

Solvent extraction of Cobalt (II) from aqueous solutions by new ligand 2-[(4-Chloro-2-methoxy phenyl) azo] -4,5-diphenyl imidazol

Shawket K. Jawad

Dept. of Chemistry, College of Education
for girls

Kufa University, Al-Najaf, Iraq

Zainab A. Muttalib

Dept. of Chemistry, College of Education
for girls

Kufa University, Al-Najaf, Iraq

Rafah Mohamed Diab

Dept. of Chemistry, College of Science
Kufa University, Al-Najaf, Iraq

الاستخلاص المذيب للكوبلت الثنائي من المحاليل المائية كمعقد ترابط أيوني باستخدام ليكاند جديد
٢-[(٤-كلورو-٢-ميثوكسي فنيل) آزو]-٤,٥-ثنائي فنيل اميدازول

زينب عبد المطلب

قسم الكيمياء، كلية التربية للبنات
جامعة الكوفة، النجف، العراق

شوكت كاظم جواد

قسم الكيمياء، كلية التربية للبنات
جامعة الكوفة، النجف، العراق

رفاه محمد ذياب

قسم الكيمياء، كلية العلوم
جامعة الكوفة، النجف، العراق

الخلاصة:

اعتمادا على قابلية مركبات الآزو على التعقيد مع العناصر الانتقالية كأيونات موجبة معطية انتقائية عالية استخدم الليكاند ٢-[(٤-كلورو-٢-ميثوكسي فنيل) آزو]-٤,٥-ثنائي فنيل اميدازول، النتائج أوضحت إن قيمة الدالة الحامضية المثلى لاستخلاص الكوبلت الثنائي كانت (pH=9) وزمن الرج المثالي كان (١٠ دقائق) أما التركيز الأمثل للكوبلت ليعطي أعلى قيمة لنسبة التوزيع كانت (٣٠ μg). دراسة تركيب المعقد المستخلص هو (١:١) (فلز:ليكاند)، دراسة تأثير المذيب العضوي يبين إن نسب التوزيع تزداد مع نقصان ثابت العزل الكهربائي للمذيبات العضوية حيث نحصل على أعلى قيمة لنسب التوزيع مع مذيب رابع كلوريد الكربون، من المحتمل إن انخفاض ثابت العزل الكهربائي للمذيب العضوي يساعد في تحطيم الغلاف التميوي للأيون الفلزي وتكوين الأيونات الحرة وزيادة قدرة التناسق بين جزيئات الليكاند والأيونات الموجبة، الدراسة الترموديناميكية أوضحت إن التفاعل بين الليكاند وأيونات الكوبلت كان تفاعل باعث للحرارة وإن التفاعل يعتمد على الانتروبي في طبيعته.

Abstract:

The solvent extraction of Co(II) by used a 2-[(4-Chloro -2-methoxy phenyl) azo]-4,5-diphenyl imidazol (4-ClMePADPI) have been studied, The results shows that the optimum pH extraction was (pH_{ex}=9) ,and the optimum shaking time was 10min. as well as Co²⁺ concentration was 30µgCo²⁺ (1.018x10⁻⁴M) ,The stoichiometry study shows the more probable structure of ion pair complex extracted was (1:1) (Metal:Ligand) Co²⁺:(4-ClMePADPI) SO₄²⁻ , organic solvent effect appear distribution ratio (D) for extraction increase with decrease of dielectric constant and higher distribution ratio(D) get with carbon tetra chloride may be decreasing dielectric constant for organic solvent help to destroy the hydration shell about metal cation Co²⁺ and giving free cation to enhancement the ability of coordination between ligand molecules and metal cation, thermodynamic study shows the reaction was exothermic reaction and the reaction was entropic region .

Key word: Solvent extraction, Cobalt.

