Extraction of Copper (II) Ion Pair Complex from Aqueous Solutions by Using the Reagent 2-[(4-chloro -2-methoxyphenyl)azo]-4,5 Diphenylimidazole

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Abstract

Extraction of Cu^{+2}ions from aqueous solutions reagent 2-[(4-chloro -2-methoxyphenyl)azo]-4,5 diphenylimidazole (4-ClMePADPAI) shows the optimum conditions for extraction was (pHex=8) ,concentration of Cu^{+2}ions in aqueous solution (30µg) (9.45×10^{-5}M),as well as shaking time (10 min) ,all these conditions giving higher distribution ratio (D) ,organic solvent effect shows there is not any linear relation between distribution ratio (D) and dielectric constant (ε),for organic solvents used but there is an the effect for organic solvent structure on the extraction method .Stoichiometric study shows the more probable structure of ion pair complex extracted for Cu^{+2}ions with reagent (4-ClMePADPAI) was1:1 (metal:reagent)$[Cu(4\text{-}ClMePADPAI)]^{+2}SO_4^{-2}$. The effect of temperature on the extraction of Cu^{+2}ions shows the reaction between Cu^{+2}ions reagent ((4-ClMePADPAI) was exothermic

الخلاصة

استخلاص النحاس Cu^{+2} من المحاليل المائية بواسطة الكاشف 2–[4- كلورو-2- ميثوكسي فنل)ازو]-5,4- ثنائي فنيل اميدازول (4-ClMePADPI) يبين إن الظروف المثلى لعملية الاستخلاص كانت (pH= 8)

والتركيز الأمثل لايونات النحاس Cu^{+2} في المحلول المائي (30µg) ($9.45x10^{-5}$) أما زمن الرج فكان مقداره (دقائق 10) .حيث إن هذه الظروف تعطي أعلى نسبة توزيع(D).تأثير المذيب العضوي انه لا توجد أية

علاقة خطية بين نسب التوزيع(D) وثوابت العزل الكهربائي للمذيبات العضوية المستخدمة وان أفضل مذيب عضوي يعطي أفضل عملية استخلاص وأعلى قيمة لنسبة التوزيع (D) لايونات النحاس Cu^{+2} هو البنزين بالرغم من انه يمتلك ثابت عزل كهربائي (Є) واطئ جدا والمذيب العضوي الثاني هو الكحول الاميلي الذي

يملك أعلى قيمة لثابت العزل الكهربائي .كما وهذه النتائج تعكس تركيب المذيب العضوي على عملية الاستخلاص .كما إن دراسة تركيب المعقد المستخلص أوضحت إن التركيب المحتمل لمعقد الترابط الأيوني هو $[Cu(4\text{-}ClMePADPI)]^{+2}$ SO_4^{-2} (Ligand :metal)(1:1) .أما دراسة تأثير درجة الحرارة أوضحت إن التفاعل بين ايونات النحاس Cu^{+2} والليكاند (4-ClMePADPI) هو تفاعل باعث للحرارة.

