

## Synthesis of new ligand as imidazole derivative 2-[ $\alpha$ -Naphthylazo]-4,5-diphenylimidazole and its application about extraction of copper (II) and Silver (I) from aqueous solutions

Shawket K. Jawad

Abdul Allah M. Ali

Alaa Kh. Hassan

Department of Chemistry – College of education for girls – Kufa University

### Abstract

New derivative for imidazole compound which is 2-[ $\alpha$ -Naphthylazo]-4,5-diphenylimidazole ( $\alpha$ -NADPI) used as ligand for extraction of copper (II) and silver (I) according to solvent extraction method, dependence on the selectivity and sensitivity of imidazole compounds, toward transition metal cations, the experiment for extraction shows the optimum pH value was for  $\text{Cu}^{+2}$  ion ( $\text{pH}_{\text{Hex}} = 7$ ) and for  $\text{Ag}^{+}$  ion was ( $\text{pH}_{\text{Hex}} = 9$ ), the study effect of metal ions concentration shows the optimum concentration giving high distribution ratio (D) was (30  $\mu\text{g}$ ) ( $4.7 \times 10^{-5}$  M) for  $\text{Cu}^{+2}$  and (50  $\mu\text{g}$ ) ( $4.63 \times 10^{-5}$  M) for  $\text{Ag}^{+}$ , in the kinetic side for extraction study shows optimum shaking time for extraction was (15 minutes) for  $\text{Cu}^{+2}$  and  $\text{Ag}^{+}$ . Organic solvents effect studies shows there is not any linear relation between distribution ratio (D) and dielectric constant ( $\epsilon$ ) for organic solvents used but there is an effect for organic solvent structure on the extraction method to increase the stability of ion pair complex extracted, as well as stoichiometric studies shows the structure of ions pair complex extracted was (1:1) (metal:ligand) for both metal ions as  $[\text{Cu}(\alpha\text{-NADPI})] + 2\text{SO}_4^{2-}$  and  $[\text{Ag}(\alpha\text{-NADPI})] + \text{NO}_3^{-}$ .

### الخلاصة

مشتق جديد للاميدازول هو ٢-[ $\alpha$ -نفثالين آزو]-٤,٥-ثنائي فنيلا اميدازول ( $\alpha$ -NADPI) حضر واستخدم كليكند لاستخلاص النحاس (II) والفضة (I) حسب نظرية الاستخلاص الساتلي، اعتماداً على انتقائية وحساسية لمركبات الاميدازول نحو الايونات الموجبة للعناصر الانتقالية، تجارب الاستخلاص اظهرت ان قيم pH لعملية الاستخلاص كانت ( $\text{pH}_{\text{Hex}} = 7$ ) لايونات النحاس و ( $\text{pH}_{\text{Hex}} = 9$ ) لايونات الفضة، أما دراسة تأثير الايون الموجب في الطور المائي على عملية الاستخلاص اظهرت ان القيمة المثلى لتركيز الايون الفلزي التي تعطي أعلى قيمة لنسبة التوزيع (D) كانت (30  $\mu\text{g}$ ) ( $4.72 \times 10^{-5}$  M) لايونات النحاس و (50  $\mu\text{g}$ ) ( $4.63 \times 10^{-5}$  M) لايونات الفضة. أما من الجانب الحركي لعملية الاستخلاص فقد اظهرت الدراسة ان زمن رج الطورين للحصول على أحسن استخلاص وأعلى قيمة لنسبة التوزيع (D) كانت (١٥) دقيقة لكلا الايونين  $\text{Cu}^{+2}$  و  $\text{Ag}^{+}$ . أما دراسة تأثير المذيب العضوي فقد اظهرت التجارب انه لا توجد علاقة خطية بين قيم نسب التوزيع (D) وقيم ثابت العزل الكهربائي ( $\epsilon$ ) للمذيبات العضوية المستخدمة، ومن جانب آخر فقد اظهرت الدراسة ان هناك تأثير لتركيب المذيب العضوي على عملية الاستخلاص لزيادة استقرار معقد الترابط الأيوني المستخلص. كذلك دراسة تركيب معقد الترابط الأيوني المستخلص أثبتت ان تركيب المعقد المستخلص كان (١:١) لكلا الايونين (فلز:ليكند)  $[\text{Cu}(\alpha\text{-NADPI})] + 2\text{SO}_4^{2-}$ ;  $[\text{Ag}(\alpha\text{-NADPI})] + \text{NO}_3^{-}$ .

### 1.Introduction

Dependence on selectivity and sensitivity of imidazole derivatives growing concern in studying of complexes formed by imidazole derivatives. [1] synthesis new azo compound and used it for spectrophotometric determination of nickel (II). [2]

studies spectral and acid base properties of some imidazole derivatives. [3] studies on the reactivity of Cis-RuCl<sub>2</sub> fragment, spectral and electrochemical characterization of the products. [4] giving derivatives of ruthenium and iron complexes with Benzotriazole and Benzimidazole as simple model for proton-coupled electron transfer systems. [5] Studies complexes of copper (II), zinc (II) and nickel (II). [6] used imidazole derivatives as antifungal for inhibition of cytochromes P450. [7] used imidazole derivatives hybrid compound with inhibitory Histamines. [8] studied comparison extraction of Zn (II) and Ni (II) by different derivatives of imidazole. [9] synthesis and crystal structure of complex for nickel (II) with imidazole derivatives. [10] studies synthesis, molecular structure and reactivity of imidazole derivatives. [11] synthesis dicatonic extended Bis-Benimidazole. [12] synthesis of chiral salen Zn (II) and its coordination with imidazole derivatives. [13] studies characterization of a new imidazole ligand and its complexes with Co<sup>+2</sup>, Ni<sup>+2</sup>, and Cu<sup>+2</sup>.

## **2. Experimental**

### **2.1. Apparatus**

Shimadzu (UV-100-O2 spectrophotometer single beam) and (UV-1700 double beam spectrophotometer, Japan) used for absorption measurement and for pH measurements used pH-meter, WTW-INOLAB, Germany, for Infrared spectrum (IR) used Pyeunicam, sp3-2001, Infrared spectrophotometer, England, and for element analyzer used Instrument (C.H.N.) EA 1108.

