Extraction of Copper (II) from aqueous solutions by using of 2-[(4-Bromo phenyl) azo]-4,5-diphenyl imidazole

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Abstract

The extraction of Copper has been studied as a complex by means of 2-[(4-Bromo phenyl) azo]-4,5-diphenyl imidazole dissolved in chloroform .The study revealed that the optimum pH value was ($pH_{ext.}$ = 9), concentrations of Cu(II) ion in aqueous solution giving highest distribution ratio (D) were (40µg) and the ligand [$1x10^{-4}$M] respectively and the optimum shaking time to reach the equilibria was ten minutes . Studies organic solvent showed there is not any linear relation between dielectric constant of organic solvents and distribution ratio (D) of extraction ,but there is an effect for the structure of organic solvent . The thermodynamic study demonstrates the complexation reaction is an exothermic at temperature degrees (20 C^0 - 70 C^0).

Key words: extraction , P-BrPAI ,copper, azo, imidazole.

الخلاصة

تمت دراسة عملية استخلاص ايونات النحاس (II) من المحاليل المائية بواسطة الكاشف 2- [(4- بروم- و فنيل) ازو]– 5,4 ثنائي فنيل أميدازول (P-BrPAI) المذاب في الكلوروفورم فقد كان هذا الكاشف جيد للاستخلاص هذه الايونات وتضمن الدراسة النواحي الاتية :

تاثير الدالة الحامضية pH حيث كانت القيمة المثلى لاستخلاص ايونات النحاس الثنائية عند pH = 9 , اما افضل تركيز للنحاس الثنائي الذي يعطي اعلى قيمة لنسبة التوزيع ويحقق لنا حالة الاستخلاص الافضل حيث كان التركيز (40 µg) (1.2×10^{-4} M) هو افضل تركيز , اما من الجانب الحركي لتفاعل التعقيد بين ايونات النحاس (II)والكاشف (P-BrPAI) فقد بينت الدراسة ان زمن الرج (10 دقائق) هو الافضل لوصول المعقد الى حالة الاتزان , كذلك تم دراسة تاثير تركيز الكاشف العضوي و وجد ان افضل قيمة لنسبة التوزيع عندما يكون التركيز $1x10^{-4}$M .كذلك تم دراسة تاثير المذيب العضوي وظهرعموما انه لاتوجد علاقة خطية بين نسبة التوزيع للاستخلاص و ثابت العزل الكهربائي للمذيبات العضوية المستخدمة ، كما اوضحت الدراسة الثرموديناميكية لتفاعل التعقيد ان التفاعل باعث للحرارة من (20 C^0 - 70 C^0) .

Introduction

Sensitivity and selectivity behavior of azo compounds and imidazoles as well as their derivatives for complex formation with metals as well as their extraction have been giving growing concern. Several studies were carried out on the extraction and determination of Cu (II) and complex formation by imidazoles compounds. Preparation and Identification of Some Transition Metal Complexes with the New Ligand 2- [*p*- (2′- Pyrimidyl sulphamyl) phenyl azo] - 4,5- diphenyl imidazole studied by A. J . Khadim and A.K.Hassan , using 2-[(α-naphthyl) azo]-4,5-diphenyl imidazole to extraction of copper and silver [1,2] Carolina et al., Studied the extraction of imidazole chelate complex with copper [3]. Synthesis of tri- and tetra substituted imidazoles carried by Daniel V. Paone and Anthony W. Shaw [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) was carried out by Ibramim and Nebahat. [6]. The extraction of Cu(II) and Ag (I) using 2-[(4-carboxy methyl phenyl)azo]-4,5-diphenyl imidazole and 2-[(3-methyl benzene) azo]-4,5diphenyl imidazole as well as Synthesis and Spectrophotometric determination of Cu (II) ,Ni (II) using the organic reagent 2-[(4-Bromo phenyl) azo]-4,5-diphenyl imidazole Fig(1) was studies by I. R. Ali [7,8]. Jose´ J. Campos et al., have 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 [9] . N. Dallali et al., have studied cloud point extraction and determination of Zn, Co, Ni and Pb by flame atomic absorption spectrometry using 2-Guanidinobenzimidazole as the complexing agent [10]. In other study used 2-[p-(2′-Pyrimidyl sulphamyl) phenyl azo]-4,5-diphenyl imidazole to extraction of Cu(II) from aqueous solutions [11].P.Giridhar et al., have studied the extraction of uranium and the effect of alkyl group on the extraction [12]. As well as T.K. Mondal et al., have studied Synthesis , structure spectra and redox properties of Ruthenium–carbonyl complexes of 1-alkyl-2-(arylazo) imidazoles [13]. studies in solvent extraction of group (IIb) metal ion by new organic reagent ",2-[(4-Chloro-2- methoxy phenyl)azo]-4,5-diphenyl imidazole.were carried out by Abdul Muttalib [14].

