

## Extraction of Copper Cu(II) from aqueous solutions by using of 2-[p-(2'-Pyrimidyl sulphamyl) phenyl azo]-4,5-diphenyl imidazole

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### Abstract:

The extraction of Copper has studies as complex means of (PSPAI) dissolved in chloroform .The search comprises the following aspects: the optimum pH values for extraction was ( $pH_{ext.} = 8$  ), so the suitable concentration of Cu(II) ions in aqueous solution which is giving highest distribution ratio (D) was (40  $\mu$ g ) ,studying effect of extraction time illustrated the optimum shaking time to reach the equilibria twenty minute . It was found from experiments that the best D of Cu(II) when the concentration of ligand equal to  $[6 \times 10^{-5} \text{ M}]$  and the probability form category enable for extraction  $[\text{Cu(PSPAI)}]^{+2}\text{SO}_4^{-2}$  from the slope of straight line of this category , that the more probable structure of ion pair (metal : ligand) complex extracted was 1 : 1.The study of organic solvent effect appear that there the D values increasing with increasing of dielectric constant of organic solvents used . The thermodynamic study demonstrates the complexation reaction is an exothermic .

**Key words: extraction ,PSPAI ,copper, azo, imidazole.**

### 1.Introduction

Since discovery imidazole compounds and its derivatives , growing concern in synthesis it and studying extraction of metals by it . Several studies were carried out to extraction of Cu (II) . P.Giridhar et al., studied the extraction of uranium and the effect of alkyl group on the extraction [1]. The extraction of Cu(II) and Ag (I) was studied by I.R.Ali using 2-[(4-carboxy methyl phenyl )azo]-4,5-diphenyl imidazole and 2-[(3-methyl benzene) azo]-4,5diphenyl imidazole [2]. A.K.Hassan , used 2-[( $\alpha$ -naphthyl) azo]-4,5-diphenyl imidazole to extraction of copper and silver [3] . Carolina et al., Studied the extraction of imidazole chelate complex with copper [4] . Ibolya Apro studied the complexation of Cu (II) ,Zn(II) and Ni(II) with imidazole as ligands and inositol derivatives [5] . Synthesis a new imidazole ligand and stadied it complexes with Co(II), Cu (II) , and Ni(II) carried by Ibramim and Nebahat. [6]. N. Dallali et al., studied cloud point extraction and determination of Zn, Co, Ni and

Pb by flame atomic absorption spectrometry using 2-Guanidinobenzimidazole as the complexing agent [7]. Jose´ J. Campos et al., Studied Coordination geometry isomerism induced by N-H -Cl, C-H-Cl, C-H-N, C-H-p and p-p supra molecular interactions in

mercury(II) complexes with tri pyridyl imidazole chelating ligands [8] . Synthesis of tri- and tetra substituted imidazoles carried by Daniel V. Paone and Anthony W. Shaw [9].As well as T.K. Mondal et al., studied

Synthesis , structure spectra and redox properties of Ruthenium–carbonyl complexes of 1-alkyl-2-(arylazo) imidazoles [10]. studies in solvent extraction of group (IIb) metal ion by new organic reagent ", 2-[4-Chloro-2- methoxy phenyl)azo]-4,5-diphenyl imidazole. carried by Abdul Muttalib [11].

#### 2.Apparatus

Used TRUV754(UV – Visible Spectrophotometer) for absorption measurements also pH measurements used 3320 Jenway pH Meter .

### **3.Materials**

CuSO<sub>4</sub>.5H<sub>2</sub>O , Dithizone (D<sub>2</sub>HZ), H<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>OH , Chloroform , Dichloromethane, Carbon tetra chloride and Toluene from B. D. H. and Merck The ligand 2- [p- (2'-Pyrimidyl sulphamyl) phenyl azo] -4,5-diphenyl imidazole synthesized as in the thesis [12].

#### 4.Procedure

i-preparation of standard stock solutions

(a) A solution of Copper (II) (1 mg/ml ) was prepared by dissolving 3.928 gm CuSO<sub>4</sub>.5H<sub>2</sub>O (0.015 mol) in 1 liter of distillation water containing 1 ml of conc. H<sub>2</sub>SO<sub>4</sub> .