Introduction

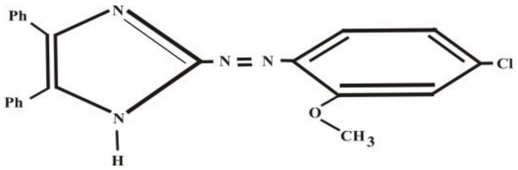
The selectivity and sensitivity of imidazole compounds for complexation reaction with transition metal ions open the door about wide spreed about applications for extraction and separation and spectrophotometric determination many transition metal ions previous study about the complexes of ruthenium and iron with benzotriazole and benzimidazole derivatives[1].Another study include equilibrium ,structure and hydrolytic activity for complexes of copper(II),zinc(II)and nickel(II)with imidazole containing reagent and inositol derivatives [2],used 1-octylimidazole and 1-octyl-2-methylimidazole for extraction of Zn(II),Ni(II) in different organic solvents[3]. Anew imidazole reagent ,benzo[15-crown-5]-1H-imidazole [4,5f] [1,10] phenanthroline has been synthesized from the reaction of 5,6-diamino-1,10 phenanthroline with 4'-formyl benzo-15-crown-5as well as prepared complexes Co(II),Ni(II),Cu(II) with this new ligand and the complex structure found to be (2:1) [4].Solvent extraction of palladium (II) with various ketons in nitrobenzene from nitric acid medium was investigated [5].The solvent extraction trivalent lanthanides (La,Nd,Eu,Ho,Lu) with mixtures of the chelating extractant 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedionethenoyltrifluoro-acetone HTTA) or 4-benzoyl-3-methyl -1-phenyl-2-pyrazoline-5-or(HP) and 4-(2-pyridyl azo)-resorcin (PAR,s) in $CHCl_3$ was studied[6].A new polystyrene divinyl benzene resin containing 2-(2-thiazolyl azo)-5-dimethyl amino-phenol (TAM) functional groups has been synthesized and its sorption behavior for nineteen metal ions ,including Zr(IV) ,Hf(W) ,V(VI) has been investigated by batch and column methods [7] .A new thiazolylazo reagent 2-[2-(5-methylbenzothiozolyl)azo]-5-dimethylamino benzoic acid (5-Me-BTAMB) was synthesized ,its chromogenic reaction with micro amounts of nickel(II) was studied as well as the stability constants for the complexes of Ni^{+2},Co^{+2},Fe^{+2},Cu^{+2} and Pd^{+2}[8].The preparation and structural identification of complexes for Fe(III),Co(II),Ni(II),Cu(II),Zn(II) and Cd(II)with 2-(2-benzimidazolylazo)-4-acetamido phenol (BIAAP) was studied [9],study the crystal and molecular structures of $[Ni(Im)_6](dtp)_2$ (Im=imidazole ,dtp=o,o'diphenyl dithiophosphate) have been determined by X-ray crystallography[10].Benzildithiosemicarbazone(BDTSC) used as sensitive and selective analytical reagent for the extractive spectrophotometric determination of cupper (II),(BDTSC) reacts with copper(II) in the pH range 1-7 to form yellowish complex [11]. A ciral complex salen Zn(II) ,was synthesized and characterized its coordination with imidazole derivatives was studied by UV-Vis spectrophotometric titrations and CD spectrpscopy[12].

Aparatus

For absorption measurements of UV-Visible electromagnetic radiation region used (UV-100-02 spectrophotometer single beam) and (UV-1700 double beam spectro photometer)Japan , as well as for pH measurements used (HANNA pH-meter) .

Reagents and standard solutions preparation :

All reagent and solvents were obtained from commercial sources and used as received .The reagent2-[(4-chloro -2-methoxyphenyl)azo]-4,5 diphenyl imidazole (4-ClMePADPAI) synthesized as in the thesis [13] .The stock solution of Cu^{+2} ions (1mg/ml) prepared by dissolved 0.3928gm of $CuSO_4.5H_2O$ in distilled water contain 1ml conc. $H_2SO_4$and then dilute the solution to 100 ml in volumetric flask by distilled water ,and other standard working solutions prepared by dilution method ,dithizone solution (1×10^{-2}M) prepared by dissolved 0.256gm of dithizone in 100 ml CCl_4 ,working solution (1×10^{-4}M) for dithizone prepared by dilution method with CCl_4.($1x10^{-2}$M)reagent solution (4-CMePADPAI) prepared by dissolved 0.3885gm of reagent in 100ml chloroform in volumetric flask ,other standard working solution prepared by dilution with chloroform organic solvent $CHCl_3$



2-[(4-Chloro-2-methoxy phenyl)azo]-4,5-diphenyl imidazole

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

General procedure

For extraction experiments have to take (5ml) of aqueous solution contain fixed quantity of Cu^{+2} ions, change the pH value for aqueous solution to optimum value of pH ,afterward adding (5ml) of (1×10^{-4}M), Reagent solution dissolved in chloroform and shaking these two layers for suitable time ,at last separate aqueous phase from organic phase and determine the remainder quantity of Cu^{+2} ions in aqueous phase by following the spectrophotometric determination method (dithizone method) [14],from the absorption values at (λ_{max}=550nm.) and calibration curve Fig(2) can be determine the quantity Cu^{+2} ions remainder in aqueous phase ,but for determine the quantity of Cu^{+2} ions transferred to organic phase to produce ion pair complex follow the stripping method which is include shaking the organic phase with three portions of nearly concentration hydrochloric acid HCl after that determine the Cu^{+2} ions in acidic aqueous phase by dithizone method ,at last divide the quantity of Cu^{+2} ions in organic phase of the ions in aqueous phase to calculate distribution ratio (D),from other hand we can be determine the quantity of Cu^{+2} ions transferred to organic phase by subtraction remainder in aqueous quantity of Cu^{+2} ions phase from the initial quantity .