Apparatus

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

Materials

$CuSO_4.5H_2O$, Dithizone (D_2H_Z), H_2SO_4, NH_4OH , Chloroform , Dichloromethane, 1,2-Dichloroethane, Carbon tetra chloride , Benzene , and Toluene from B. D. H. and Merck ,The ligand 2-[(4-Bromo phenyl) azo]-4,5-diphenyl imidazole synthesized .

Procedure

i-prepration of standard stock solutions

(a) A solution of Copper (II) (1 mg\ml) was prepared by dissolving 3.928 gm $CuSO_4.5H_2O$ (0.015 mol) in 1 liter of distillated water containing 1 ml of conc. H_2SO_4

(b) A standard solution of $1x10^{-4}$ M of (P-BrPAI) was prepared by dissolve 0.004 gm in 100 ml of $CHCl_3$.

(c) A solution of $1x\ 10^{-2}$M of Dithizone (D_2H_Z) was prepared by dissolve 0.0256 gm in 10 ml of CCl_4.

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

ii-Calibration curve :

different concentrations of (1– 40) µg of Cu(II) were prepared using D.W. after the solutions had been adjusted to pH ≤ 1, they were transfered to a separate funnel and were extracted with portion of H_2D_Z in CCl_4 with shaking it about 3 min. continuous the addition until the last

portion does not change its green colour . the removing free reagent by shaking the combined extracts with the dilute ammonia sol.after that the complex solution of $Cu(HD_Z)_2$ was diluted with CCl_4 in 10ml volumetric flask then absorbance was measured the at 550 nm , the solvent was used as reference (Dithizone method)[15],the calibration curve was illustrated in Fig(2).

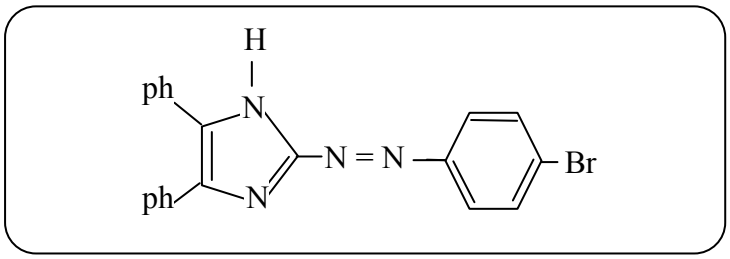
iii- Extraction of Copper (II)

A 5ml of aq. solution of Cu(II) has a specific concentration was placed in (25 ml) separating funnel with equivalent volume of ligand solution . after the separation funnel had been shaked within 10 sec . the two layer was separated .

iv-Determination of distribution ratio

A residue of Cu(II) was determinated using spectrophotometric method ,then a value of D was calculated using the relation ship below :

$$\text{Distribution ratio (D)} = \frac{\text{Conc. Of Cu(II) in organic phase}}{\text{Conc. Of Cu(II) in aqua. phase}}$$ [16].



