shows picrate anion was the best anion and giving higher distribution ratio(D), synergism effect shows there is an effect for synergism to enhancement the extraction ability by participate synergic agent in the ion pair complex extracted and increase stability of complex extracted ,and shows there is one molecule of synergic agent TBP in the complex structure $[Cu(\alpha\text{-NADPI})(TBP)]^{+2}SO_4^{-2}$, $[Ag(\alpha\text{-NADPI})(TBP)]^{+}NO_3^{-}$.

الخلاصة :

الليكاند ٢-[α-نفثايل ازو] -٤,٥ - ثنائي فنيل اميدازول حضر واستعمل كليكاند جديد لاستخلاص ايونات النحاس Cu^{+2} والفضة Ag^{+1} وقد شملت الدراسة توضيح الجانب الثرموديناميكي لعملية الاستخلاص وكذلك تأثير التمليح وتأثير الأيونات السالبة وتأثير المشاركة Synergism على عمليات الاستخلاص ،حيث أوضحت الدراسة إن تفاعل التعقيد بين الليكاند الجديد والأيونات هو تفاعل باعث للحرارة Exothermic .تأثير التمليح يوضح إن الألكتروليت $MgSO_4$ هو الأفضل من بين الألكتروليتات الأخرى حيث تعطي أعلى قيمة لنسبة التوزيع(D) كما إن زيادة قيم نسب التوزيع (D) تزداد مع زيادة تركيز الألكتروليت.أما تأثير الأيون السالب يوضح إن أيونات البكرات كانت هي الأفضل لتعطي أعلى قيمة لنسبة التوزيع(D) .أما دراسة الSynergism توضح إن هناك تأثير لجزيئات TBP لرفع قابلية الاستخلاص بمشاركة جزيئات TBP في معقد الترابط الأيوني مع زيادة استقرارية المعقد كما إن الدراسة أوضحت مشاركة جزيئة واحدة من TBP في تركيب المعقد $[Ag(\alpha\text{-NADPI})(TBP)]^{+}NO_3^{-}$ $[Cu(\alpha\text{-NADPI})(TBP)]^{+2}SO_4^{-2}$.

Introduction:

Previous study about extraction of $Cu^{+2}$and Ag^{+1}ions by ligand (α-NADPI) shows the ion pair complex extracted was (1:1) (Metal:Ligand)$[Cu(\alpha\text{-NADPI})]^{+2}SO_4^{-2}$ and $[Ag(\alpha\text{-NADPI})]^{+}NO_3^{-}$. A.E.Arifien et al (2003)[1] studied the extraction of Fe(II),Co(II),Ni(II) and Cu(II) with thiourea monophosphazene (H_2MPZ) at three temperature as well as studied synergism effect on the extraction of Co(II) with TBP .J.Rais et al (2001)[2] studied the effect of anion (Cl^-,NO_3^-,ClO_4^-) and dicarbollide anion$[(C_2B_9H_{11})_2Co]^-$ on the extraction of metal ions by use neutral ligand .Ruijuan et al (2006)[3] synthesized Achiral complex for Zn(II) with new imidazole ligand and study its coordination by UV-Vis spectroscopy and CD spectroscopy .Nguyen et al (2007)[4] extracted Pd(II)with solvent extraction method by used various Ketones .Shumin et al (1992)[5] extraction Zn(II) and Cd(II) and study synergistic effects on the extraction method .Shumin et al (2000)[6] studied about different complexation ability and extraction for Zn(II) and Ni(II) by use two different derivatives imidazole ligands. Shusheng et al(2003)[7] studied the crystal and molecular structure of $[Ni(Im)_6](dtp)_2$ by X-ray crystallography (Im=imidazole ,dtp=o,o´-diphenyl dithio phosphate).Anita et al (2004)[8] studied synthesis molecular structure and reactivity of 5-

methylidene-1,2,3,5-tetrahydroimidazole [2,1-b] quinazolines .Ibrahim et al (2006)[9] synthesized anew imidazole ligand and studied its complexes with Co(II),Ni(II),Cu(II) by FT-IR,UV-Vis, HNMR, fluorescence, spectrophotometer ,elemental analysis and mass spectra. B.K.REDDY et al (2003) [10]studied spectrophotometric determination of copper in different samples by use new ligand .

2.Experimental

2.1.Aparatus:

Used schimadzu (UV-100-02) spectrophotometric single beam) and (UV1700 double beam spectrophotometer, Japan) for absorption measurements, for pH measurements used pH-meter, WTW-INOLAB, Germany, for Infrared spectrum (IR) used Pyeunicam, SP^3-2001, Infrared spectrophotometer ,England, and for elemental analyzer used Instrument (C.H.A) EA.1108

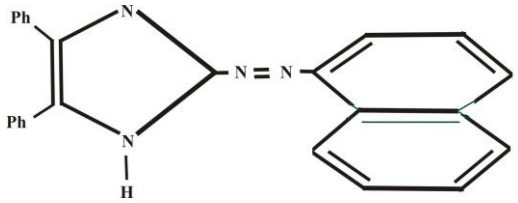
2.2.Reagents and preparation of standard solutions:

All reagents and solvents was obtained from commercial sources and used as received. Stock solutions of Cu(II)and Ag(I) ions at concentration of (1mg/ml)was prepared by dissolved fixed quantity of $CuSO_4.5H_2O$ and $AgNO_3$ in 100ml of distilled water contain 1ml of H_2SO_4 or $HNO_3$by used volumetric flask, other working solution prepared by dilution with distilled water, as well as prepared ($1x10^{-2}$M) dithizone dissolved in CCl_4 as stock solution for spectrophotometric determination of Cu^{+2} and Ag^{+1}ions in aqueous phase ,other working solution for dithizone prepared by dilution with CCl_4solvent ,stock solution for ligand (α-NADPI) dissolved in chloroform $CHCl_3$ at concentration of ($1x10^{-2}$M)was prepared, and other working solutions was prepared by dilution with chloroform $CHCl_3$ organic solvent.

2.3.Synthesis of ligand (α-NADPI)

By condensation reaction of benzyl with Hexamethylenetetramine prepare (4,5-diphenyl imidazole) [11] ,diazonium salt for Naphthylamine prepared [12], afterward added diazonium salt solution drop by drop to the imidazole solution in basic alcoholic solution at 0°to produce ligand (α-NADPI) .UV-Vis spectrum for ligand solution dissolved in chloroform shows three absorption peak ,the first peak at 234nm respect to (π-π*)electronic transition for imidazole ring[13],the second peak appear at 276nm for(π-π*)electronic transition to Benzene ring ,but the third peak appear at 463nm for intermolecular charge transfer (n-π*)[14].