1.Introduction:

Previously used the azo compounds and its derivatives for the extraction methods and used to spectrophotometric determination of transition elements, prepared the ligand 2-[2-benzimidazolyl azo]-4-acetamidophenol and studied its complexes with Fe(III) , Co(II) , Ni(II) ,Cu(II) , Zn(II) and Cd(II) [1] , comparison of extraction for Zn(II) and Ni(II) complexes with 1-octyl-2-methylimidazol was studied [2]. In other study used 4-(2-thiazolylazo) – resorcinol for spectrophotometric determination of Chromium in steel [3]. Anew imidazol ligand was prepared benzo (15-crown-5) -14-imidazol [4,5,f] [1,10] phenanthroline and studied the characterization of its complexes with Co(II) , Ni(II) and Cu(II) [4] ,other study include reactivity of Cis RuCl₂ fragments in Ru(PPh₃)₂ (TaiMe)Cl₂ with N,N-chelators (TaiMe =1-methyl -2-(p-tolylazo) imidazole)[5].For some derivatives of 2-(arylaazo)-4,5-diphenyl imidazole studies spectral and acid base properties [6] . By x-ray determined the crystal and molecular structure of [Ni(Im)₆](dtp)₂ complex (Im=imidazole dtp = o,o diphenyl dithiophosphate [7] ,salen Zn(II) was synthesized and characterized its coordination with imidazole derivatives and amino acid ester was studied [8], In previous study extracted Cu(II) and Ag(I) by used 2-[4-Carboxy methyl phenyl]azo]-4,5-diphenyl imidazole [9],another study used 2-[α-Naphthyl azo]-4,5-diphenyl imidazole for extraction Copper(II) and Silver(II)[10],studied extraction of Uranium and the effect of alkyl group on the extraction [11],studied Chelate complex of new imidazole ligand with Copper(II)[12],studies the complexes of Zn(II) and Ni(II)with imidazoles and inositol derivatives [13]. In this work used (4-ClMePADPI) as derivatives for azo compound as ligand for extraction Co(II) as well as studied the optimum conditions and effective parameters on the extraction method.

2. Experimental

2.1. Reagents

All reagents were of analytical grade quality and freshly distilled water was used.

1.697x10⁻⁴M 1mg/mL Cobalt(II) stock solution was prepared by dissolved 0.4780gm of CoSO₄·7H₂O in 100mL distilled water contain 2mL of concentration H₂SO₄, other working solutions for Co²⁺ ions prepared by dilution with distilled water. 0.5% solution of 1-Nitroso-2-Naphthol in glacial acetic acid prepared.

1x10⁻²M stock solution of 2-[(4-Chloro-2-methoxy phenyl)azo]-4,5-diphenyl imidazole prepared by dissolved 0.03885gm in 10mL chloroform by used 10mL volumetric flask. Other working solutions prepared by dilution with chloroform.

2.2. Apparatus

Spectrophotometer measurements were made in Shimadzu UV-100-02 spectrophotometric single beam and UV-1700 double beam spectrophotometer, Japan. The pH measurements were performed with HANNA Japan.

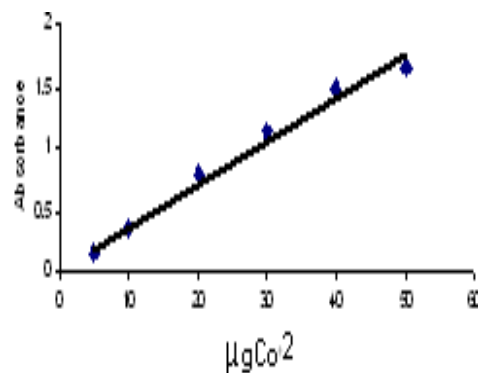
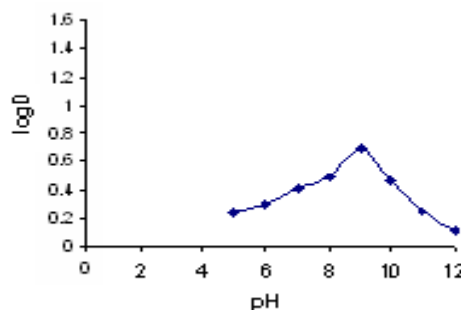
2.3. Procedure

5mL of aqueous phase contain fixed quantity of Co²⁺ ions at optimum condition, add to it 5mL of organic phase (ligand solution) at fixed concentration, shaking the two layers for suitable time afterward separate organic phase from aqueous phase and determine remainder quantity of Co²⁺ ions in aqueous phase by followed Spectrophotometric method (1-Nitroso-2-Naphthol method) [1], after that calculate transfer quantity of Co²⁺ ions to the organic phase and distribution ratio (D).