2-[(4-Bromo phenyl) azo]-4,5-diphenyl imidazole[8]

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

Results and Discussion

Table (1) and Fig (3) was shown that, (pH_{ex}=9) was the optimum value of pH extraction. At pH less than optimum value the imidazole molecule ligand had been protonated to occupy the pair of electron and then can not coordinated strongly with Cu(II) ions and ion pair complex less stable and was minimized the distribution ratio (D) [3],also at pH more than optimum value distribution ratio (D) will be decreased by reason concentration of $[Cu(PSPAI)]^{+2}(HO^-)_2$ complex was increased this complex more soluble in aqueous phase and less extracting to organic phase and it was suffered the dissociation equilibria [7] .

The optimum Conc. Of Cu(II) ions in aqueous phase , which is (40µg) (1.2×10^{-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. was not allowed to reach the equilibria therefore, the value of D was minimized, according to Lechatlier principle [17].

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

$$Cu^{+2} + (\text{P-BrPAI}) + SO_4^{-2} \rightleftharpoons [Cu(\text{P-BrPAI})]^{+2} SO_4^{-2}$$

Table (3) and Fig(5) was shown that 10 minutes was the best time for shaking, this time was required to reaching the complex to equilibrium state .

The study also was illustrated of effect of P-BrPAI concentration on the extraction process in Table (4) and Fig(6) that probability forming two species enable for extraction $[Cu(P\text{-}BrPAI)]^{+2}SO_4^{-2}$) $[Cu(P\text{-}BrPAI)]^{+2}(HO^{-1})_2$, from the straight line slop of these species was (1 : 1) (metal : ligand), that the more probable structure of ion pair complex was extracted ,in Table (5) was shown the relation between dielectric constant of organic solvents and distribution ratio (D) wasn't linear due to extracted complex charge less and it was affected by stereo structure of organic solvent and nature of complex soluble[18]. The Table (6) ,(7) and Fig. (7) were demonstrated values of free energy of transition of ions from aqua. phase to organic phase and the $\Delta H_{ex.}$ values were shown that the extraction of Cu(II) decrease with increasing temperature (i.e process is exothermic) from study different heat degree (20 C^0 - 70 C^0) depending on (Vant- Hoff) relation ship [19]

$$\log K_{ex.} = \frac{-\Delta H}{2.303RT} + Cons\tan t \cdots\cdots(1)$$

The $\log K_{ex.}$ verses ($1/T\ k^0$) show the slope equal to $\frac{-\Delta H}{2.303R}$ from this relation ship calculate the Value $\Delta H_{ex.}$ =-27.397 k_J . $mole^{-1}$

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

and

$$\Delta G_{ex.} = \Delta H_{ex.} \_ T\Delta S_{ex.} \cdots\cdots(3)$$

we used log D instead of $\log K_{ex.}$.
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 $\Delta H_{hyd.}$

$\Delta H_{ex.} = \Delta H_{solv.} - \Delta H_{hyd.} \cdots\cdots(4)$ [11].

While at low heat degree (0 C^0, 10 C^0) decreasing the distribution ratio

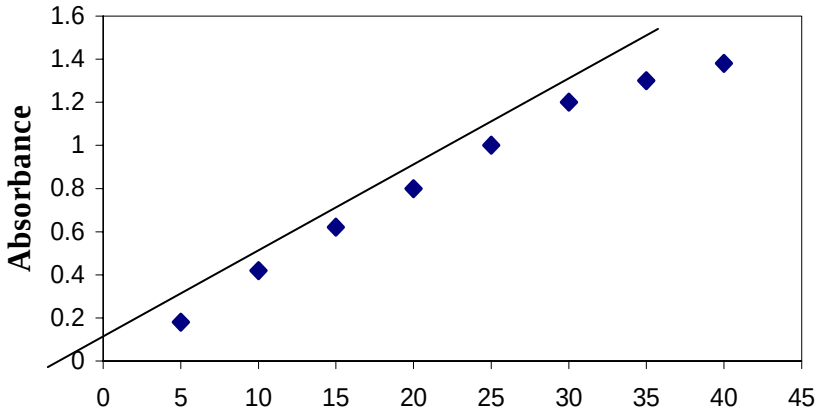


Fig.(2): Calibration Curve of Cu (II)