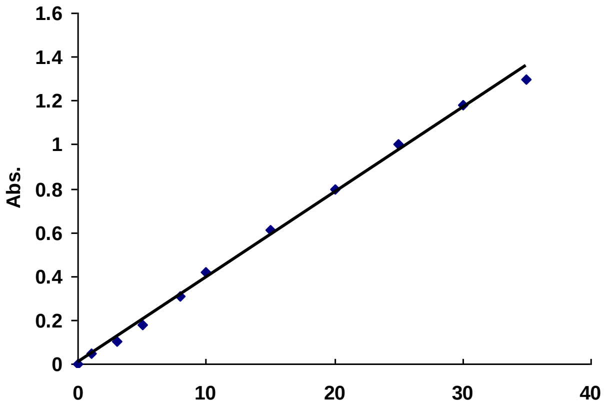
Results and Discussion

Effect of pH

Extraction of (30μg)(9.45×10^{-5}M) of Cu^{+2} ions in 5ml aqueous solution at different pH values (5-10) by (1×10^{-3}M) reagent solution (4-ClMePADPI) dissolved in chloroform $CHCl_3$,after shaking for (15min) separate the aqueous phase from organic phase ,and determine the remainder quantity in aqueous phase and transferred quantity to the organic phase Cu^{+2} ions and calculate the distribution ratio (D) and percentage of extraction (E) according to dithizone method detailed in general procedure .The results in Table(1) and Figure (3) shows the optimum value for pHex was pH=8 which is giving higher distribution ratio .

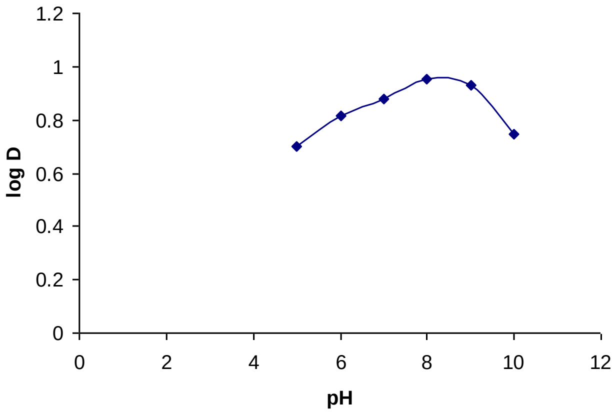
Table (1) :Effect of pH on extraction of Cu^{+2} ions.

pH	5	6	7	8	9	10
D	5	6.5	7.57	9	8.057	5.6
E	83.3%	86.7%	88.3%	90%	89.6%	84.8%



μg Cu^{+2} ions

Fig(2) :Calibration curve for Cu^{+2} ions.



Fig(3) :Effect of pH on the extraction of Cu^{+2} ions .

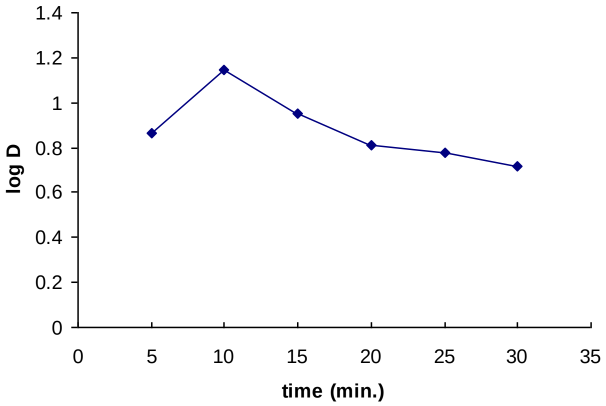
The pH lower than optimum value of aqueous phase effect to may be protonated the reagentmolecule and occupy the lone pair electron and minimizing the complexation ability and decrease the distribution ratio (D) and percentage of extraction (E) ,as well as the pH higher than optimum value effect to decrease distribution ratio (D) and percentage of extraction by reason of produced stable species of Cu^{+2} ions in aqueous phase can not be extracted in addition of produced ion pair complex contain hydroxyl ion (OH^-) as anion which is more stable in aqueous phase and minimizing extraction ability .