3. Results and discussion

3.1. Effect of pH

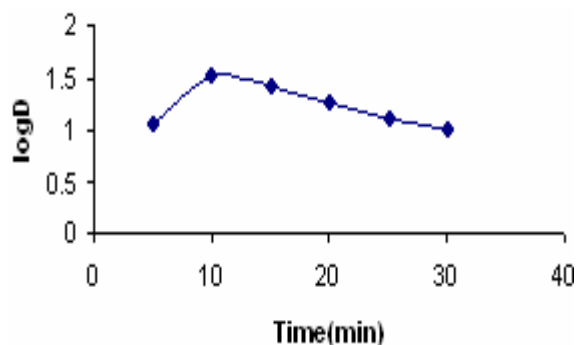
Prepared 5mL aqueous solutions contain 20µg Co²⁺ ions (6.78 x 10⁻⁵M) at different pH (5 – 10), adding to these solutions 5mL of 1 x 10⁻³M ligand solution (4-ClMePADPI) in chloroform, which is synthesized according to the procedure detailed in previous study [2], after that separate of organic phase from aqueous phase and determine remainder Co²⁺ ions in aqueous phase according to spectro photometric method [1] and calibration curve figure(1) afterward calculate distribution ratio (D) at each pH get the results at figure (2).

Fig.1: Calibration curve for Co²⁺ ionsFig.2: Effect of pH on extraction of Co²⁺ ions

The results in figure (2) shows the optimum pH for extraction Co²⁺ ions was (pH_{ex} = 9) , pH less than optimum value not suitable for extraction Co²⁺ ions because may be giving stable species can not be extracted and dominate dissociation constant as well as at pH higher than optimum value .

3.2. Effect of shaking time

5mL aqueous solution contain 20μg (6.7×10^{-5} M) Co²⁺ ions at (pH_{Cx} = 9) was extracted with 5mL of 1×10^{-3} M ligand (4-ClMePADPI) in chloroform at different shaking time (5-30 minutes) after complete shaking separate organic phase from aqueous phase and determine remainder quantity of Co²⁺ ions in aqueous phase as well as transferred quantity to organic phase by followed (1-Nitroso-2-Naphthol method) [1] , later calculate distribution ratio (D), plot logD values against shaking time get figure (3) .

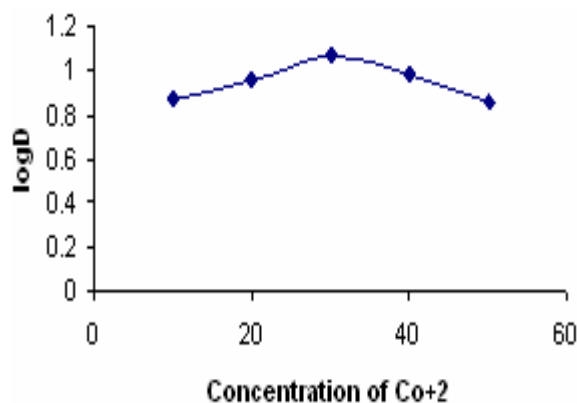
Fig 3: Effect of shaking time on extraction Co²⁺ ions

The results in figure (3) shows the optimum shaking time for extraction was (10 minutes) , shaking time less than 10 minutes it is not enough to reach equilibrium state and decline distribution ratio(D) as well as shaking for longer time minimizing distribution ratio(D) by reason of dominate dissociation equilibria .