### **2.2. Reagents and preparation of standard solutions**

All reagents and solutions were obtained from commercial sources and used as received. The stock solution of Cu<sup>+2</sup> ions (1 mg/ml) prepared by dissolved (0.3928 gm) from CuSO<sub>4</sub>.5H<sub>2</sub>O in (100 ml) distilled water contain (1 ml) of conc. H<sub>2</sub>SO<sub>4</sub>, other working standard solution prepared by dilution with distilled water, stock solution of Ag<sup>+</sup> ions prepared by dissolved (0.1575 gm) from AgNO<sub>3</sub> in 100 ml distilled water contain (1 ml) conc. HNO<sub>3</sub> by used volumetric flask, other working standard solutions prepared by dilution with distilled water. (1×10<sup>-2</sup> M) dithizone stock solution prepared by dissolved (0.0256 gm) in (10 ml) of CCl<sub>4</sub> by used volumetric flask, afterward prepared (1×10<sup>-4</sup> M) dithizone working standard solution by dilution with CCl<sub>4</sub>, needful for extraction method prepare (1×10<sup>-2</sup> M) stock solution for ligand (α-NADPI) by dissolved (0.374 gm) from ligand in (100 ml) of Chloroform by used volumetric flask.

### **2.3. Synthesis of ligand (α-NADPI)**

The synthesis of ligand (α-NADPI) include two steps, first step preparation of (4,5-Diphenyl imidazole)[14], the second step preparation of diazonium salt for α-Naphthylamine, afterward addition the solution of diazonium salt to the alcoholic basic solution of (4,5-Diphenyl imidazole) and by coupling reaction produced ligand, by followed condensation of Benzil with Hexamethylene tetramine produced (4,5-Diphenyl imidazole) afterward prepared diazonium salt for Naphthylamine according to shibuta method[15], at later added diazonium solution drop by drop to imidazole solution in basic alcoholic solution at (0 °C) to produced the ligand (α-NADPI).

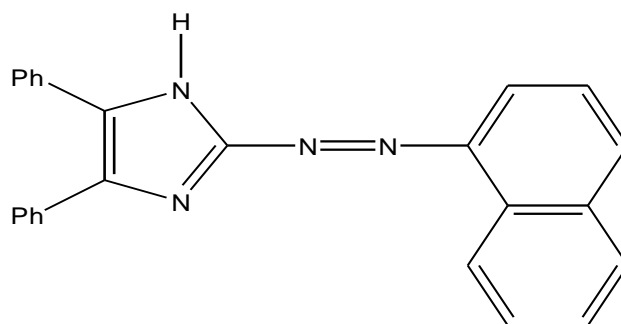
For detection the structure of synthesized ligand Uv-Vis-spectrum for ligand

solution dissolved in chloroform shows three absorption peaks, the first peak at 234 nm respect to ( $\pi$ -  $\pi^*$ ) electronic transition for imidazole ring[16], the second peak appear at 276 nm for ( $\pi$ -  $\pi^*$ ) electronic transition of benzene ring, and the third peak appear at 463 nm intramolecular charge transfer ( $\pi$ -  $\pi^*$ )[17].

IR spectrum shows many peak respects to stretching vibrations for functional groups and giving peak at wave number 3350  $\text{cm}^{-1}$  respect to stretching vibration for (N-H) in imidazole ring, another peak at 3100  $\text{cm}^{-1}$  respect to stretching vibration for aromatic band (C-H) as well as (C=N) giving peak at 1600  $\text{cm}^{-1}$  and appear two peaks at 1450  $\text{cm}^{-1}$  and 1500  $\text{cm}^{-1}$  for (-N=N-) group, another peak appear at 700  $\text{cm}^{-1}$  and 750  $\text{cm}^{-1}$  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-[ $\alpha$ -Naphthylazo]-4,5-diphenylimidazole

**Fig (1): The structure of ligand ( $\alpha$ -NADPI)**

## **2.4. General procedure**

For extraction of  $\text{Cu}^{+2}$  ions and  $\text{Ag}^{+}$  ions giving (5 ml) aqueous solution contain fixed quantity of metal ions at optimum pH and optimum shaking time after added (5 ml) of ligand solution ( $\alpha$ -NADPI) dissolved in organic solvent at fixed concentration, after complete shaking time separate organic phase from aqueous phase, afterward determine remainder quantity of metal ions in aqueous phase by application spectrophotometric method (Dithizone method) for each metal ions[8].from absorbance value accoding this method and calibration curve Fig (2) determine remainder quantity of metal ions in aqueous phase, after that determine the quantity of metal ions transferred to organic phase to produced ion pair complex by shaking the organic phase with three portions of conc. HCl each portion (2 ml), by this method dissociation the ion pair complex and return metal ion to the aqueous solution, at last determine the quantity of metal ion by (dithizone method), and its possible determine the quantity of metal ion transferred to organic phase by subtraction the quantity of metal ions in aqueous phase from the initial quantity of metal ions, afterward divided the quantity of metal ions transferred to the organic phase on quantity of metal ions remainder in aqueous phase to calculate distribution

ratio (D).