(b) A standard solution of  $4 \times 10^{-4}$  M of (PSPA) prepared by dissolve 0.0192 gm in 100 ml of CHCl<sub>3</sub>.

(c) A solution of  $1 \times 10^{-2}$  M of Dithizone (D<sub>2</sub>HZ) prepared by dissolve 0.0256 gm in 10 ml of CCl<sub>4</sub>.

(d) A dilute solution of ammonia prepared by add 1 drop of conc. ammonia in 25 ml of D. W

ii-Calibration curve :

A different concentration of (1– 40 ) ìg of Cu(II) was prepared using D.W. then adjust a solutions to pH = 1, transfer the solution to a separate funnel and extract with portion of H<sub>2</sub>DZ in CCl<sub>4</sub> until the last portion does not change its green colour . With dithizone each extraction separate the organic Phase before the green dithizone reagent is completely complexed as the violet Cu(HDZ)<sub>2</sub> shake the aquase sample with the final portion of the dithizone sol. not less than 3 min., remove free by shaking the combined extracts with the dilute ammonia sol. Dilute the violet with CCl<sub>4</sub> in 10ml volumetric flask and measure the absorbance at 550 nm ,using the solvent as reference (Dithizone method)[13],the calibration curve illustrated in Fig(1).

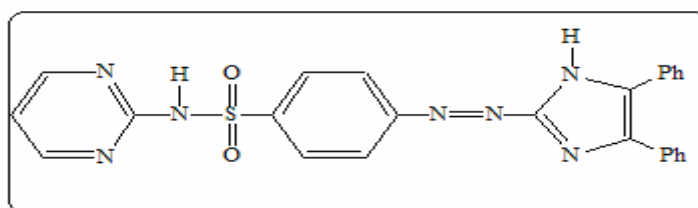
**iii- Extraction of Copper (II)**

A 5ml of aq. solution of Cu(II) has a specific concentration placed in (25 ml) separating funnel with equivalent volume of organic solution of ligand . Then shake the separation funnel within 20 sec . A two layer was separate .

**iv-Determination of distribution ratio**

A residue of Cu(II) was determined using spectrophotometric method ,then. A value of D was calculated using the relationship below :

$$\text{Distribution ratio (D)} = \frac{\text{Conc. Of Cu(II) in organic phase}}{\text{Conc. Of Cu(II) in aqua. Phase}} \quad [14,15].$$



**2-[p-(2-Pyrimidyl sulphamyl) phenyl azo]-4,5-diphenyl imidazole**

**Fig (1) : structure of ligand used in extraction method**

**4. Results and Discussion:**

Table (1) and Fig (3) show that the optimum value of pH extraction was ( $pH_{EX}=8$ ) . At pH less than optimum value effect to protonated the imidazole molecule ligand to occupy the pair of electron and then can not coordinate strongly with Cu(II) ions and give less stable ion pair complex and minimize the distribution ratio (D) ,also at pH value more than optimum value effect to decrease distribution ratio (D) by reason increase concentration of  $[Cu(PSPAD)]^{+2}(HO^-)_2$  complex this complex more soluble in aqueous phase and less extracted to organic phase and sovereignty the dissociation equilibria [16] .

The optimum Conc. Of Cu(II) ions in aqueous phase , which is (40ìg) ( $6 \times 10^{-4}$  M) was illustrated by Table (2) and Fig. (4).

Due to that conc. which was giving highest distribution ratio .The conc. Of Cu(II) ions less than optimum Conc. not allow to reach the equilibria therefore, the value of D minimizes, according to Lechatlier principle .

These results demonstrate the effect of metal ion conc. on the equilibria of complexation reaction

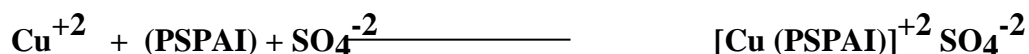


Table (3) and Fig (5) show that the best time for shaking was 20 minutes , and this show that the complex reach to equilibrium state, and this time was adopted in a residue of experiments .