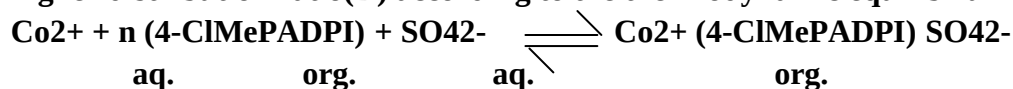
3- Effect of metal ion concentration

5mL aqueous solutions contain different quantities of Co²⁺ ions (10 μ g $\rightarrow$ 50 μ g) at pH_{Hex} = 9 extracted by 5mL of 1 x 10⁻³M ligand 4-ClMePADPI dissolved in chloroform after shaking these two layers for 10 minutes separate organic phase from aqueous phase and determine remainder quantity of Co²⁺ ions in aqueous phase by followed (1-Nitroso-2-Naphthol method) [1], after that determine transferred quantity to the organic phase and distribution ratio (D) and percentage of extraction E.

Plot logD values against μ gCo²⁺ ions giving the figure (4)

Fig 4: Effect of Co²⁺ ions concentration on extraction method

The results in figure (4) shows 30 μ g (1.018 x 10⁻⁴M) Co²⁺ ions in 5mL aqueous phase giving higher distribution ratio(D) according to the thermodynamic equilibrium



This quantity of Co^{2+} ions its necessary to reached the thermodynamic equilibrium but any concentration less than $30\mu\text{g}$ not able to reached complexation reaction to the equilibrium and concentration more than $30\mu\text{g}$ effect to dominate dissociation equilibria according to Leschatlier principle.

3.4. Stoichiometry

3.4.1. Slope analysis method

Form 5mL aqueous phase contain $30\mu\text{g}$ ($1.018 \times 10^{-4}\text{M}$) Co^{2+} ions at $\text{pH} = 9$ extracted by different concentrations of ligand 4-ClMePADPI dissolved in chloroform ($1 \times 10^{-6}\text{M}$ – $5 \times 10^{-4}\text{M}$) at 5 mL volume after shaking 10minutes separate the two layers and determine remainder quantities of Co^{2+} ions in aqueous phase by followed spectrophotometric method [1] and transferred quantities to organic phase as well as distribution ratio(D) after plot $\log D$ values against $\log [4\text{-ClMePADPI}]$ giving the figure (5) .

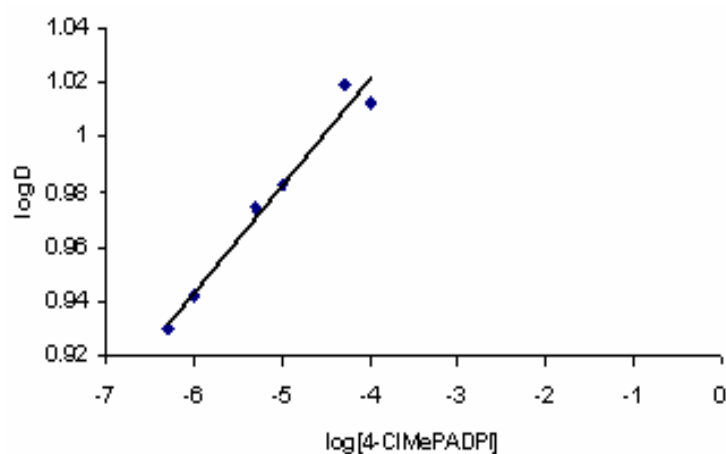


Fig 5: Slope analysis method

The results in figure (5) shows the more probable structure of ion pair complex extracted was $1 : 1 : 1 \text{ Co}^{2+} : (4\text{-ClMePADPI}) \text{ SO}_4^{2-}$.

3.4.2. Mole ratio method

Extracted Co^{2+} ions from 5mL aqueous phase contain $30\mu\text{g}$ Co^{2+} ions ($1.018 \times 10^{-4}\text{M}$) at $\text{pH}=9$ by 5mL organic phase contain different concentration of ligand 4-ClMePADPI dissolved in chloroform ($1 \times 10^{-6}\text{M}$ – $5 \times 10^{-4}\text{M}$) at 10 minutes shaking time ,then separated of two layers and determined the absorbance of organic phase at $\lambda_{\text{max}}=514\text{nm}$ which is the wave length for maximum absorbance to the complex and plot absorbance values (A) against mole ratio CL/CM get the figure(6).