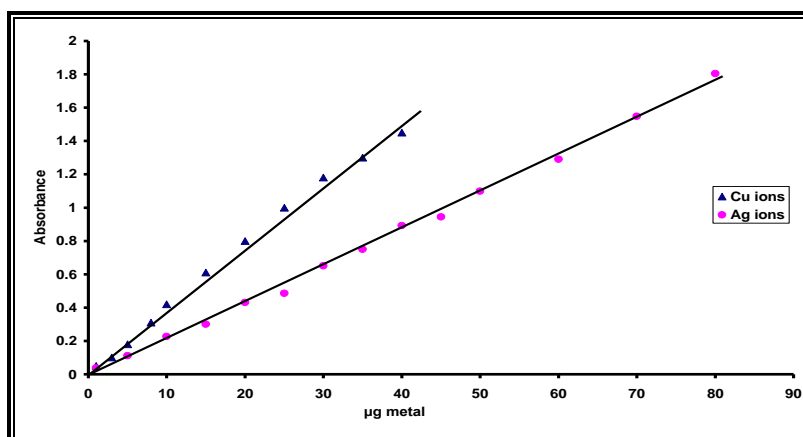
### 3- Results and Discussion

#### 3.1 Effect of pH

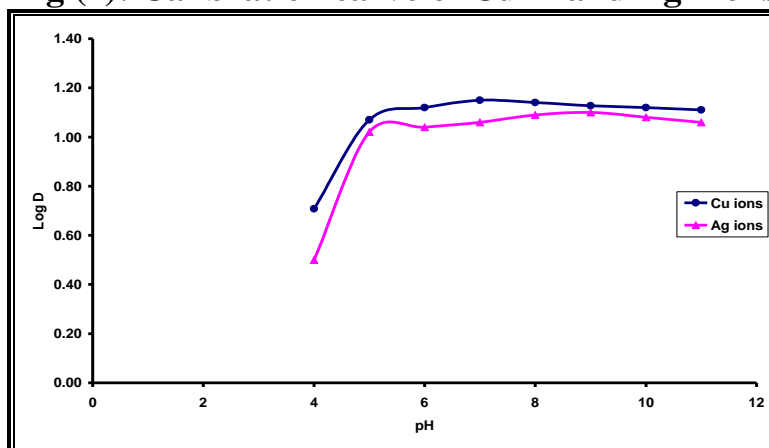
Extraction (20  $\mu\text{g}$ ) of each metal ions in (10 ml) aqueous solution ( $3.15 \times 10^{-5}$  M  $\text{Cu}^{+2}$ ) and ( $1.86 \times 10^{-5}$  M  $\text{Ag}^{+}$ ) at different pH (pH = 4-11) by (10 ml) ligand solution ( $\alpha$ -NADPI) dissolved in chloroform at ( $1 \times 10^{-4}$  M), after shaking the two layers for 15 minutes, separate organic phase from aqueous phase and determine the remainder metal ions in aqueous phase and transferred quantity to organic phase according to method detailed in general procedure, afterward calculate distribution ration (D) and percentage of extraction (E%). The results in Table (1) and Figure (3) shows the optimum pH for extraction metal ions by ligand ( $\alpha$ -NADPI) was (pH<sub>ex</sub>= 7) for  $\text{Cu}^{+2}$  and (pH<sub>ex</sub>= 9) for  $\text{Ag}^{+}$  ions.

**Table (1): Effect of pH on extraction of  $\text{Cu}^{+2}$  and  $\text{Ag}^{+}$  ions**

pH		4	5	6	7	8	9	10	11
$\text{Cu}^{+2}$	D	5.1	11.74	13.18	14.12	13.8	13.41	13.18	12.88
	%E	83.6	92.2	92.95	93.4	93.2	93.06	92.95	92.8
$\text{Ag}^{+}$	D	3.16	10.47	10.96	11.48	12.3	12.58	12.02	11.48
	%E	75.96	91.3	91.64	92	92.48	92.64	92.32	92



**Fig (2): Calibration curve of  $\text{Cu}^{+2}$  and  $\text{Ag}^{+}$  ions**



**Fig (3): Effect of pH on extraction of  $\text{Cu}^{+2}$  and  $\text{Ag}^{+}$  ions**

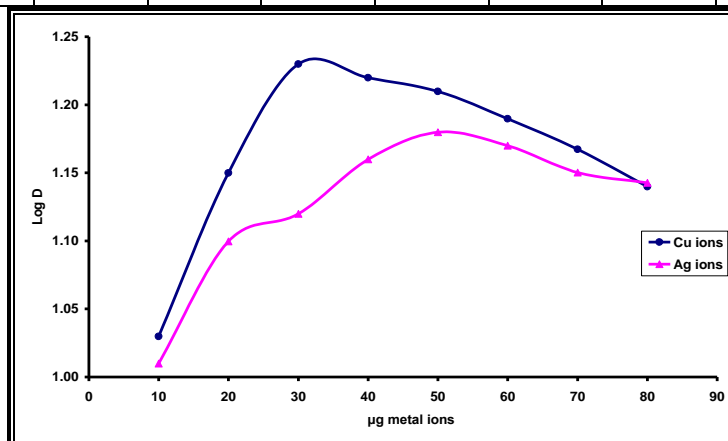
The results shows optimum pH for extraction of  $\text{Cu}^{+2}$  ions was ( $\text{pH}_{\text{ex}} = 7$ ), but for  $\text{Ag}^{+}$  ions was ( $\text{pH}_{\text{ex}} = 9$ ), at pH less than optimum value maybe effect to protonated ligand molecules and occupancy the lone pair electron on ligand atom and decrease the ability of complexation as well as minizing distribution ration (D) and percentage of extraction (E%) from other hand pH values more than optimum value effect to decrease distribution ratio (D) and percentage of extraction (E%) by reason of maybe produce stable species for metal ions can not be extracted and it is possible participate hydroxyl ion in the structure of ion complex which is more soluble in aqueous phase and decrease extraction ability, as well as the charge density of  $\text{Cu}^{+2}$  ions is more than for  $\text{Ag}^{+}$  ions this is effect to give good interaction between ligand molecule and  $\text{Cu}^{+2}$  ions than  $\text{Ag}^{+}$  ions and this behavior shows optimum pH for  $\text{Cu}^{+2}$  ions is less than for  $\text{Ag}^{+}$  ions.