The study of effect of PSPAI concentration on the extraction process illustrated in Table (4) and Fig. (6) that probability forming category enable for extraction  $[\text{Cu}(\text{PSPAI})]^{+2}\text{SO}_4^{-2}$  , from the slop of straight line of this category ,that the more probable structure of ion pair complex extracted was ( 1 : 1 ) (metal : ligand) . The results in Table (5) shows that there the distribution ratio (D) of Cu(II) ions increasing with increasing of dielectric constant of organic solvent this results reflect the effect of polarity of organic solvent on extraction, Table (6) ,(7) and Fig. (7)

demonstrate increasing values of free energy of transition of ions from aqua. phase to organic phase and the  $\Delta H_{ex}$ . values shows that the extraction of Cu(II) decrease with increasing temperature ( i.e process is exothermic ) from study different heat degree ( 20 k<sup>0</sup> -50 k<sup>0</sup> ) depending on (Vant- Hoff) relation ship [17].

$$\log K_{ex.} = \frac{-\Delta H}{2.303RT} + Constant \dots\dots(1)$$

The log K<sub>ex.</sub> verses (1/T k<sup>0</sup>) show the slope equal to  $\frac{-\Delta H}{2.303R}$  from this relation ship

calculate the Value  $\Delta H_{ex.} = -50.97 \text{ kJ} \cdot \text{mole}^{-1}$

$$\Delta G_{ex.} = -RT \ln K_{ex.} \dots\dots(2)$$

and

$$\Delta G_{ex.} = \Delta H_{ex.} - T\Delta S_{ex.} \dots\dots(3)$$

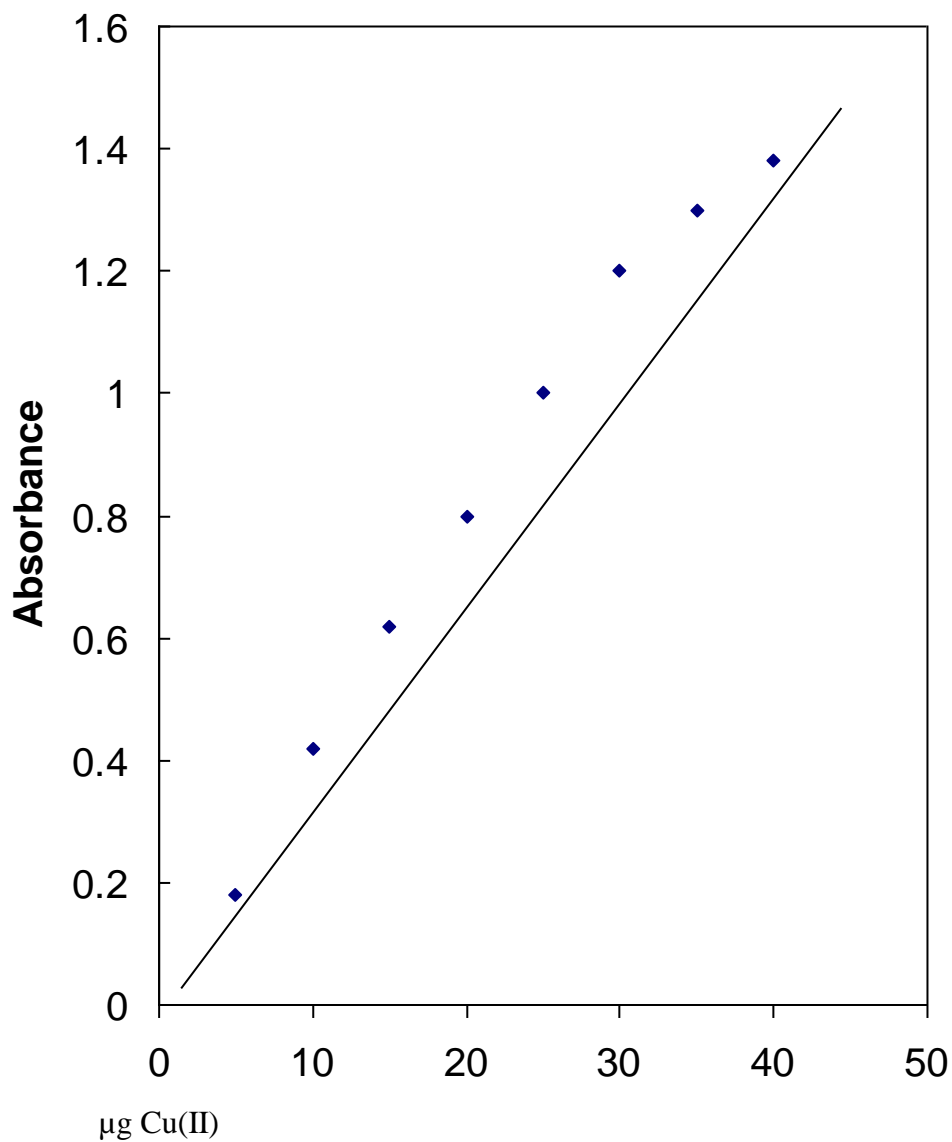
we used log D instead of log K<sub>ex.</sub> .