Table (1) : Effect of pH on extraction of Cu(II) ions

pH	5	6	7	8	9	10	11	12
D	0.11	0.73	3.84	5.15	31	7.35	0.09	___
Log D	-0.95	-0.13	0.71	0. 58	1.49	0.86	-1.04	___

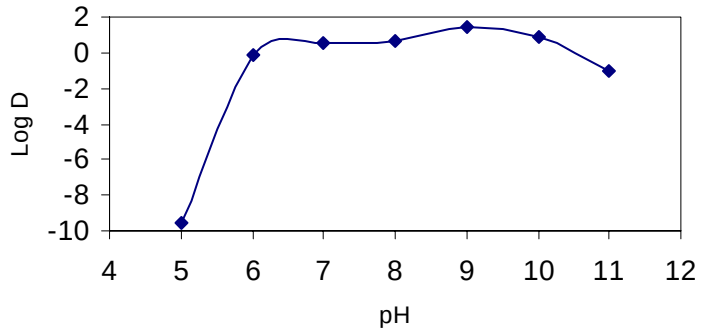


Fig.(3): pH effect on the extraction of Cu(II) ions

Table(2) : Effect of Cu(II) ions concentration on the extraction method

µg Cu(II)	10	20	30	40	60	80	120
ppm	2	4	6	8	12	16	24
D	0.1	1.42	9	19	22	79	13.7
Log D	-0.95	0.153	0.95	1.27	1.34	1.89	1.136

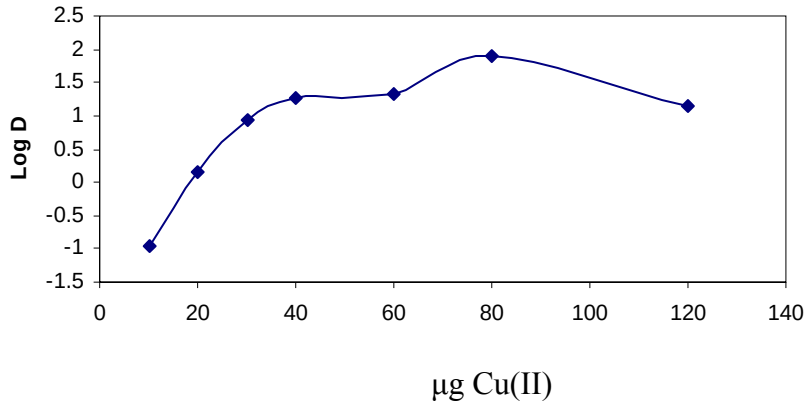


Fig.(4):The effect of Cu(II) ions concentration on the extraction method

Table (3) : Effect of shaking time on extraction of Cu(II) ions

Time(min.)	5	10	15	20	25	30
D	12.33	31	25.6	19	12.3	12.3
Log D	1.09	1.49	1.4	1.27	1.09	1.09

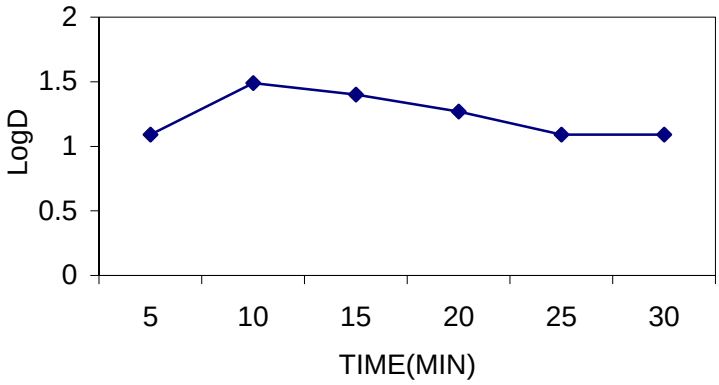


Fig.(5):The effect of shaking time on the extraction method

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

[ligand] x 10^{-5} M	1	2	3	6	8	10
D	3.98	7.16	25.66	9.66	9.38	31
Log D	0.6	1.1	1.409	0.97	1.2	1.49