IR spectrum shows many peak respects to stretching vibration for functional groups and giving strong peak at wave number $3350cm^{-1}$respect to stretching vibration for (N-H) in imidazole ring ,another peak at $3100cm^{-1}$belong to stretching vibration for aromatic bond (C-H) as well as (C=H)giving peak at $1600cm^{-1}$and appear two peaks at $1450cm^{-1}$and $1500cm^{-1}$for (-N=N-)group ,another peak appear at $700cm^{-1}$ and $750cm^{-1}$respect to the rings binding to the imidazole ring. Elemental analysis C.H.N shows the percentage of elements in ligand molecule identify with the theoretical percentage calculated, theoretical values was (C=80.20%,H=4.81%,N=14.97%) found values (C=80.11%,H=4.9%,N=14.66%) from the results of spectrum and elemental analysis suggested the structure of ligand was:-



2-[α-Naphthyl azo] -4,5-diphnyl imidazole

Figure(1):The structure of ligand (α-NADPI)

2.4 General procedure

Extraction method include taking 5ml aqueous phase contain fixed quantity of each ion (30µg)(4.72×10^{-5}M) of Cu^{+2}or (50µg)(4.63×10^{-5}M) of Ag^{+1}at optimum pH value adding 5ml of ligand solution dissolved in organic solvent and fixed concentration ,after shaking these two phases for suitable time separate the aqueous phase ,afterward determine the remainder quantity of metal ions Cu^{+2}or Ag^{+1}in aqueous phase by followed the method of spectrophotometric determination (dithizone method)[14],at later calculate distribution ratio(D) and percentage of extraction (E),can be by followed this method to study many different parameters effect on the extraction of metal ions by used ligand (α-NADPI),and from calibration curve Fig(2) to prepared by taking 5ml of aqueous solutions contain different quantity of Cu^{2+} or Ag^{+} 3µg to 40µg (0.472×10^{-5}M - 6.29×10^{-5}M) for Cu^{2+} and (0.278×10^{-5}M -3.71×10^{-5}M) for Ag^{+} at (pH=2-3) for Cu^{2+} and (pH=4-5) for Ag^{+} ,after that transfer each solution into 25ml separation funnel and added successive (1ml) of (1×10^{-4}M) dithizone solution dissolved in CCl_4 organic solvent, collect all portions in 10ml volumetric flask and shaking with (5ml) dilute ammonium solution at that complete the organic solution to (10ml) with CCl_4 and determine the absorbance at λ_{max}=550nm for Cu^{2+} and at λ_{max}=462nm for Ag^{+} and plot absorbance values against quantity of each ion in µg and the values of absorption always determine the remainder quantity metal ions in aqueous phase.

3.Results and Discussion

3.1.Temperature effect on the extraction method

Extracted (30µg)of Cu(II)ions ($4.72x10^{-5}$M) and (50µg) of Ag(I) ions ($4.63x10^{-5}$ M) in 10ml aqueous solution at (pH=7) for Cu(II)ions and (pH=9) for Ag(I) which is the optimum pH_{ex} values for extraction of each ion by (10ml) of ligand solution (α-NADPI) dissolved in suitable organic solvent at ($1x10^{-4}$M) concentration after shaking these two layer for (15min) at different temperature (10-50C°),separate the organic phase from aqueous phase and determine the remainder quantity of each ion extracted in aqueous solution by followed the spectrophotometric determination (dithizone method)[14],afterward calculate the metal ion quantity transferred to the organic phase and distribution ratio(D)at each temperature .The results in Table(1)and Figures(3,4)shows the reaction between the ligand (α-NADPI)and both metal ions Cu(II) and Ag(I) was exothermic reaction .

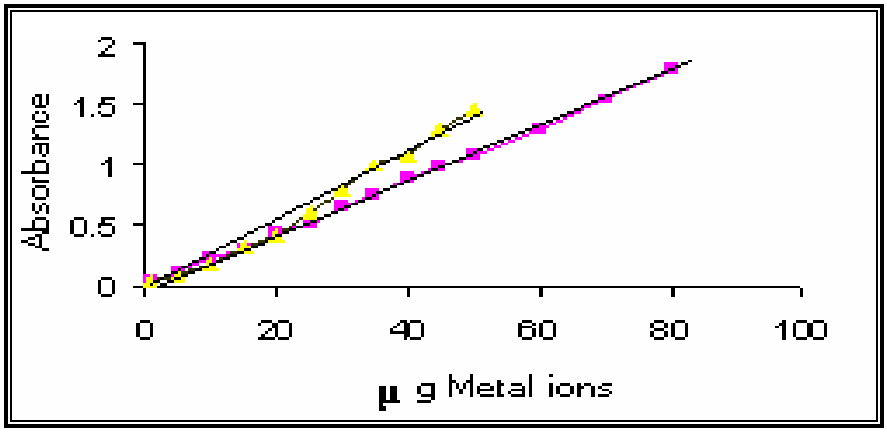
Table (1): Effect of temperature on extraction of Cu (II) and Ag (I).

T °C	T K°	1/Tx10^{-3} K°	D_{Cu}			D_{Ag}		
			$CHCl_3$	CH_2Cl_2	CCl_4	$CHCl_3$	CH_2Cl_2	CCl_4
10	283	3.53	29	25.9	22.56	22.08	18.64	17.15
20	293	3.41	24	21.22	19.49	19.83	16.59	14.62
30	303	3.3	21.22	18.19	16.59	18.01	14.62	12.85
40	313	3.19	17.7	16.47	14.79	15.5	12.88	10.96
50	323	3.09	15.5	14.63	13.45	12.69	11.09	9.33

After plot log D against 1/T obtained the Figures (3) (4) ,afterward calculate the extraction constant K_{ex} by application of relation below :

$$K_{ex}=\frac{D}{[M^{+n}]_{aq.}\,[L]_{org.}}$$

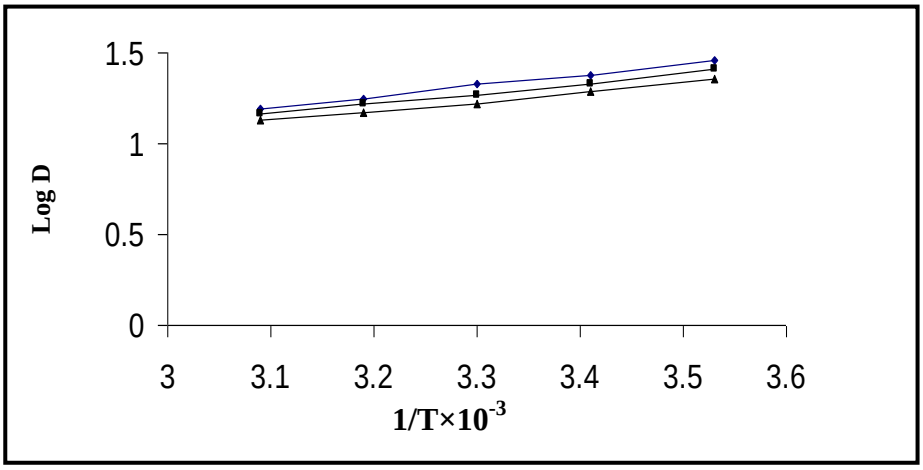
Where D is distribution ratio for each cation,[M^{+n}] the molar concentration of each cation in aqueous phase,[L] the molar concentration of ligand (α-NADPI)in organic phase.