After application of these relations , the values of Gibbs free energy and entropy values showed by Table (7) .

This result suggested that the extraction of Cu(II) is easy and the negative value of  $\Delta H_{ex.}$  and this mean decrease in value of  $\Delta H_{solv.}$  and increase of  $\Delta H_{hyd.}$

$$\Delta H_{ex.} = \Delta H_{solv.} - \Delta H_{hyd.} \dots\dots(4) \text{ [18-20].}$$

and the value of  $\Delta H_{ex.}$  provide additional evidence about activity of (PSPAI) to extraction Copper ions.



**Fig.(2): Calibration Curve of Cu (II)**

**Table ( 1 ) : Effect of pH on extraction of Cu(II) ions  
( $6 \times 10^{-5}$  M of Cu(II) , 10 min. ,  $6 \times 10^{-5}$  M(PSPAI) in  $\text{CHCl}_3$ )**

pH	5	6	7	8	9	10
D	1.6	1.807	2.55	9	2.07	—

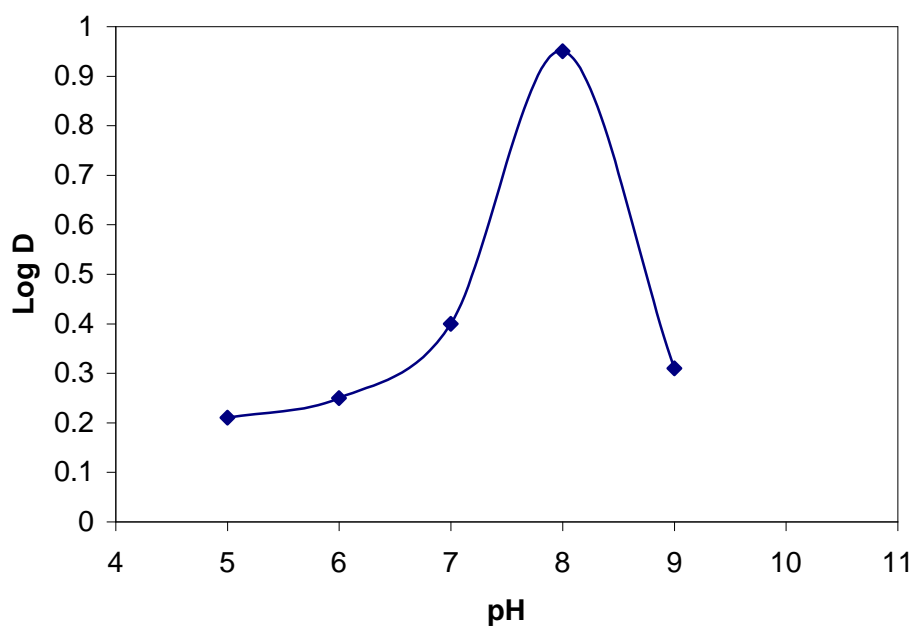
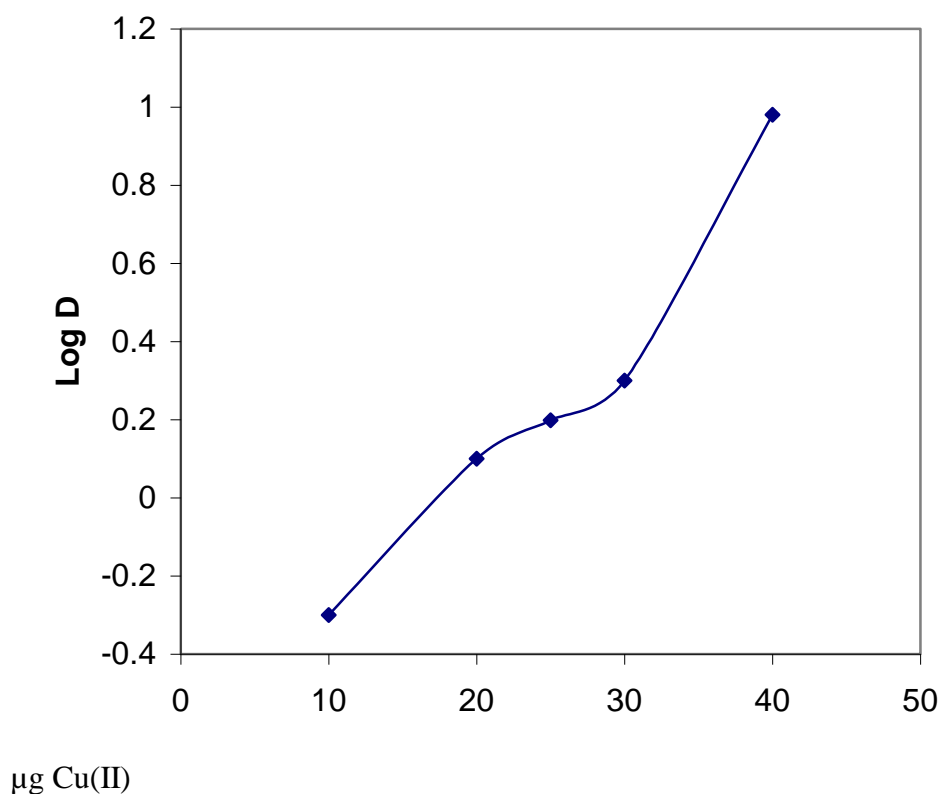