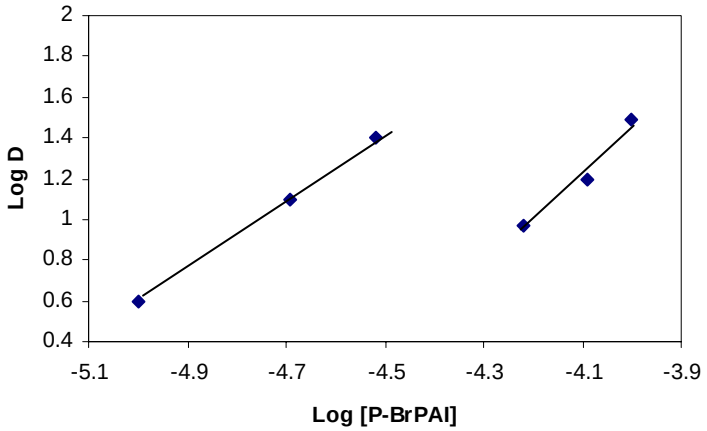


Fig.(6):The effect of ligand concentration on the extraction method

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

Organic solvent	ε	D
1,2-Dichloro ethane	10.65	7.69
Chloroform	5.708	31
Toluene	2.438	12.33
Carbon tetra chloride	2.38	25.6
Benzene	2.804	9.66
DCM	9.08	16.2

Table(6) : Effect of temperature on the extraction of Cu(II) ions

T ^{o}C	T ^{o}K	1/T ^{o}K x10^{-3}	D
0	273	3.6	25.8
10	283	3.5	27.4
20	293	3.4	31.0
30	303	3.3	27.5
40	313	3.2	20.0
50	323	3.1	12.5
60	333	3	10.0
70	343	2.9	7.0

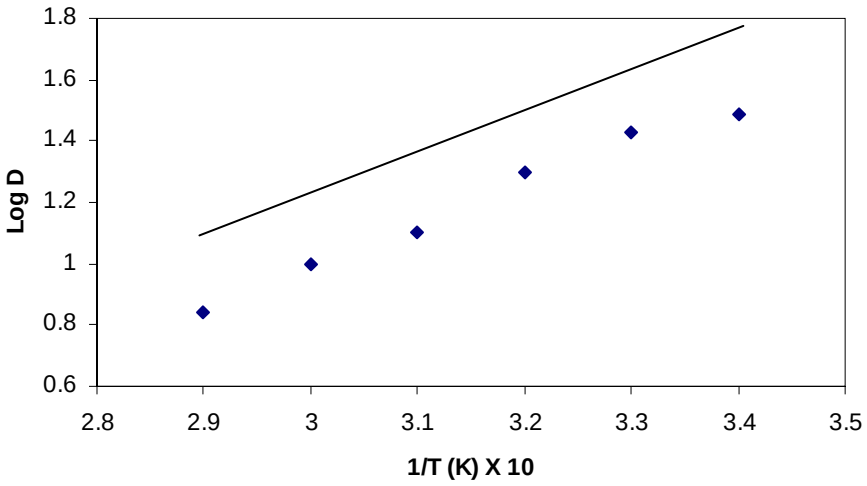


Fig (7) : Effect of temperature on the extraction of Cu(II) ions

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

T k^0	$\Delta H_{ex.}$ KJ $mole^{-1}$	$\Delta G_{ex.}$ KJ $mole^{-1}$	$\Delta S_{ex.}$ J $mole^{-1}$
293	-27.397	- 8.344	-65
303		-8.282	-63
313		-7.777	-62
323		-6.791	-63.7
333		-6.365	-63.1
343		-5.507	-63.8

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