Effect of shaking time

Extracted (30µg) (9.45×10^{-5}M) Cu^{+2}ions in 5ml aqueous phase at (pHex=8) by 5ml of (1×10^{-3}M) reagent solution (4-ClMePADPI) dissolved in chloroform ,after shaking these two layers for different time (5-30min) ,separate the organic phase from aqueous phase and determine the remainder quantity and transferred of Cu^{+2}ions in these two layers by followed spectrophotometric method (Dithizone method) detailed in general procedure ,afterward calculate distribution ratio(D) and percentage of extraction (E) .The results in Table (2) and Figure(4) demonstrate the optimum shaking time was (10min) .

Table (2) :Effect of shaking time on the extraction of Cu^{+2}ions.

Shaking time Min	5	10	15	20	25	30
D	7.3	14	9	6.5	6	5.3
E	88%	93%	90%	86.7%	85.7%	84.13%



Fig(4) :Effect of shaking time on the extraction of Cu^{+2}ions.

The shaking for optimum time allow to reach the equilibrium of reaction to give stable ion pair association complex , but shaking for time less than optimum time not allow to reach the equilibrium and minimizing the extraction ability and decrease distribution ratio (D) ,as well as shaking for time more than optimum time effect to favorite the dissociation equilibrium and decrease the distribution ratio (D) also .

Effect of Metal ion concentration

Extraction Cu^{+2}ions from 5ml aqueous phase at (pH=8) contain different quantity of ions (5-70μg) ($1.57\times10^{-5}\rightarrow2.2\times10^{-4}$M) of Cu^{+2}ions ,by 5ml of (1×10^{-3}M) reagent solution (4-ClMePADPI) dissolved in chloroform $CHCl_3$ after shaking these two layers for (10min) ,separate the aqueous phase from the organic phase and determine the quantity of Cu^{+2}ions remainder in aqueous phase and quantity transferred to the organic phase according to the (Dithizone method) detailed in general procedure afterward calculate distribution ratio(D) and percentage of extraction (E) .The results at Table (3) and Figure (5) shows the optimum concentration of Cu^{+2}ions which is giving higher distribution ratio (D) and percentage of extraction (E) was (30μg) (9.45×10^{-5}M) of Cu^{+2}ions .

Table (5) :Effect of Cu^{+2}ions concentration on extraction .

μg Cu^{+2}	5	10	20	30	40	50	60	70
D	1.5	3	4.7	14	10.43	7.66	6.5	5.3
E	60%	75%	82.5%	93.3%	91.3%	88.5%	86.7%	84.1%

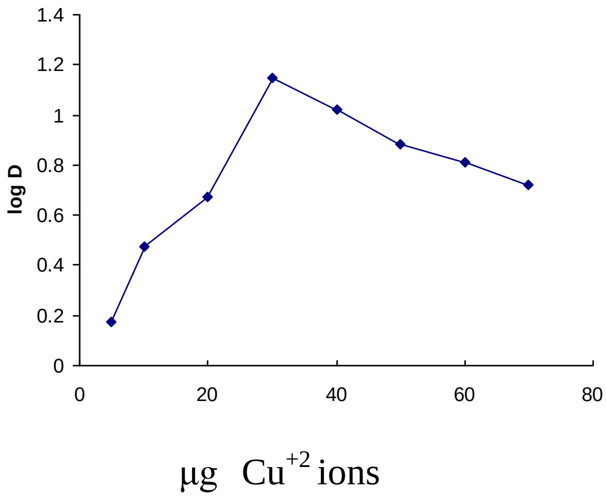


Fig (5) :Effect of Cu^{+2}ions concentration on extraction method .

The equilibrium of complexation reaction as in the relation

$$\mathbf{Cu^{+2} + n\ 4\text{-}ClMePADPI + SO_4^{-2} \rightleftharpoons [Cu(4\text{-}ClMePADPI)]^{+2}\ SO_4^{-2}}$$

aq. org. aq. org.

This relation shows the equilibrium effect by Cu^{+2}ions concentration to give more stable ion pair association complex , the concentration of Cu^{+2}ions in aqueous phase (30μg) (9.45×10^{-5}M) give the suitable concentration of Cu^{+2}ions to predominate complex formation and high extraction and higher distribution ratio(D) but lower concentration than optimum value not allow to reach the equilibrium and giving stable complex but at concentration of Cu^{+2}ions more than optimum value effect to decline distribution ratio also according to Leshatelier principle and predominate dissociation equilibrium.