Fig.(3): pH effect on the extraction of Cu(II) ions

Table(2) : Effect of Cu(II) ions concentration on the extraction method  
( pH=8, 10 min. , $6 \times 10^{-5}$  M(PSPA) in  $\text{CHCl}_3$  )

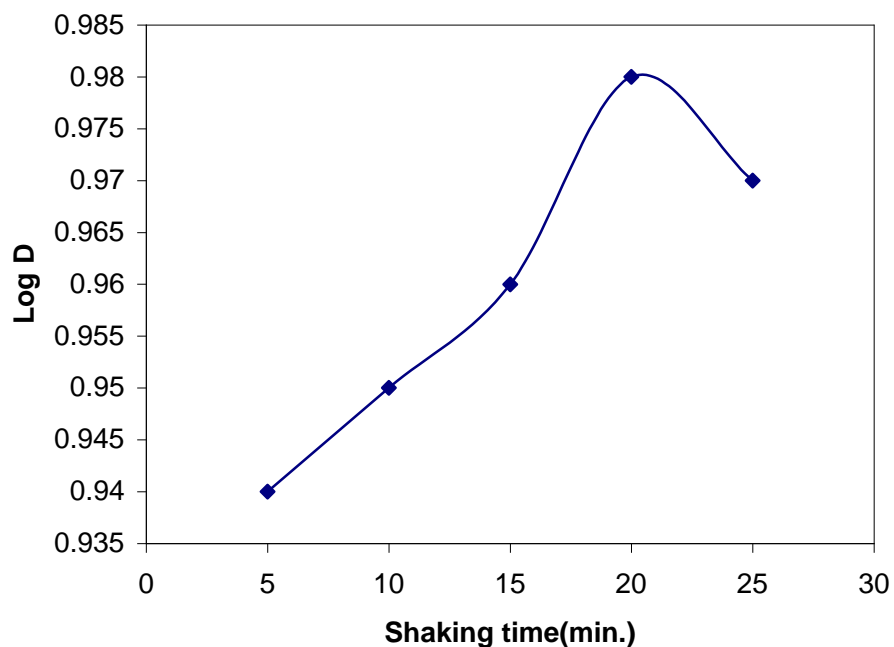
$\mu\text{g Cu(II)}$	10	20	25	30	40
$[\text{Cu(II)}] \times 10^{-5}$	1.5	2	4	5	6
D	0.5	1.28	1.58	2.018	9