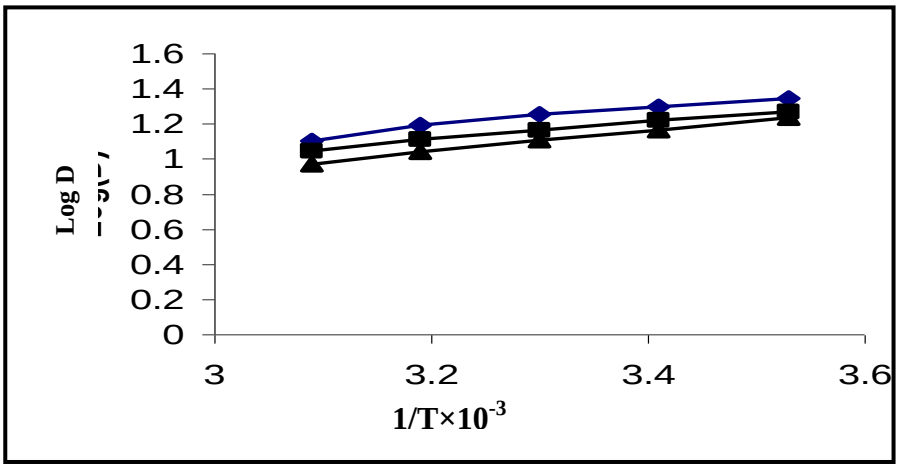
Fig(2):Calibration curve of ▲Cu(II) ■Ag(I)

For Ag^{+}
RSD=0.03%
RE=±0.2
D.L=1×10^{-6}M

For Cu^{2+}
RSD=0.04%
RE=±0.1
D.L=5×10^{-5}M



Fig(3):Temperature effect on extraction of Cu(II) in different solvents
♦$CHCl_3$■CH_2Cl_2▲CCl_4

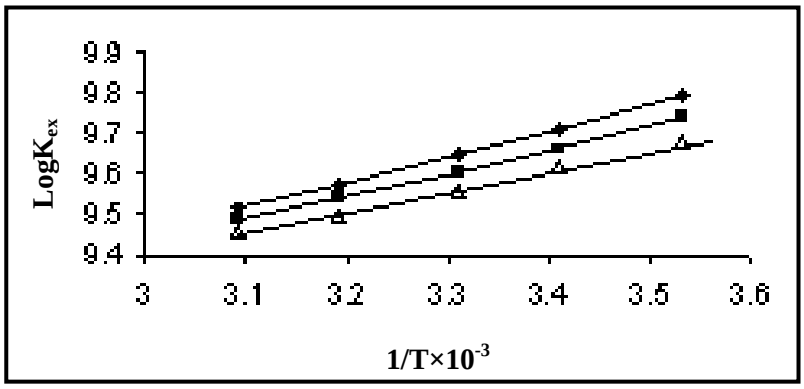


Fig(4):Temperature effect on extraction of Ag(I) in different solvents
♦$CHCl_3$■CH_2Cl_2▲CCl_4

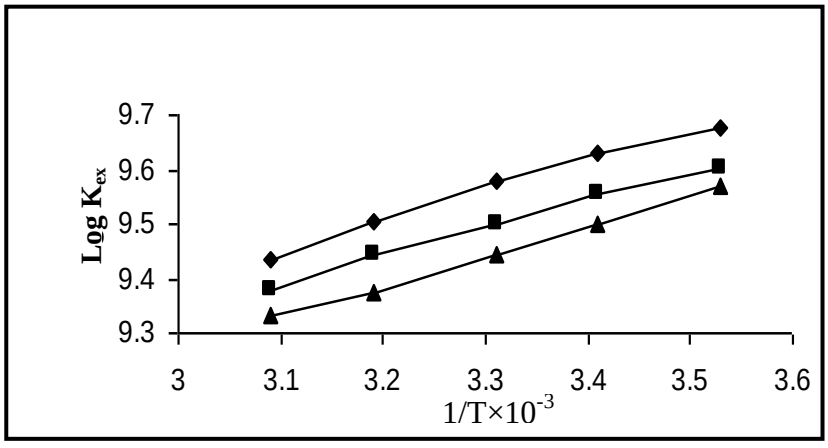
Table (2): Extraction constant K_{ex} for Cu (II) & Ag(I).

$1/T°K\times10^{-3}$	$K_{ex}\times10^{9}$Cu(II)			$K_{ex}\times10^{9}$Ag(I)		
	$CHCl_3$	CH_2Cl_2	CCl_4	$CHCl_3$	CH_2Cl_2	CCl_4
3.53	6.144	5.487	4.779	4.769	4.026	3.704
3.41	5.089	4.494	4.129	4.283	3.583	3.157
3.3	4.495	3.854	3.515	3.889	3.158	2.775
3.19	3.75	3.489	3.133	3.348	2.782	2.367
3.09	3.284	3.099	2.849	2.741	2.395	2.015

Plot log K_{ex} against 1/T°K for each ion at each organic solvent afterward determine the slope of each straight line.



Fig(5):Extraction constant for Cu(II)
♦$CHCl_3$■CH_2Cl_2▲CCl4
Slope $CHCl_3$ =0.63
CH_2Cl_2 =0.576
CCl4 =0.52



Fig(6):Extraction constant for Ag(I)
♦$CHCl_3$■CH_2Cl_2▲CCl4
Slope $CHCl_3$ =0.558
CH_2Cl_2 =0.526
CCl4 =0.614

Afterward calculate enthalpy for extraction of each ion by Vant-Hoff equation :

$$\frac{\Delta \text{Log}K_{ex}}{\Delta 1/T} = \frac{-\Delta H}{2.303R}$$

$$\text{Slope} = \frac{-\Delta H}{2.303R}$$

Free energy of extraction for each ion determine by relation below

$\Delta G_{ex} = -RT \ln K_{ex}$

At later calculate the entropy of extraction by relation.

$\Delta G_{ex} = \Delta H_{ex} - T\,\Delta S_{ex}$

Table (3): Thermodynamic data for extraction of Cu(II),Ag(I).