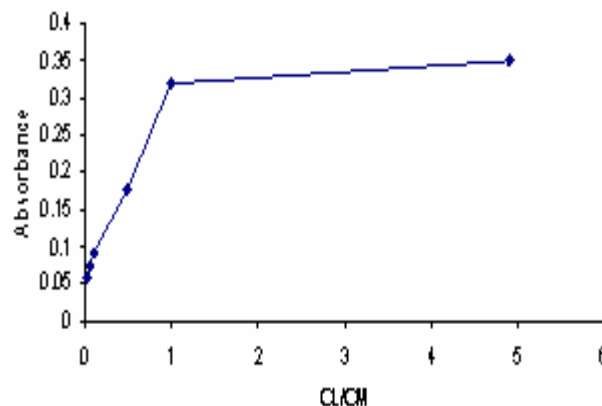


Fig 6. Mole ratio method

Results in figure (6) shows the more probable structure of ion pair complex extracted was 1:1 metal: ligand $\text{Co}^{2+}:(4\text{-ClMePADPI}) \text{SO}_4^{2-}$ identify with result in slope analysis .

3.4.3. Continuous Variation method

Prepared aqueous solution for Co^{2+} ions and organic solutions of ligand 4-ClMePADPI in chloroform at same concentration $1 \times 10^{-3}\text{M}$, mixing different volume of these solutions to maximum volume 5mL and controlled pH at $\text{pH} = 9$, shaking these two layers for 10min. separate these two layers and determine absorbance of organic phase at 514 nm . After plot absorbance (A) against volume ratio giving figure (7).

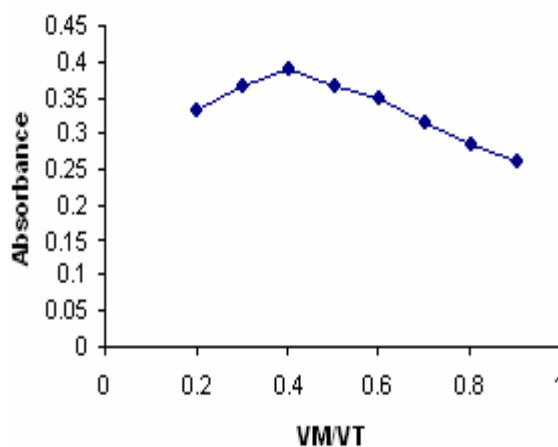


Fig 7. Continuous variation method

The results show more probable structure of ion pair complex extracted was 1:1 metal: ligand $\text{Co}^{2+} (4\text{-ClMePADPI}) \text{SO}_4^{2-}$ as in slope analysis and mole ratio.

3.5. Organic solvents effect

Extracted of 30 μ g Co²⁺ ions (1.018 x 10⁻⁴M) in 5 mL aqueous phase at pH = 9 by 5mL organic solution of ligand 4-ClMePADPI dissolved in different organic solvents differ in dielectric constant (ϵ) after shaking for 10 minutes separate the two layers and then calculate the distribution ratio(D) with each organic solvent used by followed spectrophotometric method [1] and get the results in figure (8) by application of equation below for calculate the transition energy ΔG_t and extraction constant K_{ex} as well as free energy of extraction ΔG_{ex} .

$$\Delta G_t = Z^2 / 2r (1/\epsilon_w - 1/\epsilon_o)$$

$$K_A = \frac{[Co(4-ClMePADPI)^{+2}SO_4^{=}]_{org.}}{[Co^{2+}]_{aq.} [4-ClMePADPI]_{org.}}$$

$$K_{ex} = \frac{K_A \cdot D [Co(4-ClMePADPI)^{+2}SO_4^{=}]_{org.}}{[Co^{2+}]_{aq.} [4-ClMePADPI]_{org.}}$$

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

Table (7) : Organic solvents effects .