### 3.2 Effect of metal ion concentration

Extraction different concentrations of  $\text{Cu}^{+2}$  and  $\text{Ag}^{+}$  ions in 10 ml aqueous phase ( $10 - 80 \mu\text{g}$ ) ( $1.57 \times 10^{-5} - 12.59 \times 10^{-5} \text{ M}$   $\text{Cu}^{+2}$ ) and ( $0.927 \times 10^{-5} - 7.41 \times 10^{-5} \text{ M}$   $\text{Ag}^{+}$ ) at ( $\text{pH} = 7$ ) for  $\text{Cu}^{+2}$  and ( $\text{pH} = 9$ ) for  $\text{Ag}^{+}$  ions by 10 ml of ligand solution ( $\alpha\text{-NADPI}$ ) dissolved in chloroform at ( $1 \times 10^{-4} \text{ M}$ ), after shaking the two layers for 15 minutes, separate organic phase from aqueous phase and determine the reminder metal ions in aqueous phase and transferred quantity of metal ions to organic phase to produce ion pair complex by followed the spectrophotometric method (dithizone method) detailed in general procedure, after that calculate distribution ratio (D) and percentage of extraction (E%). The results in Table (2) and Figure (4) shows the optimum concentration of metal ions giving higher distribution ration (D) and percentage of extraction (E%) was ( $30 \mu\text{g}$ ) ( $4.724 \times 10^{-4} \text{ M}$ ) for  $\text{Cu}^{+2}$  ions and ( $50 \mu\text{g}$ ) ( $4.63 \times 10^{-5} \text{ M}$ ) for  $\text{Ag}^{+}$  ions.

**Table (2): Effect of metal ion concentration on extraction method**

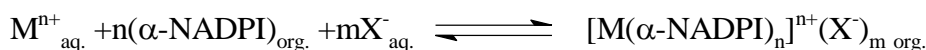
$\mu\text{g Mn}^{+}$		10	20	30	40	50	60	70	80
$\text{Cu}^{+2}$	D	10.71	14.12	16.98	16.59	16.21	15.48	14.7	13.8
	%E	91.5	93.4	94.4	94.3	94.19	93.9	93.6	93.2
$\text{Ag}^{+}$	D	10.23	12.58	13.18	14.45	15.13	14.79	14.13	13.89
	%E	91.1	92.6	92.95	93.5	93.8	93.7	93.4	93.3



**Fig (4): Effect of metal ions concentration on extraction method**

The extraction and ion pair complex formation depend on thermodynamic equilibria

as below



The equilibrium relation shows there is an effect for metal ion concentration on thermodynamic equilibria for ion pair complex formation and extraction method from the extraction constant value.

$$K_{ex} = \frac{[M(\alpha\text{-NADPI})_n]^{n+}(X^{-})_{m\text{ org.}}}{[M^{n+}]_{aq.} [X^{-}]_{aq.} [\alpha\text{-NADPI}]_{org.}}$$

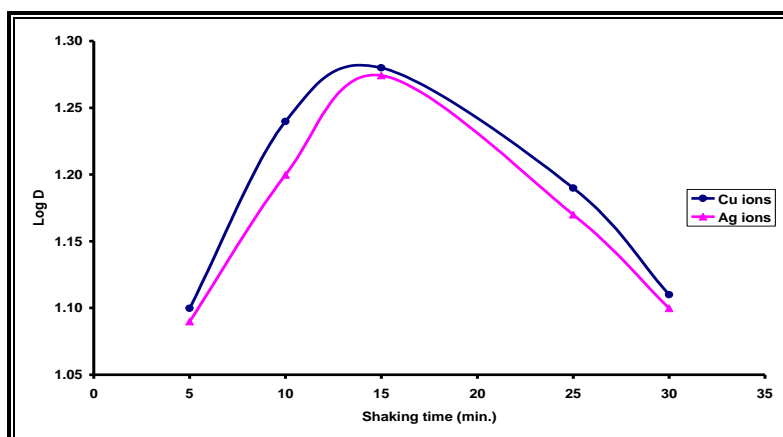
The results shows always the concentration of metal ions less or more optimum concentration effect to decline the distribution ratio (D) and percentage of extraction (E%), when the lower concentration don't allow to reach the equilibrium and minimizing the extraction ability and (D) values but the concentration more than optimum effect to dominate the dissociation equilibria according to le shatelier principle and also minimizing (D) values, from other hand the extraction method dependence on many energies which is controlled the extraction method such as  $\Delta G_{hydr.}$ ,  $\Delta G_{solv.}$ ,  $\Delta G_{ex}$ ,  $\Delta G_{part}$  and  $\Delta G_{ass}$ , the charge density of metal ions is very effective parameter effect on these energy values, the results appear by reason of charge density of Cu+2 more than Ag+ ions, the optimum concentration of Cu+2 ions (30  $\mu\text{g}$ ) less than for Ag+ ions (50  $\mu\text{g}$ ).

### 3.3 Effect of shaking time

Extraction (30  $\mu\text{g}$ ) ( $4.72 \times 10^{-5}$  M) Cu+2 ions at (pH<sub>ex</sub>= 7) and (50  $\mu\text{g}$ ) ( $4.63 \times 10^{-5}$  M) Ag+ ions at (pH<sub>ex</sub>= 9) in (10 ml) aqueous solution by (10 ml) organic solution of ligand ( $\alpha\text{-NADPI}$ ) dissolved in chloroform at ( $1 \times 10^{-4}$  M), after shaking the two layers for different times (5-30 minutes), separate these two layers and determine the reminder metal ions in aqueous phase and transferred quantity of metal ions to organic phase to produce ion pair complex by followed spectrophotometric method detailed in general procedure, after that calculate distribution ratio (D) and percentage of extraction (E%). The results in Table (3) and Figure (5) shows the optimum shaking time for extraction of both ions Cu+2 and Ag+ was (15 minutes).

**Table (3): Effect of shaking time on extraction method**

Shaking time (min.)		5	10	15	25	30
Cu+2	D	12.58	17.37	19.05	15.48	12.88
	E%	92.64	94.56	95	93.93	92.8
Ag+	D	12.3	15.84	18.80	14.79	12.58
	E%	92.48	94.06	94.95	93.67	92.64



**Fig (5): Effect of Shaking time on extraction method**

The results shows the shaking time less than optimum shaking time effect to not allow to reach equilibrium state and decline distribution ratio (D) and percentage of extraction (E%), but shaking for time more than optimum shaking effect to dominate the dissociation equilibria and minimizing distribution ratio (D) and percentage of extraction (E%).