Thermodynamic Data	Cu(II)			Ag(I)		
	$CHCl_3$	CH_2Cl_2	CCl_4	$CHCl_3$	CH_2Cl_2	CCl_4
ΔH_{ex} KJmole^{-1}	-0.0118	-0.0108	-0.0097	-0.0104	-0.0098	-0.0115
ΔG_{ex} KJmole^{-1}	-51.86	-51.6	-51.28	-51.27	-50.88	-50.69
mole$^{-1}\Delta S_{ex}$ J k^{-1}	183.2	182.3	181.17	181.13	179.75	179.11

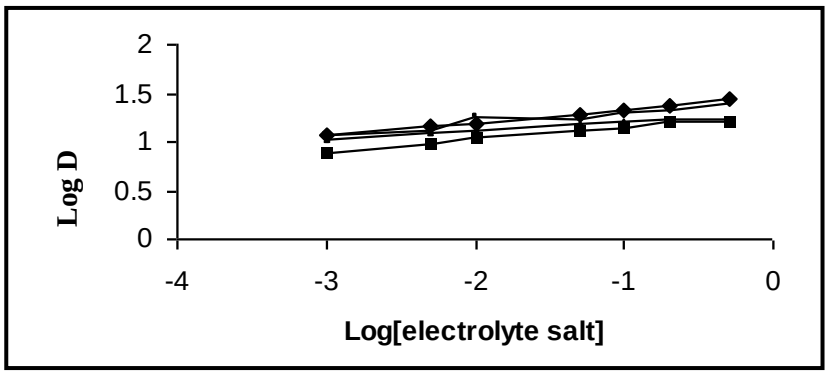
The results in Tables(2,3)shows the reaction between both metal ions Cu(II)&Ag(I) with ligand(α-NADPI) was exothermic in the three organic solvents was more suitable for this reaction and extraction method .As well as the results shows the effect of organic solvent structure on the complexation reaction for both ions, where chloroform organic solvent to contribute to giving more stable ion pair complex may be contact ion pair or solvent separated ion pair, decrease distribution ratio D and extraction constant K_{ex} with temperature increase may be by increase the steric effect of Naphthyl group in ligand molecule with temperature increase and dominate the dissociation equilibria of ion pair complex. The enthalpy of extraction for Cu(II)&Ag(I) reflect the structure of ion pair complex extracted was 1:1:1 Cu^{+2} (α-NADPI)SO_4^{-2} and Ag^{+}(α-NADPI)NO_3^{-} ,the high value of entropy of extraction ΔS_{ex} demonstrate the complexation reaction was entropic in region ,in addition to participate the organic solvent to increase the stability and complex formation which is appear chloroform organic solvent was more suitable for extraction method.

3.2.Salting -out Effect on Extraction Method

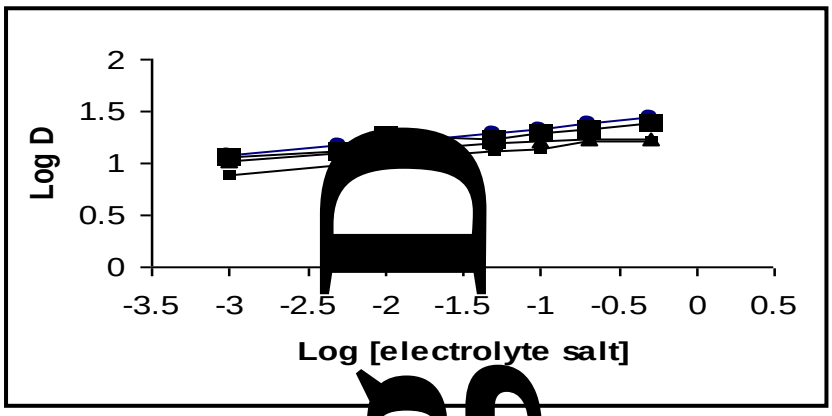
For appear the effect of inorganic electrolyte salt on qualification of extraction method, extracted 30µg Cu^{+2}(4.72×10^{-5}M) &50µg Ag^{+1}(4.63×10^{-5}M) at optimum condition pH=7 for Cu(II) and pH=9 for Ag(I) as well as (15min) shaking time in foundation different concentration (1×10^{-3}M-1M) of inorganic electrolyte salts $LiNO_3$,$(NH_4)_2SO_4$,$MgSO_4$,$NaNO_3$ by use 1×10^{-4}M of ligand solution (α-NADPI) dissolved in chloroform after complete shaking time separate organic phase from aqueous phase determine the remainder quantity of metal ion Cu(II)or Ag(I) in aqueous phase and the transferred quantity of each metal ion to organic phase by follow the spectrophotometric method (dithizone method) as detailed in general procedure, afterward determine distribution ratio (D) and percentage of extraction(E) as in Table(4) after plot logD values against values of log [electrolyte salt] to obtain Figure(6)(7)
.

Table (4):Salting out effect on extraction method

Electrolyte salt[M]	Cu(II)								Ag(I)							
	$MgSO_4$		$LiNO_3$		$NaNO_3$		$(NH_4)_2SO_4$		$MgSO_4$		$LiNO_3$		$NaNO_3$		$(NH_4)_2SO_4$	
	D	%E	D	%E	D	%E	D	%E	D	%E	D	%E	D	%E	D	%E
1×10^{-3}	14	93.3	13.26	93	11.48	92	8.09	89	12.02	92.3	11.5	92	10.61	91.4	7.62	88.4
5×10^{-3}	16.65	94.3	15.6	93.97	14.7	93.6	12.04	92.3	14.6	93.6	13.2	93	12.5	92.6	11.19	91.8
1×10^{-2}	19	95	17.4	94.6	15.6	94	13.28	93	15.6	94	14.62	93.6	13.2	93	11.82	92.2
5×10^{-2}	22.07	95.7	20.4	95.3	19.6	95.1	15.6	94	19.83	95.2	17.51	94.6	15.6	94	13.2	93
1×10^{-1}	24	96	22.07	95.7	20.4	95.3	16.65	94.3	21.72	95.6	19.83	95.2	16.8	94.4	13.7	93.2
2×10^{-1}	26.27	96.3	24	96	21.2	95.5	18.35	94.8	24	96	21.73	95.6	17.18	94.5	16.52	94.3
5×10^{-1}	29	96.7	27.3	96.5	20.4	95.3	19.68	95.2	27.24	96.5	24.64	96.1	17.18	94.5	16.8	94.4
1	29.61	96.73	26.27	96.3	20.1	95.2	21.22	95.5	28.4	96.6	24	96	17.51	94.6	17.18	94.5



Fig(7):Salting out effect on extraction method of Cu(II)
● $MgSO_4$, ♦ $LiNO_3$,▲ NaNO3 ,■ $(NH_4)_2SO_4$



Fig(8):Salting out effect on extraction method of Ag(I)
● $MgSO_4$, $LiNO_3$, ▲ $NaNO_3$, ■ $(NH_4)_2SO_4$

The results in Table(4) and Fig.(7&8) shows $MgSO_4$ was the best electrolyte salt for extraction Cu(II) and Ag(I) which is giving enhancement in distribution ratio (D) for the range ($5x10^{-2}M \rightarrow 1M$) when distribution ratio (D) with out using electrolyte salt was D=19.05 for Cu(II) and D=18.8 for Ag(I),the second effective electrolyte salt was $LiNO_3$and the third was $NaNO_3$ for Cu(II) but $(NH_4)_2SO_4$was not effective electrolyte salt for extraction both ions Cu(II)&Ag(I) and $NaNO_3$not effective for extraction Ag(I) ,the high charge density for Mg^{+2}ions appear high effective for destroy the hydration shell about Cu(II)&Ag(I) cation in aqueous phase to produce free ions and to increase complexation ability and increase distribution ratio ,as well as effective salting out on Cu(II) more than Ag(I) reflect the behavior of cation in aqueous phase.