Organic solvent effect

Extracted(30μg) (d 9.45×10^{-5}M) Cu^{+2}ions in (5ml) aqueous solution at (pH=8) by (5ml) reagent solution (4-ClMePADPI) dissolved in different organic solvents differ in dielectric constant (ε) at concentration of (1×10^{-3}M).After shaking these two layers for (10min) ,separate the organic phase from the aqueous phase and determine the remainder quantity of Cu^{+2}ions in aqueous phase and transferred quantity of Cu^{+2}ions to the organic phase to form ion pair association complex by followed the spectrophotometric method (Dithizone method) detailed in general procedure ,afterward calculate distribution ratio (D) and percentage of extraction (E) .The results at Table (6) shows there is not any linear relation between distribution ratio (D) and dielectric constant (ε) for organic solvents used .

Table (6) :Organic solvents effect on extraction Cu^{+2}ions .

Organic solvents	ε	D	E
n-Amyl alcohol	15.8	19	95%
Chloroform	5.708	14	93.3%
Bromo Benzene	5.4	5.66	84.98%
Benzene	2.804	29	96.67%
Toluene	2.498	14	93.3%

The results reflect the effect of organic solvent structure on the extraction of Cu^{+2}ions ,where benzene giving higher distribution ratio in spite of having lower dielectric constant ,from other hand the results demonstrate the participation of organic solvent in the structure of ion pair complex extracted by form of contact ion pair (tight ion pair)or solvent separated ion pair complex (loose ion pair).

Stoichiometry

Slope Analysis Method

Extracted (30µg) (9.45×10^{-5}M) Cu^{+2}ions in 5ml aqueous solution at (pH=8) by 5ml organic solution of reagent (4-ClMePADPI) dissolved in chloroform at different concentration ($1\times10^{-2}\rightarrow1\times10^{-5}$M) ,after shaking these two layers for (10min) separate organic phase from aqueous phase ,and determine the remainder quantity of Cu^{+2}ions in aqueous phase and transferred quantity of Cu^{+2}ions to the organic phase by followed spectrophotometric method (Dithizone method) as detailed in general procedure afterward calculate distribution ratio(D) .The results at Table (7) and Fig (6) illustrate the more probable structure of ion pair complex extracted was (1:1) (Metal : Ligand) $[Cu(4\text{-}ClMePADPI)]^{+2}SO_4^{-2}$.

Table (7) :Slope analysis method .

[ligand]	1×10^{-5}	5×10^{-5}	8×10^{-5}	1×10^{-4}	2×10^{-4}	3×10^{-4}	5×10^{-4}	8×10^{-4}	1×10^{-3}	5×10^{-3}	1×10^{-2}
D	2.82	4.36	5.01	5.6	6.31	7.5	8.2	9	10	15.85	20

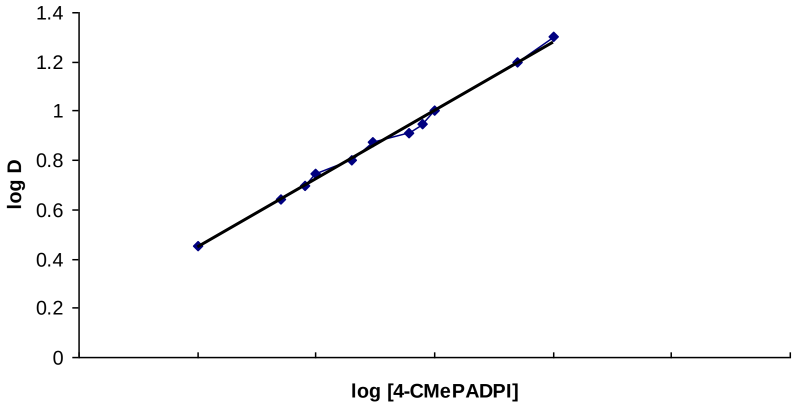


Fig (6) :Slope analysis for extraction Cu^{+2} ions.

Mole Ratio Method

Extracted (30µg) (9.45×10^{-5}M) Cu^{+2}ions in 5ml aqueous solution at (pH=8) by 5ml organic solution of reagent (4-ClMePADPI) dissolved in chloroform at different concentration ($1\times10^{-5}\rightarrow1\times10^{-3}$M) ,after shaking these two layers for (10min) separate organic phase from aqueous phase, afterward determine the absorbance of organic phase at (λ = 518nm) Vs reagent solution as blank ,at last calculate the mole ratio of ligand over metal C_L / C_M and plot these values against absorbance values the results of Table (8) and Figure(7) demonstrate the more probable structure of ion pair complex extracted was (1:1) (Metal :Ligand) $[Cu(4\text{-}ClMePADPI)]^{+2}SO_4^{-2}$.