### **3.4 Organic solvent effect**

To illustrated the role of organic solvent in extraction method and ion pair complex extracted formation and stability, extracted (30  $\mu\text{g}$ ) ( $4.72 \times 10^{-5}$  M) Cu+2 ions at (pH<sub>ex</sub>= 7) and (50  $\mu\text{g}$ ) ( $4.63 \times 10^{-5}$  M) Ag+ ions at (pH<sub>ex</sub>= 9) in 10 ml aqueous phase by 10 ml of organic solution of ligand ( $\alpha$ -NADPI) dissolved in different organic solvent differ in dielectric constant ( $\epsilon$ ) at ( $1 \times 10^{-4}$  M), after shaking the two layers for (15 minutes), separate organic phase from aqueous phase, afterward determine the reminder quantity of metal ions in aqueous phase and transferred quantity of metal ions to organic phase to produce ion pair complex, and calculate distribution ratio (D) and percentage of extraction (E%) by followed method detailed in general procedure. The results in Table (4) shows there is not any linear relation between dielectric constant ( $\epsilon$ ) of organic solvents used and distribution ratio (D), but shows there is an effect for organic solvents structure on the extraction method and stability of ion pair complex extracted, maybe by participate the organic solvent in ion pair complex formation to produced (tight ion pair complex) or (loose ion pair), as well as, the results demonstrate chloroform was favorable organic solvent for extraction both ions Cu+2 and Ag+ ions.

**Table (4): Organic solvent effect on extraction of Cu+2 and Ag+ ions**

Organic solvent	$\epsilon$	Cu (II)		Ag (I)	
		D	E%	D	E%
Dichloromethane	9.08	14.79	93.67	14.45	93.53
Chloroform	5.708	19.05	93.93	18.80	93.68
Benzene	2.804	13.28	93	13.03	92.87
Toluene	2.438	12.45	92.6	12.85	92.78
Carbon tetrachloride	2.238	14	93.33	13.18	92.95

To understand the role of organic solvents in the extraction method by determined thermodynamic data by used different organic solvents such as free energy of

transition ( $\Delta G_t$ ) and association constant ( $K_A$ ) and extraction constant ( $K_{ex}$ ) as well as free energy of extraction ( $\Delta G_{ex}$ ) by application the relation below

$$\Delta G_t = \frac{Z^2}{2r} \left( \frac{1}{\epsilon_w} - \frac{1}{\epsilon_0} \right)$$

$$K_A = \frac{[ML_m]^{n+} X_{n \text{ org.}}^-}{[M^{n+}]_{aq.} [L]_{org.}}$$

$$K_{ex} = \frac{K_A D [ML_m]^{n+} X_{n \text{ org.}}^-}{[M^{n+}]_{aq.} [L]_{org.}}$$

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

**Table (5): Thermodynamic data by organic solvent effect**

Organic solvents	$\Delta G_t$ KJmole-1		$K_A \times 10^4$		$K_{ex} \times 10^{10}$		$-\Delta G_{ex}$ KJmole-1	
	Cu(II)	Ag (I)	Cu(II)	Ag (I)	Cu(II)	Ag (I)	Cu(II)	Ag (I)
CH <sub>2</sub> Cl <sub>2</sub>	-0.245	-0.038	37	33.6	51.7	44.6	15.3	15.08
CHCl <sub>3</sub>	-0.405	-0.064	45.5	35.7	57.15	50.12	19.65	15.4
C <sub>6</sub> H <sub>6</sub>	-0.857	-0.135	23.3	28.6	28.12	33.79	13.9	14.4
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	-0.992	-0.157	19.2	25.1	21.26	28.9	13.2	13.99
CCl <sub>4</sub>	-1.067	-0.169	30.3	31.3	38.6	37.2	14.7	14.6

The results in Table (5) demonstrate the transition of metal ion increase with decrease of dielectric constant ( $\epsilon$ ), but the values  $K_A$ ,  $K_{ex}$  and  $\Delta G_{ex}$  giving higher values with chloroform organic solvent in spite of this organic solvent have not higher or lower dielectric constant this truth reflect the participation of organic solvent in the formation of ion pair complex extracted through the organic solvent structure but not the polarity.

### **3.5 Stoichiometry**

#### **3.5.1 Slope Analysis Method**

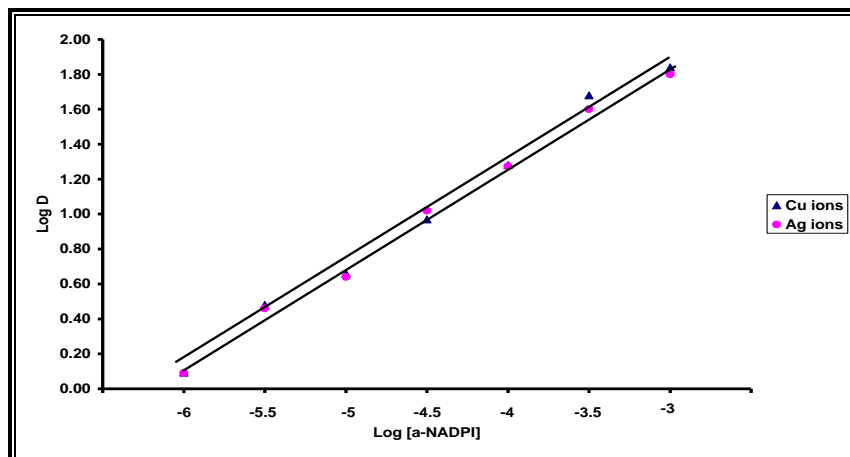
Extracted (30  $\mu$ g) ( $4.72 \times 10^{-5}$  M) Cu<sup>+2</sup> ions at (pH= 7) and (50  $\mu$ g) ( $4.63 \times 10^{-5}$  M) Ag<sup>+</sup> ions at (pH= 9) in (10 ml) aqueous phase by (10 ml) organic solution of different concentration ( $1 \times 10^{-6}$ - $1 \times 10^{-3}$  M) of ligand ( $\alpha$ -NADPI) dissolved in chloroform, after shaking the two layers for (15 minutes), separate organic phase from aqueous phase and determine the remainder quantity of metal ions in aqueous phase and transferred quantity of metal ions to organic phase, after that calculate distribution ratio (D) according to method detailed in general procedure. The results in Table (6) and Figure (6) shows the structure of ion pair complex extracted was (1:1) (metal:ligand) for both ions Cu<sup>+2</sup> and Ag<sup>+</sup> [Cu( $\alpha$ -NADPI)]<sup>+</sup>2SO<sub>4</sub><sup>-2</sup> ; [Ag( $\alpha$ -



NADPI)]+NO<sub>3</sub><sup>-</sup>.