3.3.Anion Effect on Extraction Method

According to extraction equilibria below appear the effect of anion on the complex formation and stability

$$M^{+n}_{aq.} + nL_{org.} + mX^{-n}_{aq.} \rightleftharpoons [ML_n]^{+n}X_m^{-n}{}_{org.}$$

Extraction (30µg)of Cu(II)ions ($4.72x10^{-5}M$) and (50µg) of Ag(I) ions ($4.63x10^{-5}M$) in 10ml aqueous solution at (pH_{ex}=7) for Cu(II)ions and (pH_{ex}=9) for Ag(I) contain 0.1M electrolyte salt for anion used by 10ml of ligand solution (α-NADPI)dissolved in chloroform at($1x10^{-4}M$) after shaking the two layers for 15min separate organic phase from aqueous phase ,afterward determine the remainder quantity of metal ion in aqueous phase and transferred quantity to the organic phase and calculate distribution ratio (D) and percentage of extraction(E) according to dithizone method detailed in general procedure[14],get the results in Table(5).

Table (5):Anion effect on the extraction method.

Electrolyte salt 0.1M	Cu(II)		Ag(I)	
	D	% E	D	% E
Sodium picrate $C_7H_2O_8N_3Na$	29.92	96.76	28.41	96.6
Sodium oxalate $Na_2C_2O_4$	26.27	96.33	19.83	95.2
Potassium di chlorate $K_2Cr_2O_7$	23.59	95.93	16.8	94.38
Potassium chromate $K_2Cr_2O_4$	16.7	94.35	15.51	93.94
Potassium permanganate $KMnO_4$	14.33	93.47	12.51	92.6

The results at Table(5) shows favorite picrate anion for extraction Cu^{+2}& Ag^{+1}ions which is giving higher distribution ratio(D) and percentage of extraction for both cation Cu^{+2}& Ag^{+1} as well as oxalate , but dichromate giving enhancement in distribution ratio (D) for Cu^{+2}only,chromate and permanganate not effective anion for extraction this cation may be reason of the behavior of this anion in aqueous solution.

3.4.Synergisitic Effect on the Extraction Method

Extracted (30µg)($4.72x10^{-5}$M) from Cu(II) and (50µg) ($4.63x10^{-5}$M) for Ag(I) in 10ml aqueous phase at (pH_{ex}=7) for Cu(II) and (pH_{ex}=9) for Ag(I) by 10ml of ($1x10^{-4}$M) ligand solution (α-NADPI) dissolved in chloroform and different concentration of Tributylphosphate TBP($5x10^{-7}$ - $5x10^{-4}$M) after shaking these two layers for 15min at room temperature and determine distribution ratio (D) and percentage of extraction E get the result in Table(6) as well as extracted (30µg)($4.72x10^{-5}$M) of Cu(II) and (50µg) ($4.63x10^{-5}$M) of Ag(I) in 10 ml aqueous phase at (pH_{ex}=7) for Cu(II) and (pH_{ex}=9) for Ag(I) by 10ml of organic solution contain ($1x10^{-4}$M) TBP and different concentration of ligand(α-NADPI)($1x10^{-6}$-$5x10^{-4}$M) and determine distribution ratio(D) and percentage of extraction (E) by followed dithizone method as detailed in general procedure [14],get the results in Table(7) after plot logD against log(TBP] or log[α-NADPI] to obtain Figures(8,9).From other hand extracted Cu(II)&Ag(I) at optimum conditions and concentrations by used 10ml organic solution contain $1x10^{-4}$M from (α-NADPI) and TBP dissolved in chloroform at different temperature (10°C-50°C),the results demonstrated at Table(8) and Figure(10).

Table (6):Effect of different concentration of TBP at constant concentration of (α-NADPI) on the extraction method.

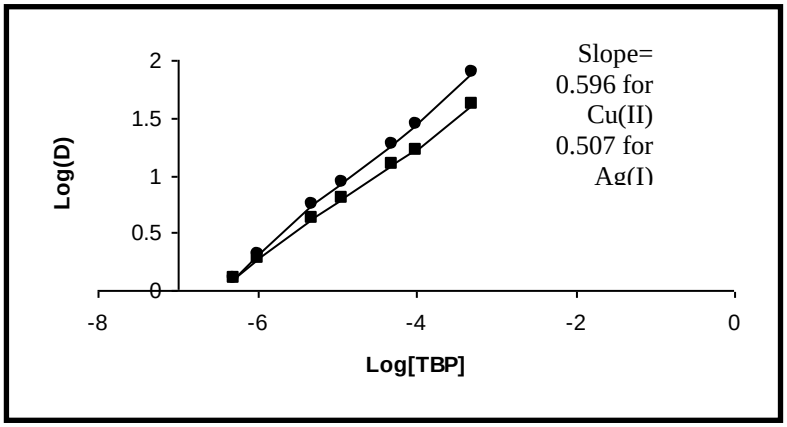
[TBP]	Cu(II)		Ag(I)	
	D	%E	D	E%
$5x10^{-7}$	١.٢٩	٥٦.٣	١.٢٦	٥٥.٧٥
$1x10^{-6}$	2.09	67.64	1.91	65.64
$5x10^{-6}$	5.6	٨٥84.	4.2	80.77
$1x10^{-5}$	9.5	90.48	6.31	.32٨٦
$5x10^{-5}$	17.7	94.65	12.4	92.53
$1x10^{-4}$	28.18	96.57	14.5	93.55
$5x10^{-4}$	79.43	98.76	41.68	97.66

Table (7): Effect of different concentration of (α-NADPI) at constant concentration of TBP on the extraction method.

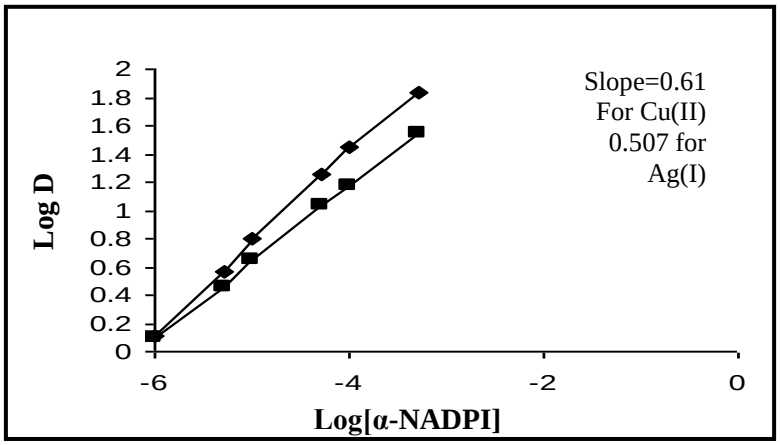
[α-NADPI]	Cu(II)		Ag(I)	
	D	E%	D	E%
$1x10^{-6}$	1.29	56.3	1.27	55.95
$5x10^{-6}$	3.9	79.59	2.82	73.82
$1x10^{-5}$	6.4	86.49	4.47	81.72
$5x10^{-5}$	18.6	94.9	10.72	91.47
$1x10^{-4}$	23	95.83	15.1	93.79
$5x10^{-4}$	70.79	98.61	29.7	96.74