**Fig.(4):The effect of Cu(II) ions concentration on the extraction method**

**Table ( 3 ) : Effect of shaking time on extraction of Cu(II) ions ( pH = 8 ,  $6 \times 10^{-5}$  M of Cu(II) ,  $6 \times 10^{-5}$  M(PSPAI) in  $\text{CHCl}_3$  )**

Time(min.)	5	10	15	20	25
D	8.75	9	9.178	9.6	9.4



**Fig.(5):The effect of shaking time on the extraction method**

**Table(4) : Effect of ligand concentration on the extraction method**

[ligand] x 10 <sup>-5</sup> M	1.5	2	3	5	5.5	6
D	3.40	3.09	4.51	7.24	8.51	9.60

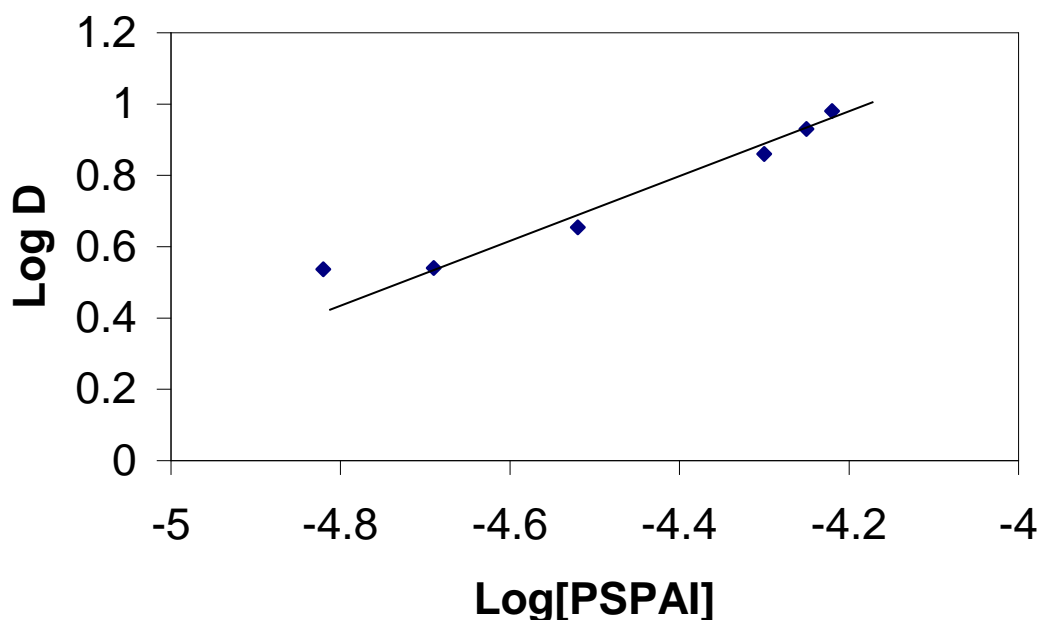


Fig.(6):The effect of ligand concentration on the extraction method

Table(5) : Effect of organic solvent on the extraction

Organic solvent	$\epsilon$	D
1,2-Dichloro ethane	10.65	11.2
Chloroform	5.708	9.6
Toluene	2.438	5.4
Carbon tetra chloride	2.38	4.3