**Table (6): Slope analysis method**

[ $\alpha$ -NADPI]	$1 \times 10^{-6}$	$5 \times 10^{-6}$	$1 \times 10^{-5}$	$5 \times 10^{-5}$	$1 \times 10^{-4}$	$5 \times 10^{-4}$	$1 \times 10^{-3}$
D Cu <sup>2+</sup>	1.24	3.02	4.57	9.33	19.05	74.86	69.18
D Ag <sup>+</sup>	1.23	2.88	4.37	10.47	18.80	39.81	63.10



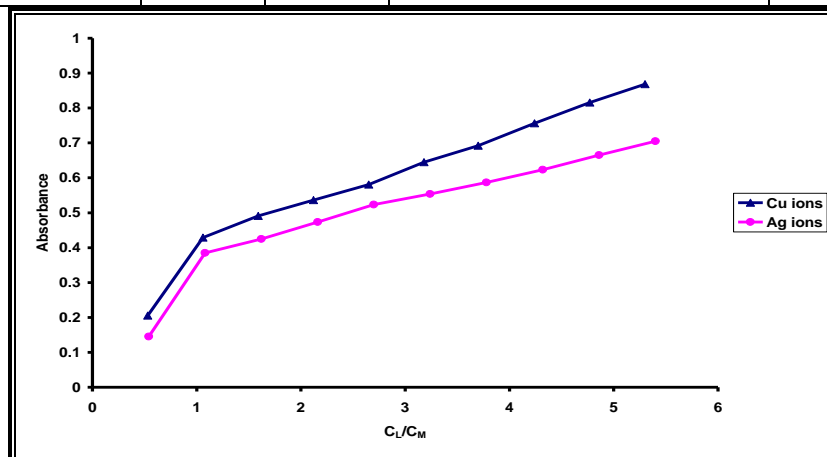
**Fig (6): Slope analysis method**

### 3.5.2 Mole Ratio Method

Extracted (30  $\mu$ g) ( $4.72 \times 10^{-5}$  M) Cu<sup>2+</sup> ions at (pH= 7) and (50  $\mu$ g) ( $4.63 \times 10^{-5}$  M) Ag<sup>+</sup> ions at (pH= 9) in (10 ml) aqueous solution by (10 ml) organic solution of ligand ( $\alpha$ -NADPI) dissolved in chloroform at different concentrations ( $2.5 \times 10^{-5}$  –  $2.5 \times 10^{-4}$  M), after shaking the two phases for (15 minutes), separate organic phase from aqueous phase and determine absorbance of organic phase at (533 nm) for Cu<sup>2+</sup> ion pair complex and at (527 nm) for Ag<sup>+</sup> ion pair complex against ligand solution as plank, afterward plot the absorbance values Vs mole ratio CL/CM. The results in Table (7) and Figure (7) shows the more probable structure of ion pair complex extracted for both ions Cu<sup>2+</sup> and Ag<sup>+</sup> was (1:1) (metal:ligand) as in the slope analysis [Cu( $\alpha$ -NADPI)]+2SO<sub>4</sub><sup>2-</sup> ; [Ag( $\alpha$ -NADPI)]+NO<sub>3</sub><sup>-</sup>.

**Table (7): Mole ratio method for extraction of Cu+2 and Ag+ ions**

[ $\alpha$ -NADPI]	CL/CM		Abs. Cu-complex (533 nm)	Abs. Ag-complex (527 nm)
	Cu+2	Ag+		
$2.5 \times 10^{-5}$	0.53	0.54	0.205	0.145
$5 \times 10^{-5}$	1.06	1.08	0.429	0.385
$7.5 \times 10^{-5}$	1.59	1.62	0.491	0.425
$1 \times 10^{-4}$	2.12	2.16	0.536	0.473
$1.25 \times 10^{-4}$	2.65	2.7	0.581	0.523
$1.5 \times 10^{-4}$	3.18	3.24	0.645	0.531
$1.75 \times 10^{-4}$	3.7	3.78	0.692	0.587
$2 \times 10^{-4}$	4.24	4.32	0.733	0.623
$2.25 \times 10^{-4}$	4.77	4.86	0.816	0.665
$2.5 \times 10^{-4}$	5.3	5.4	0.849	0.705

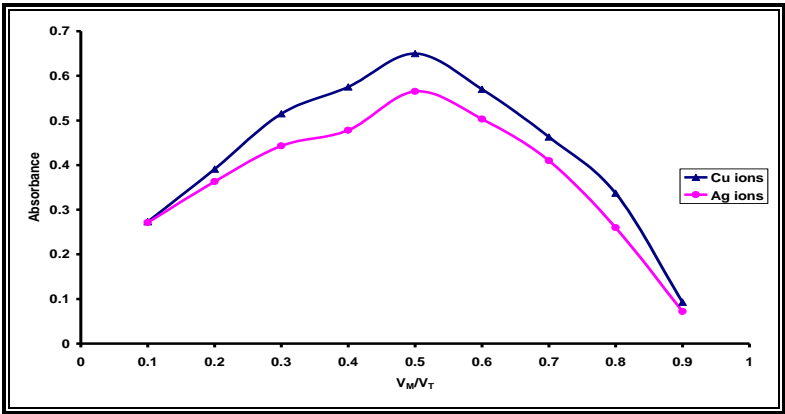
**Fig (7): Mole ratio method for extraction of Cu+2 and Ag+ ions**