Table (8): Effect of temperature

T°C	T°K	Cu(II)		Ag(I)	
		D	%E	D	% E
10	283	31.62	96.93	28.84	96.65
20	293	28.18	96.57	25.71	96.26
30	303	24.54	96.08	22.38	95.72
40	313	19.05	95.01	17.37	94.56
50	323	16.59	94.31	15.13	93.80



Fig(9):Effect of TBP conc.
• Cu(II) ■Ag(I)



Fig(10):Effect of ligand conc.
• Cu(II) ■Ag(I)

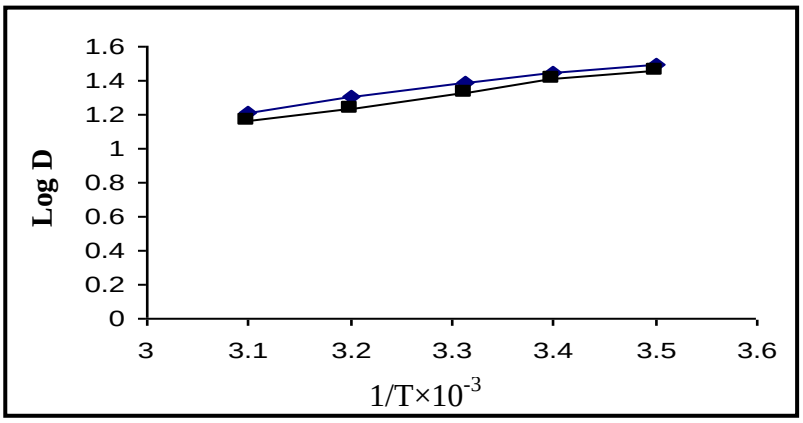


Fig (11): Effect of temperature.
• Cu (II) ■Ag (I)

After calculate extraction constant K_{ex} at each temperature by use the relation below to get the results in Table (9) .

$$K_{ex} = \frac{D}{[M^{+n}]_{aq}.[\alpha\text{-NADPI}]_{org}.[TBP]_{org.}}$$

Table (9): Effect of temperature on extraction constant Kex.

T°C	T°K	$1/T\times10^{-3}$	Cu(II) $K_{ex}\times10^{13}$	Ag(I) $K_{ex}\times10^{13}$
10	283	3.5	6.699	6.22
20	293	3.4	5.97	5.54
30	303	3.3	5.19	4.82
40	313	3.2	4.03	3.74
50	323	3.1	3.51	3.26

Plot log K_{ex} against 1/T to get Figure (12).

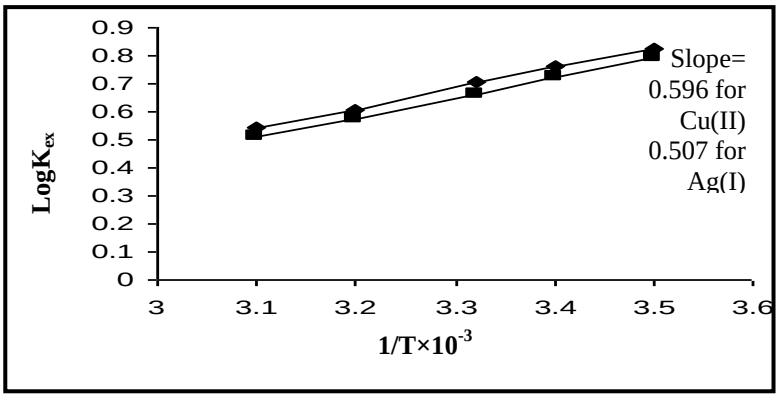


Fig (12):Effect of temperature on extraction constant K_{ex}.

Table (10): Thermodynamic data for extraction Cu^{+2}&Ag^{+1}.

Metal ions	ΔH_{ex} KJmole^{-1}	ΔG_{ex} KJmole^{-1}	ΔS_{ex} Jmole^{-1}K^{-1}
Cu^{+2}	-0.0131	-73.25	258.8
Ag^{+1}	-0.0131	-73.076	258

The results in Table(6,7) and Figure(8,9) shows the ion pair complex structure[1:1:1]$^{+n}$ anion [Metal:Ligand:TBP]$^{+n}$anion that is mean there is one ligand molecule and one molecule of TBP in the structure of one molecule of ion pair complex [Cu(α-NADPI)(TBP)]$^{+2}SO_4^{-2}$,[Ag(α-NADPI)(TBP)]$^{+}NO_3^{-}$from other hand synergistic molecules TBP participate in the formation of ion pair complex molecules but not change the structure of ion pair complex but only enhancement the stability of ion pair complex and extraction ability. .

The results in Table (8,9,10) and Figures(10,11) shows synergistic effect to increase free energy of extraction ΔG_{ex} for both ions by effect of increase spontaneous of complexation reaction in presence of TBP, the values of entropy higher than the same values in absence of TBP molecules by reason of increase free water molecules after binding TBP molecules in the coordination shell of complex. .