Table (8) :Mole ratio method for extraction Cu^{+2}ions .

C_L / C_M	0.106	0.53	0.85	1.06	2.13	3.2	5.3	8.6	10.6
Abs.	**0.008**	**0.11**	**0.21**	**0.221**	**0.25**	**0.262**	**0.30**	**0.360**	**0.38**

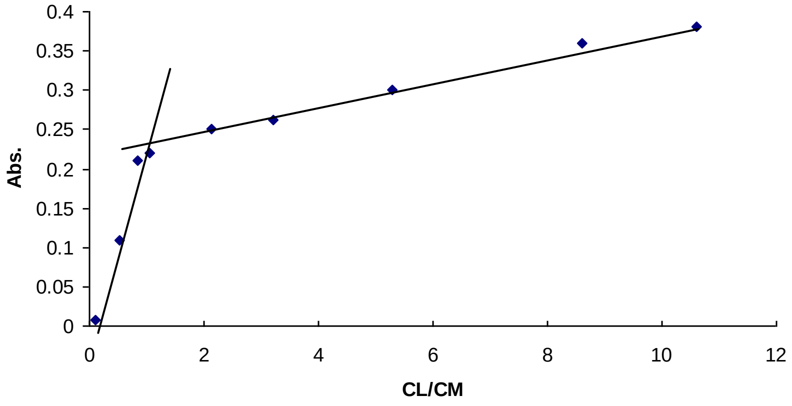


Fig (7) :Mole ratio method for extraction Cu^{+2}ions .

Continuous Variation Method

Prepared aqueous solution for Cu^{+2}ions and organic solution of reagent (4-ClMePADPI) dissolved in chloroform at the same concentration (1×10^{-4}M),afterward mixing different volume for two solution to final volume (5ml) at (pH=8) ,after shaking for (10 min) separate the organic phase from aqueous phase ,after that determine the absorbance of organic phase at (λ = 518nm) against reagent solution as blank .The results at Table (9) and Fig (8) shows the more probable structure of ion pair complex extracted was (1:1) (Metal :reagent) $[Cu(4\text{-}ClMePADPI)]^{+2}SO_4^{-2}$.

Table (9) :Continuous variation method for extraction Cu^{+2}ions .

V_M	1	1.5	2	2.5	3	3.5	4
V_L	4	3.5	3	2.5	2	1.5	1
Abs.	0.002	0.005	0.01	0.023	0.037	0.043	0.024

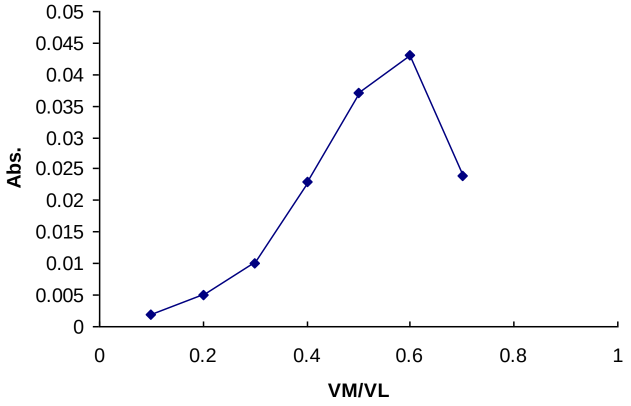


Fig (8) :Continuous variation for extraction Cu^{+2}ions .