Organic solvents	ϵ	ΔG_t KJmole ⁻¹	D	E	K _{ex}	ΔG_{ex} KJmole ⁻¹
Amyl alcohol	15.8	-0.1302	8.375	89.33	8.23×10 ⁷	-44.16
Dichloro methane	9.08	-0.64	10	90.9	9.8×10 ⁷	-44.58
Chloroform	5.708	-1.07	11.5	92	11.3×10 ⁷	-44.92
Bromo benzene	5.4	-1.13	12.9	92.8	12.7×10 ⁷	-45.2
Benzene	2.804	-2.262	20.9	95.4	20.53×10 ⁷	-46.37
Toluene	2.438	-2.6	22.91	95.82	22.5×10 ⁷	-46.59
Carbon tetra chloride	2.38	-2.64	24	96	23.58×10 ⁷	-46.71

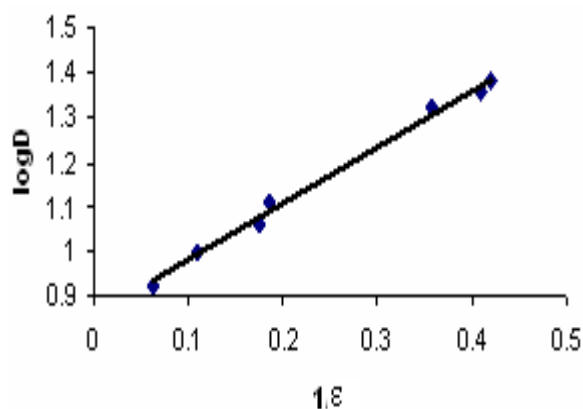


Fig 8. Organic solvents effect

The results shows extraction ability increase with dielectric constant decrease for organic solvents which is help to increase association complex concentration with increase rate of complex formation.

3.6. Effect of temperature

Extracted of 30 μ g Co²⁺ ions (1.018×10^{-4} M) in 5mL aqueous phase at pH = 9 by 5mL ligand solution 4-ClMePADPI dissolved in chloroform at 1×10^{-3} M at different temperature (2 $\rightarrow$ 30 $^{\circ}$ C) after shaking for 10 minutes at each temperature and calculate distribution spectrophotometrically get the results at table (8) .

Table (8): Temperature effect on extraction Co²⁺ ion.

T	2	8	16	20	30
T	275	281	289	293	303
D	15.66	13.49	11.99	10.47	8.5
K	15.38×10^3	13.25×10^3	11.54×10^3	10.28×10^3	8.36×10^3

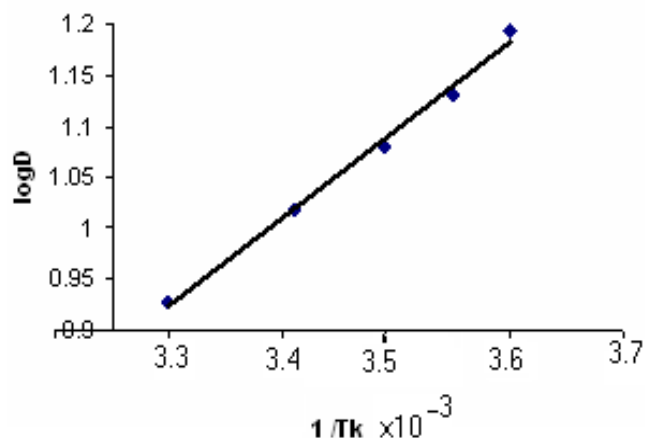


Fig 9. Thermodynamic effect on extraction

The results show the reaction between ligand 4-ClMePADPI and Co^{2+} ions was exothermic reaction. After plot $\log K_{\text{ex}}$ against $1/T_K$ and from the slope of this straight line calculate ΔH_{ex} according to

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

After that calculate ΔG_{ex} and ΔS_{ex} from the equations

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

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

Table (9): Thermodynamic data for extraction Co^{2+} ions.

ΔH_{ex}	ΔG_{ex}	ΔS_{ex}
-0.0154K j mole	-42.15K j mole	153.22 j mole-1k

The enthalpy value reflect the good binding between ligand and metal cation and the large value of entropy demonstrate the reaction was entropic in region.

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