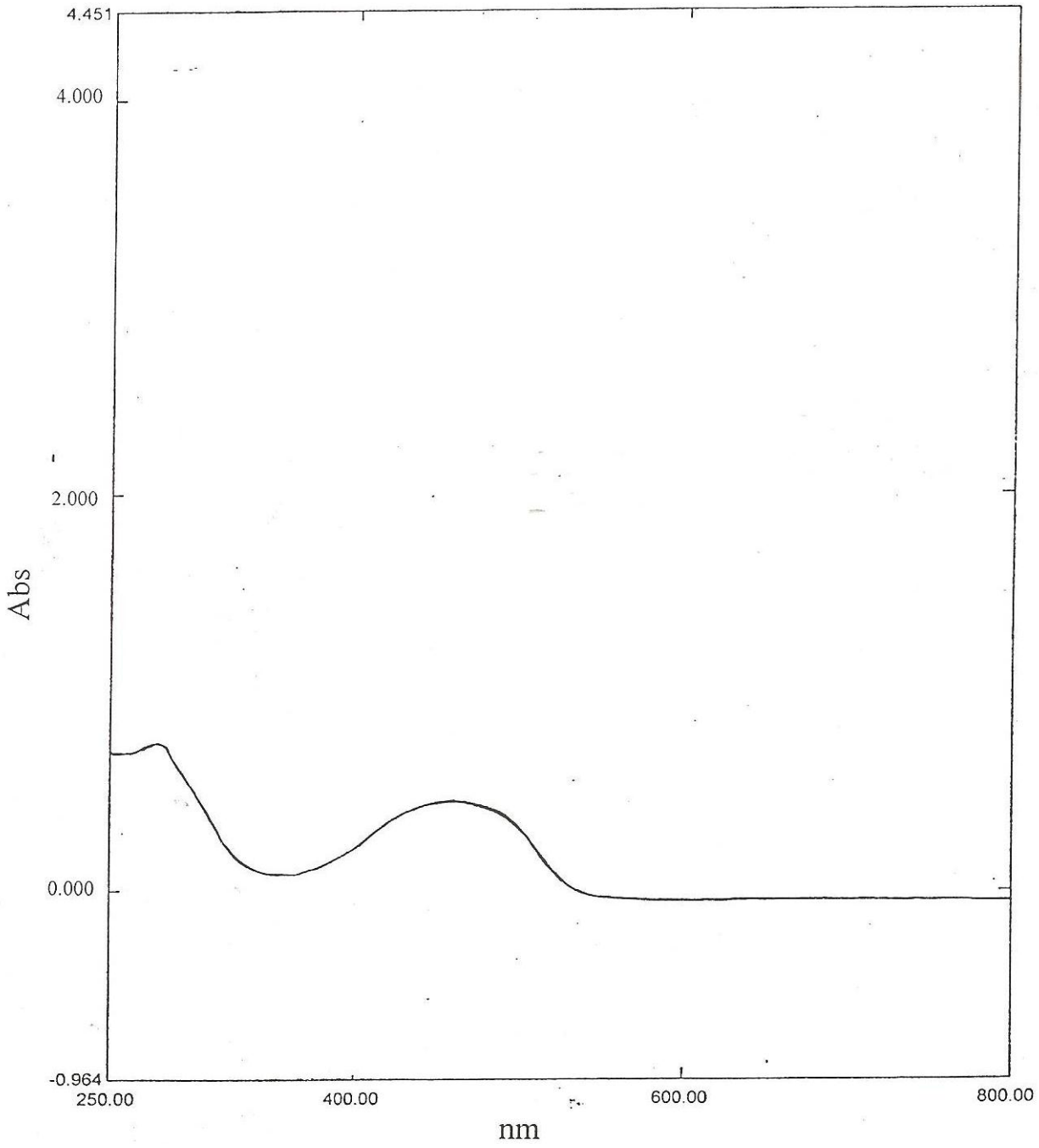


Fig (13):UV-Vis spectrum for ligand α-NADPI dissolved in chloroform.