### 3.5.3 Continuous Variation Method

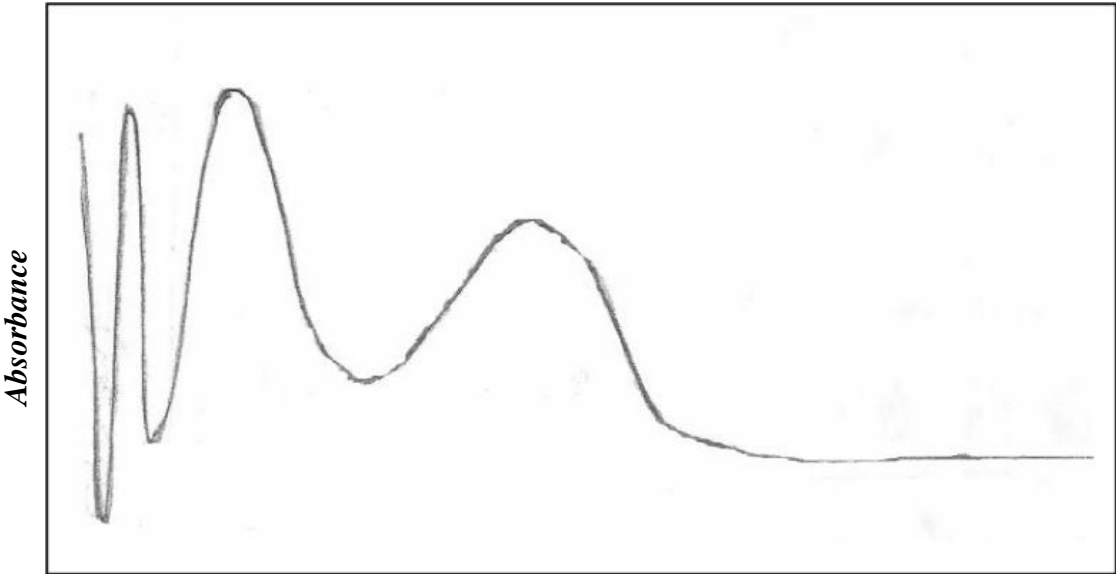
Prepare aqueous solutions for Cu+2 ions and Ag+ ions and organic solution of ligand ( $\alpha$ -NADPI) dissolved in chloroform at concentration of ( $1 \times 10^{-4}$  M) for all solutions, and then mix different volume of the two solutions to maximum volume (10 ml) at (pH= 7) for Cu+2 ions and (pH= 9) for Ag+ ions, after shaking these two layers for (15 minutes), separate organic phase from aqueous phase, determine absorbance of organic phase at ( $\lambda = 533$  nm) for Cu+2 ions and at ( $\lambda = 527$  nm) for Ag+ ions against ligand solution as plank, afterward plot absorbance value against the proportion of metal solution volume V<sub>M</sub> over total volume of solution after mixed V<sub>T</sub>. The results in Table (8) and Figure (8) shows the more probable structure of ion pair complex extracted was (1:1) (metal:ligand) [Cu( $\alpha$ -NADPI)]+2SO<sub>4</sub>-2 ; [Ag( $\alpha$ -NADPI)]<sup>+</sup>NO<sub>3</sub><sup>-</sup>.

**Table (8): Continuous variation method for extraction Cu+2 and Ag+ ions**

VM (ml)	VL (ml)	Absorbance Cu-complex $\lambda = 533 \text{ nm}$	Absorbance Ag-complex $\lambda = 527 \text{ nm}$
1	9	0.273	0.271
2	8	0.391	0.363
3	7	0.515	0.443
4	6	0.575	0.478
5	5	0.650	0.565
6	4	0.570	0.503
7	3	0.463	0.41
8	2	0.337	0.260
9	1	0.093	0.072



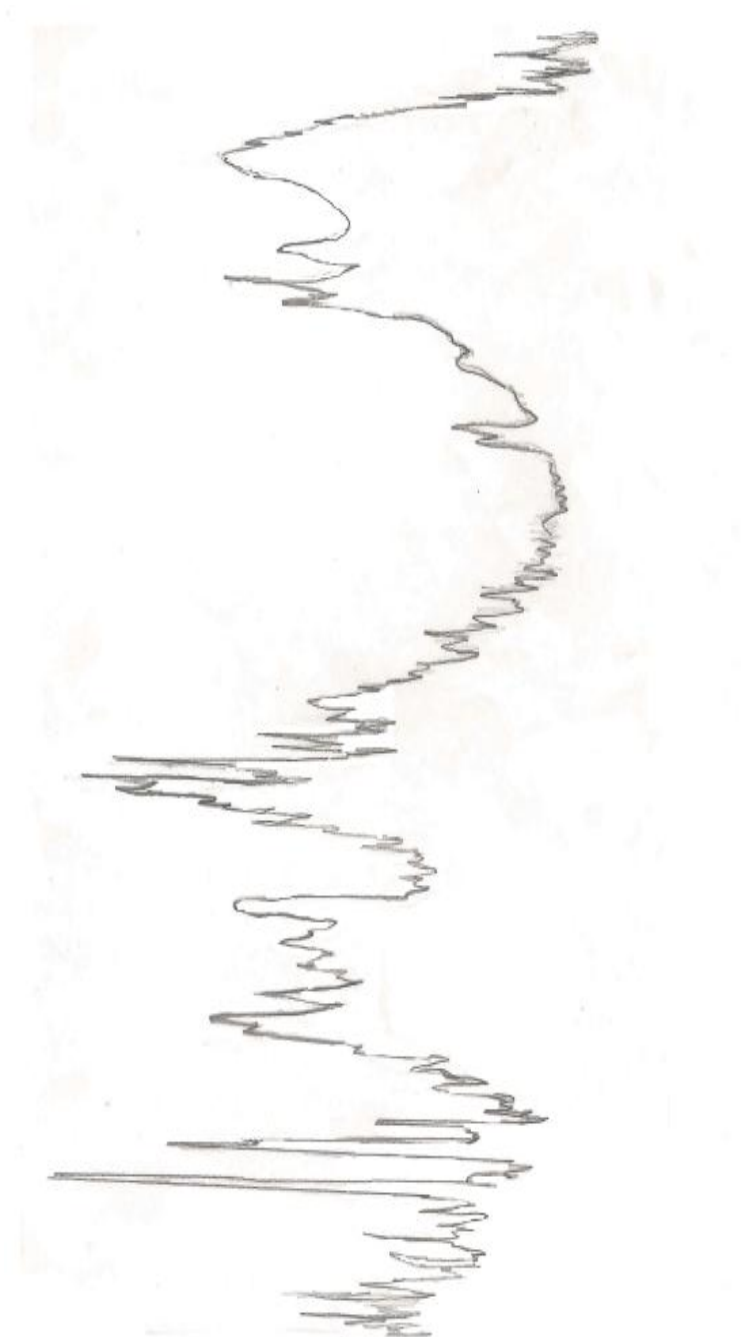
**Fig (8): Continuous variation method for extraction Cu+2 and Ag+ ions**