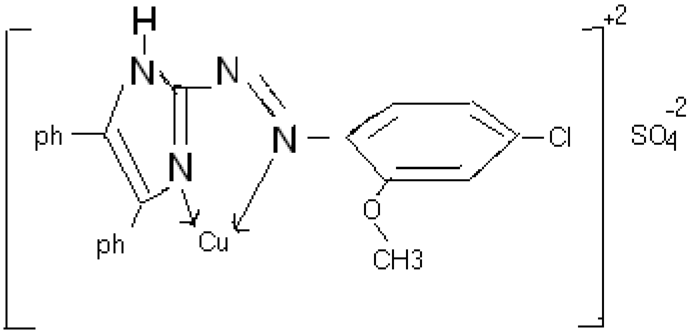


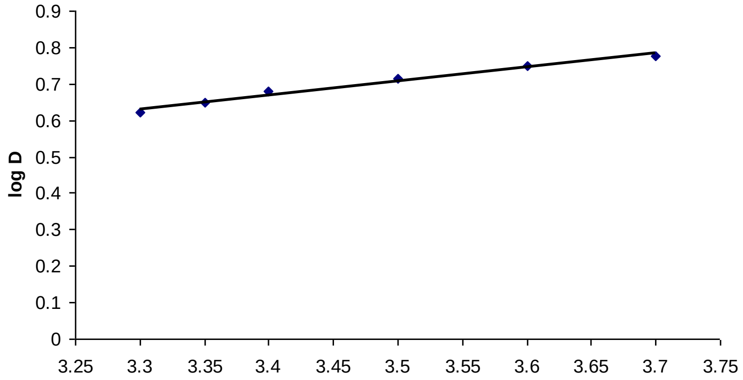
Fig (9) :Ion pair complex structure of Cu^{+2}ions with (4-ClMePADPI) .

Effect Of Temperature

Extracted (30μg) (9.45×10^{-5}M) Cu^{+2}ions in 5ml aqueous solution at (pH=8) by 5ml organic solution of ligand (4-ClMePADPI) dissolved in chloroform at different temperature (0-30 C°) ,after shaking for (10min) separate organic phase from aqueous phase ,and determine the remainder quantity of Cu^{+2}ions in aqueous phase and transferred quantity of Cu^{+2}ions to the organic phase according to (Dithizone method) as detailed in general procedure ,afterward calculate distribution ratio(D) at each temperature.The results at Table (10) and Fig (10) illustrate the reaction between Cu^{+2}ions and (4-ClMePADPI) was exothermic reaction.

Table (10) :Effect of Temperature on extraction of Cu^{+2}ions.

TC°	0	5	10	20	25	30
T°K	273	278	283	293	298	303
1 / T°K	3.7×10^{-3}	3.6×10^{-3}	3.5×10^{-3}	3.4×10^{-3}	3.35×10^{-3}	$303\text{x}10^{-3}$
D	6.0	5.6	5.2	4.76	٤,٤٥	٤,١٦٨



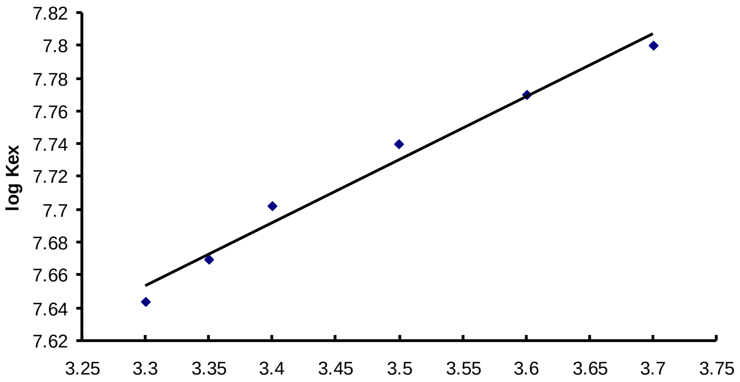
$1/T\ K^0\ x10^{-3}$

Fig (10) :Temperature effect on extraction of Cu^{+2}ions.

Calculate extraction constant Kex at each temperature by the relation above

$$\mathbf{Kex} = \frac{\mathbf{D}}{[\mathbf{Cu}^{+2}]\mathbf{aq.}\ [\mathbf{4\text{-}ClMePADPI}]}$$

Afterward plot Kex values against 1/T giving Figure (11).



1/T K^0 x10^{-3}

Fig (11) :Extraction constant of different temperature .

To determine the thermodynamic data have to application the relation below

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

$$\Delta G = -RT \ln Kex$$

$$\Delta G = \Delta H - T\Delta S$$

The results shows the enthalpy of extraction ΔHex was , ΔHex = -0.0080 $KJmole^{-1}$,as well as the free energy of extraction was (ΔGex = -56.46 $KJmole^{-1}$) and the entropy was (ΔSex = 206.8 $Jmole^{-1}$),these data prove the structure of ion pair complex extracted was (1:1) as stoichiometry from the very small value of enthalpy, and the reaction was spontaneous reaction from free energy of reaction which is identify with exothermic reaction of complexation , from other hand the large value of entropy reflect the complexation was entropic in region .

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