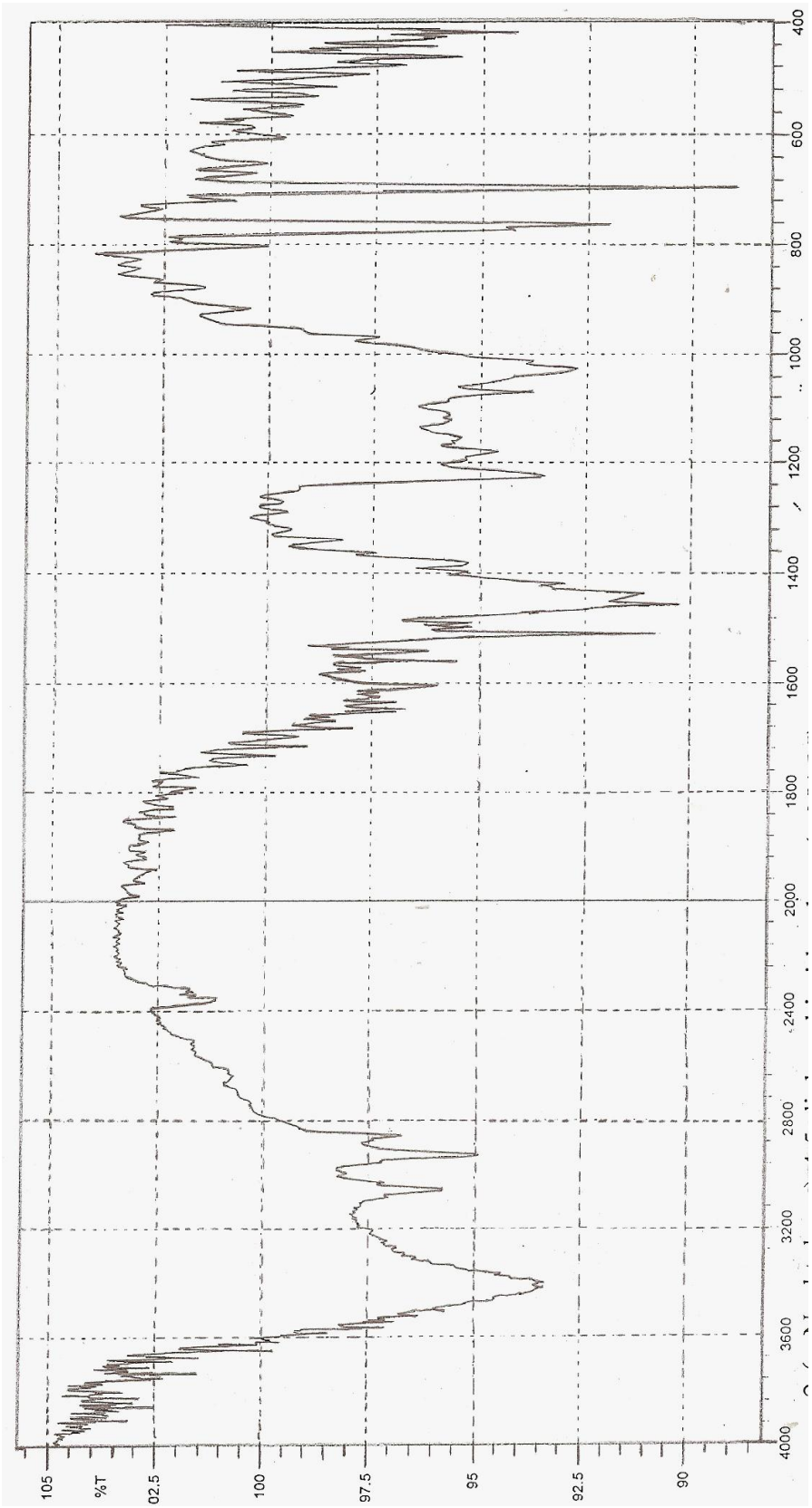


Fig (14):IR spectrum for ligand α-NADPI

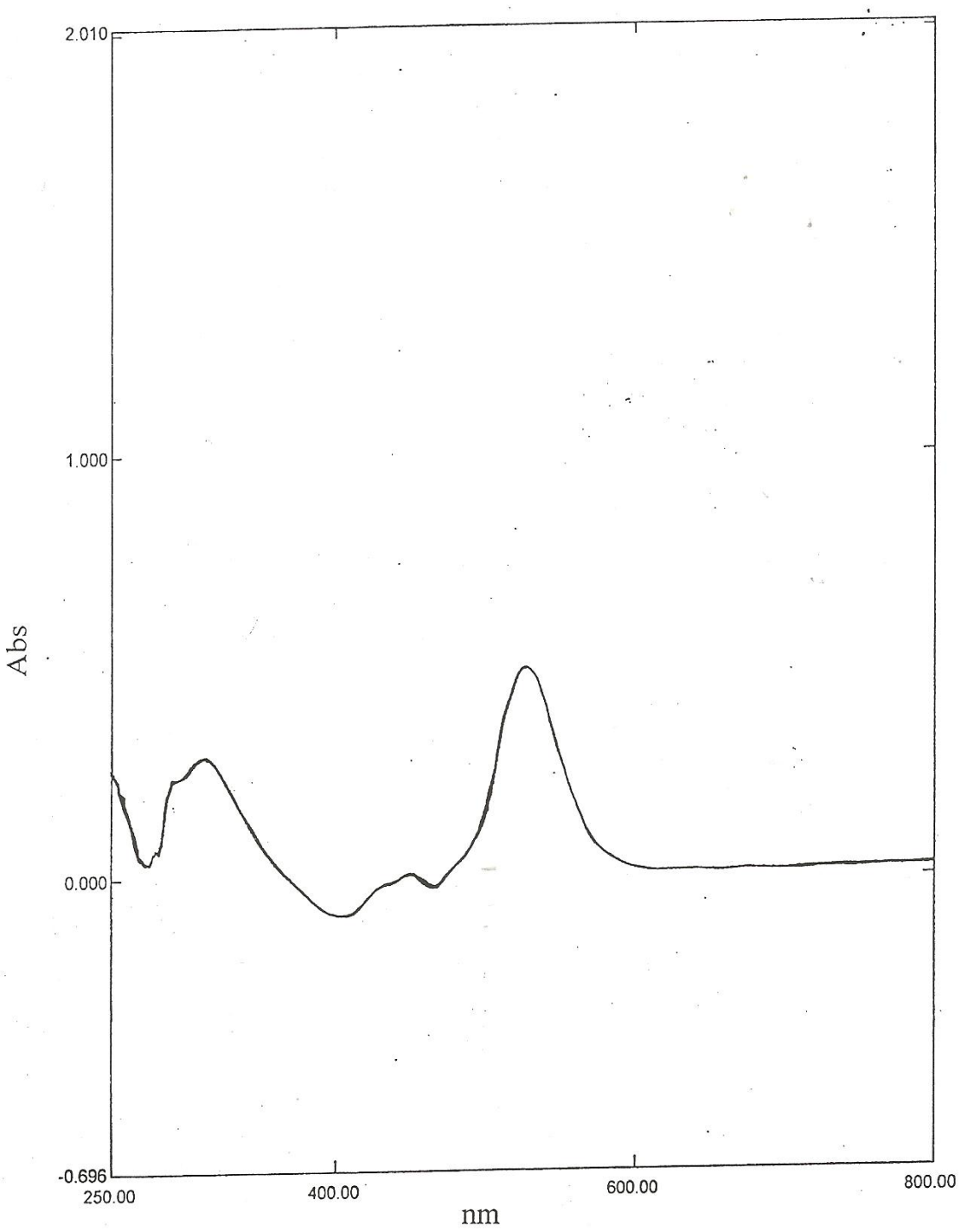


Fig (15): UV-Vis spectrum for complex of Cu^{2+} with ligand α-NADPI

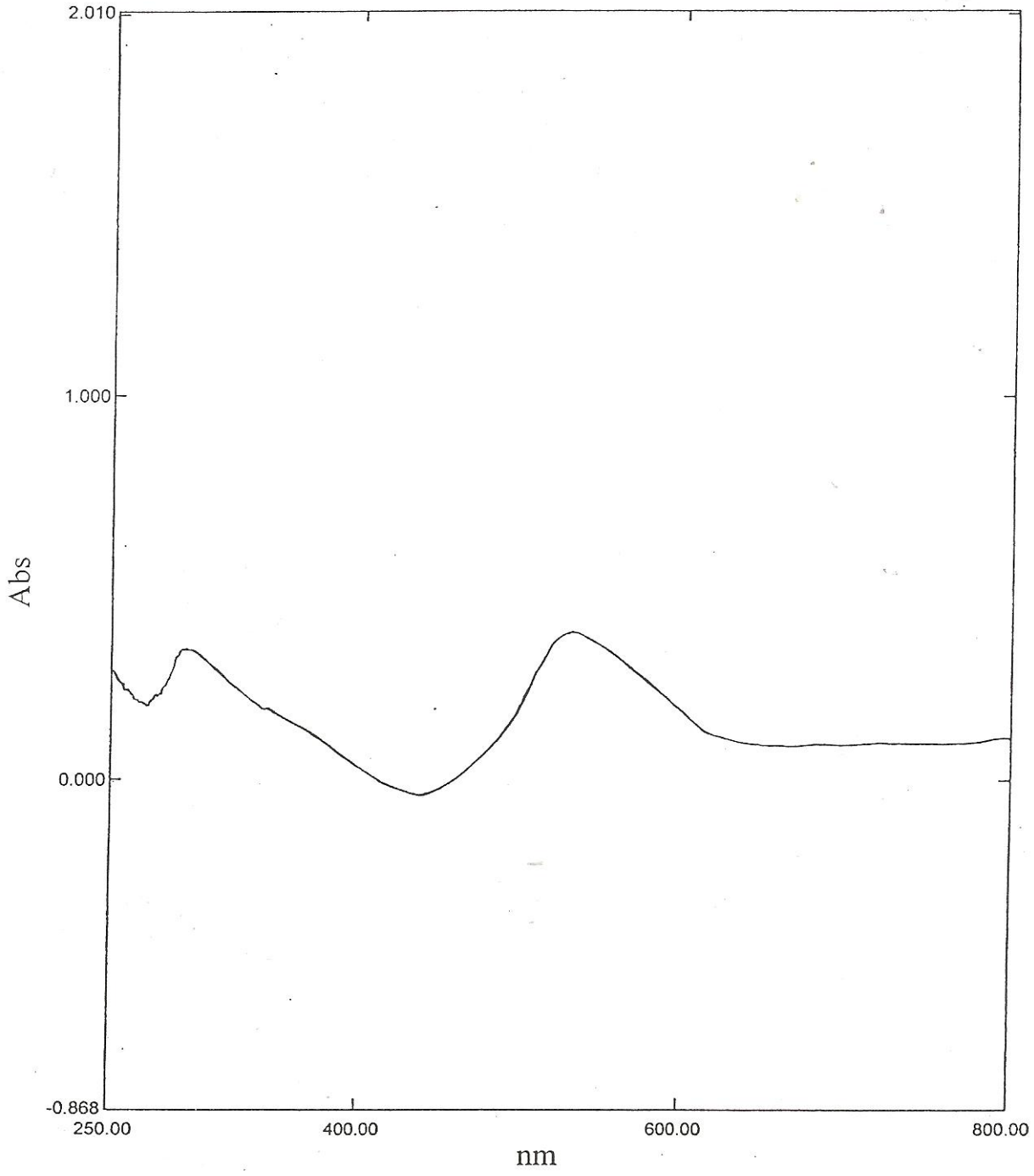


Fig (16): UV-Vis spectrum for complex of Ag^{+} with ligand α-NADPI

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