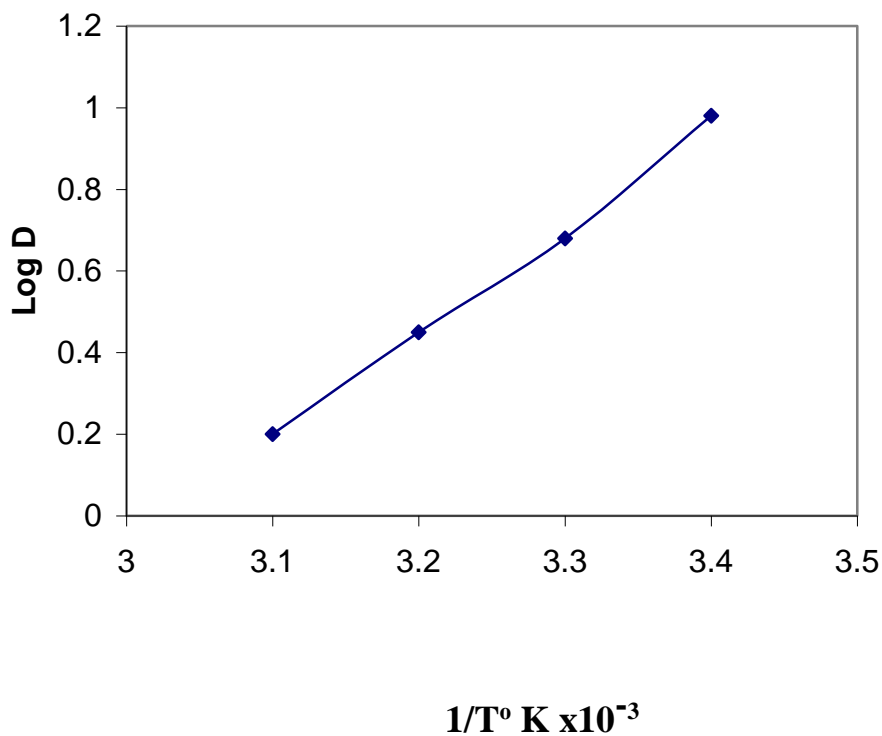
Table(6) : Effect of temperature on the extraction

T °C	T °K	$1/T^{\circ} K \times 10^{-3}$	D
20	293	3.4	9.60
30	303	3.3	4.70

40	313	3.2	2.80
50	323	3.1	1.58

**Table (7) : values of Gibbs free energy and entropy values of extraction For each temperature degrees**

T k <sup>0</sup>	ΔH <sub>ex.</sub> KJ mole <sup>-1</sup>	ΔG <sub>ex.</sub> KJ mole <sup>-1</sup>	ΔS <sub>ex.</sub> J mole <sup>-1</sup>
293	-50.97	-5.498	-155.194
303		-3.891	-155.376
313		-2.6736	-154.301
323		-1.222	-152.620



**Fig.(7): Temperature effect on the extraction of Cu(II) ions**

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## استخلاص النحاس (II) من المحاليل المائية بواسطة الكاشف 2-[بارا-(2-بريميديل سلفاميل) فنيل أزو]-4,5-ثنائي فنيل إמידازول

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### الخلاصة :

قد تم في هذا البحث دراسة استخلاص ايونات النحاس (II) من المحاليل المائية بواسطة الكاشف 2-[بارا-(2-بريميديل سلفاميل) فنيل أزو]-4,5-ثنائي فنيل إמידازول (PSPAI) المذاب في الكلوروفورم فقد كان هذا الكاشف جيد للاستخلاص هذه الايونات وتضمن البحث النواحي الاتية :  
دراسة تأثير الدالة الحامضية PH حيث كانت القيمة المثلى لاستخلاص ايونات النحاس الثنائية عند PH = 8 حيث كان التركيز (40 µg) ( $6 \times 10^{-5} M$ ) هو افضل تركيز.  
اما من الجانب الحركي لتفاعل التعقيد بين ايونات النحاس (II) والليكاند (PSPAI) فقد اظهرت الدراسة ان زمن الرج التالي لعملية الاستخلاص للطورين المائي الحاوي على ايونات النحاس الثنائية والعضوي الحاوي على الكاشف العضوي 20 دقيقة هو الافضل للوصول الى حالة الاتزان .  
كذلك تم دراسة تأثير تركيز الكاشف العضوي ووجد ان افضل قيمة لنسبة التوزيع عندما يكون التركيز  $6 \times 10^{-5} M$  كذلك تبين ان الصنف المحتمل استخلاصه  $[Cu(PSPAI)]^{+2}(SO_4)^{-2}$ ، كذلك تم دراسة تأثير المذيب العضوي وظهر عموما ان نسبة التوزيع للاستخلاص تزداد مع زيادة ثابت العزل الكهربائي للمذيبات العضوية المستخدمة ، كما اوضحت الدراسة الترموديناميكية لتفاعل التعقيد ان التفاعل باعث للحرارة .