**Fig (9): UV-Visible spectrum of Ligand 2-[α-Naphthylazo]-4,5-diphenylimidazole**

4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 400

Wave number  $\bar{\nu}$



**Fig (10): infrared spectrum of ligand Ligand 2-[ $\alpha$ -Naphtholazo]-4,5-diphenylimidazole**

## References

- 1) Xue Zhang Van, Guafang Zhang and Chunbua Zhu "Synthesis of 2-[2 (methylbenzothiazolyl) azo]-5-dimethyl aminobenzoic acid and its application the spectrophotometric determination of nickel" *Analyst*, January 1998 Vol. 123 (109-112).
- 2) M.R. Mahmood, A.M. Hamman and S.A. Ibrahime "Spectral and acid- properties of some 2-(arylozo)-4,5-diphenylimidazole derivatives" *Z. Phys. Chemie*, Leipzig 265 (1984) 2, 5, 302-312.
- 3) Sanjib Pal, Chittaranjan Sinha "Studies on the reactivity of Cis-RuCl<sub>2</sub> fragment Ru(pph<sub>3</sub>)<sub>2</sub> (TaiMe)Cl<sub>2</sub> with N,N-chelators, spectral and electrochemical characterization of the products" *Proc. Indian Acad. Sci. (Chem. Sci.)* Vol. 113, No3, June 2001. pp. 123-183.
- 4) Reginaldo C. Rocha, Francissa N. Rein and Heurique E. Toma "Ruthenium and iron complexes with Benzotriazole and Benzimidazole derivatives as simple Model for proton coupled electron transfer systems" *J. Braz. Chem. Soc.* Vol. 12 No. 2, 234-242 (2001).
- 5) Ibolya Apro Torok "Copper (II), zinc (II) and Nickel (II) complexes of imidazole containing ligand and inositol derivatives, equilibrium, structure, hydrolytic activity " Ph.D. thesis University of Szeged, Department of Inorganic and Analytical Chemistry (2002).
- 6) Wejiang Zhang, Yamini Ramamoorthy, Tansel Kilicarslan, Helma Nolte, Rachel F. Tyndate and Edward M. Sellers "Inhibition of cytochromes P450 by antifungal imidazole derivatives" *Drug metabolism and disposition* Vol. 30, Issue 3, 314-318 March (2002).
- 7) Sve Grabmann, Joachim Apelt, Wolfgang Sippl, Xavier Ligneau, Heinz H. Pertz, Yuan Hui Zhao, Jean-Michel Arrang, C. Robin Ganellin, Jean Charlv Schwartz, Walter Schunack and Holyer Stark "Imizadazole derivatives as Novel class of hybrid compounds with inhibitory histamine N-Methyl transferase proteins and histamine hH<sub>3</sub> Receptor Affinities" *Bioorganic and Medical Chemistry* (2003) 2163-2174.
- 8) Beniamin Lenarcik, Teresa ranckyte and Agnieszka Kierzkowska "The comparison of Zn (II) and Ni (II) complexes with 1-octylimidazole and 1-octyl-methylimidazole" XVIII-th ARS separator-zlotopotok, Poland 2003.
- 9) Shusheny Zhang, Shiyang Wang, Yonghong Wen and Kui Jiao "Synthesis and crystal strcture of Hexakis (imidazole) nickel (II) O,O`-diphenyldithiophosphate [Ni(Im)<sub>6</sub>](Ph<sub>2</sub>O<sub>2</sub>PS<sub>2</sub>)<sub>2</sub>" *Molecular* 2003, 8, 866-872.
- 10) Anita Kornika, Franciszek sqczewski and Maria Gdaniec "Synthesis, Molecular, structure and reactivity of 5-Methylidene-1,2,3,5-tetra hydroimidazo[2,1-b] quinazolines" *Molecular*, 2004, 9, 86-101.
- 11) Zhang Kang, Christine C. Dykstra and David W. Boyskin "Tho synthesis of Dicationic extracted Bis-Benimidazole" *Molecular*, 2004, 9, 158-163.
- 12) Ruijhen Yuan, Wenjuan Ruan, Shujun Wany, Yinghui Zhany, Xiaoli Li Zhu " Synthesis of chiral salen Zn (II) and its coordination with imidazole derivaties and amino acid ester derivatives" *Journal of Coordination Chemistry*, Volume 59, Issue 6, April 2006. pp. 585-595.

- 13) Ibrahim Erden, Nebahat Demirhan, Uvi Acata "Synthesis and characterization a new imidazole ligand and its complexes with cobalt (II), Nickel (II) and copper (II)" Synthesis and reactivity in inorganic, metal organic and Nano metal chemistry, Volume 36, Issue 7 August 2006. pp. 559-562.
- 14) ((General and inorganic chemistry)) N.S. Akhmetov Moscow (1970).
- 15) S. Shibata, Furukawa and Nakashima Anal. Chem. Acta. 81, 131 (1976).
- 16) M.R. Mahmad; A.M. Hamman and S.A. Ibrahim, Z. Phys. Chem. 265, 203 (1984).
- 17) G. Leandri, A. Magini, F. Montanari and R. Fassering, Gazz. Chem. Ital., 85, 769 (1955)