# Extraction of Zn(II) by use 2-[4-chloro-2-Methoxy phenyl azo]-4,5diphenyl imidazole

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استخلاص الخارصين (II) باستعمال الليكاند ٢-[٤-كلورو-٢-مثيوكسي فنيل آزو]-٤,٥-ثنائي

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#### الخلاصة:

باستخدام صفة انتقائية التعقيد لمركبات الآزو مع العناصر الانتقالية كايونات موجبة. فقد تم استخلاص ايونات الخارصين 2n<sup>2+</sup> -2n<sup>2</sup> بطريقة الاستخلاص بالمذيب على هيئة معقد ترابط أيوني باستعمال الليكاند ٢-[٤-كلورو-٢-ميثوكسي فنيل آزو]-٤,٥-ثنائي فنيل اميدازول (CIMePADI-). الدارسة أظهرت أن القيمة المثلى للدالة الحامضية pH<sub>ex</sub> لاستخلاص أيونات الخارصين 2n<sup>2+</sup> من المحلول المائي كانت (β = θ). كذالك فان التركيز الأمثل لأيونات الخارصين <sup>+2</sup> مقي المحلول المائي كانت g 2n<sup>2+</sup> من المحلول المائي كانت (β = θ). كذالك فان التركيز الأمثل لأيونات الخارصين <sup>+2</sup> مقي المحلول المائي كانت g 2n<sup>2+</sup> بما يعادل (M<sup>4</sup> - 10<sup>4</sup> ) والتي تعطي أعلى قيمة لنسبة التوزيع (D). من الجانب الحركي لعملية الاستخلاص فان الدراسة أوضحت ان زمن الرج الأمثل للطورين المائي والعضوي المستعملة كانت ( 15 دقيقة) أما الدراسة حول تأثير المذيب العضوي أوضحت ان زمن الرج الأمثل للطورين المائي والعضوي المستعملة كانت ( 15 دقيقة) أما الدراسة حول تأثير المذيب العضوي المستعمل في عمليات الاستخلاص و أوضحت انه لا توجد أية علاقة خطية بين قيم نسب الاستخلاص (D) وثابت العزل الكهربائي الماستعمل في عمليات الاستخلاص و أوضحت انه لا توجد أية علاقة خطية بين قيم نسب الاستخلاص (D) وثابت العزل الكهربائي المانيبات العضوية المستخلص و أوضحت انه لا توجد أية علاقة خطية بين قيم نسب الاستخلاص (D) وثابت العزل الكهربائي المذيبات العضوية المستخلص و أوضحت أن هناك تأثير لتركيب المذيب العضوي على عملية الاستخلاص، من جانب آخر الخارصين <sup>+2</sup> Zn هو (2 : 1) (Metal : ligand) <sup>2</sup>[Zn(4-ClMePADI)<sub>2</sub>]. أما من الجانب الثرموديناميكي لعملية الاستخلاص فقد بينت الدراسة أن تفاعل التعقيد بين أيونات الخارصين <sup>+2</sup> R و الليكاند (4-ClMePADI) هو تفاعل ماص المحرارة endothermic.

## Abstract:

By use complexation selectivity for azo compounds with transition metal elements as cations in aqueous solutions, extracted Zn(II) ions by solvent extraction method as ion pair complex by using 2-[4-chloro-2-Methoxy phenyl azo]-4,5-diphenyl imidazole [4-ClMePADI]. The study shows the optimum pH<sub>ex</sub> for extraction of Zn<sup>2+</sup> ions from aqueous solution was (pH<sub>ex</sub> = 8), also the optimum concentration of Zn<sup>2+</sup> ions in aqueous solution was (80  $\mu$ g/10 mL) (1.223×10<sup>-4</sup>M) which is giving higher distribution ratio (D), in side of kinetic for extraction method the study shows that the optimum shaking time for the two layers was (15 min.), the study about effect of organic solvent used in extraction method demonstrate there is not any linear relation between distribution ratio (D) and dielectric constant of organic solvents used as well as shows the effect of organic solvent structure on the extraction method, from other hand the stoichiometric study shows the more probable structure of ion pair complex extracted for Zn<sup>2+</sup> ions was (1 : 2) (metal : ligand) [Zn(4-ClMePADI)<sub>2</sub>]<sup>2+</sup>(Cl)<sub>2</sub>, thermodynamic study illustrated the complexation reaction between Zn<sup>2+</sup> ions and ligand [4-ClMePADI] was endothermic.

Key word: Solvent extraction, Zinc.

#### **<u>1. Introduction:</u>**

The extra ordinary applications of azo compounds as reagents for complexation with different metal cations open the door about another application for spectrophotometric determination of metal cations in aqueous phase, this compounds have attracted much attention as analytical reagents owing to the high sensitivity and selectivity. Fan et al [1998] synthesized azo compound for spectrophotometric determination of Ni<sup>2+</sup> ions [1]. Mohamed et al [2001] studied complexation of Zn(II) and Cd(II) with 2-[2-benzimidazolylazo]-4-acetamidophenel.[2] Beniamin et al [2003] studied comparison of the extraction process of Zn(II) and Ni(II) complexes with 1-octylimidazole and 1-octyl-2-methylimidazole [3]. Lenarcik et al, [1979] studied the optimum conditions for extraction of Co(II), Ni(II) and Zn(II) by 1-methylimidazole and 2-methylimidazole [4]. Lenarcik and Glowaki [1979] studied the comparison for extraction of

Co(II), Ni(II) and Zn(II) by 1-ethyl imidazole and 2-ethyl imidazole [5]. Lenarcik and Rauekyte [2002] studied the effect of alkyl chain length on the stability and extraction properties of Ni(II) by 1-alkyl imidazoles [6]. Lenarcik and Kierzkowska [2002] studied the effect of alkyl chain length on the stability and extraction properties of Zn(II) by us 1-alkylimidazoles [7]. Ruijuan et al [2006] synthesis chiral complex of Zn(II) with imidazole derivatives and amino acid ester derivatives. [8]. Ibolya [2002] studied complexes of Cu(II), Zn(II), Ni(II) with imidazole ligands and inositol derivatives [9]. Ibrahim et al [2006] synthesis a new imidazole ligand benzo [15-crown-5]-1H-imidazole [4,5-f] [10] phenanthroline (bip) and studied it complexes with Co(II), Ni(II) and Cu(II) [10]. Wemjiany et al [2002] studies the effect of antifungal imidazole derivatives for inhibition cytochrome  $P_{450}$  [11]. Reginaldo et al [2001] studied the complexes of Ruthenium and Iron with Benzotriazole and Benzimidazole derivatives [12]. Grabmann et al [2005] studied series of imidazole derivatives as a Noval Class compounds with inhibitory Histamin N-Methly transfere and Histamin hH<sub>3</sub> Recepter [13].

# 2. Experimental:

All reagents and solvents were obtained from commercial sources and used as received, absorption and spectrophotometric measurements were made using a single beam UV–Visible spectrophotometer (Shimadzu–UV–100–02) and double beam UV–1700UV–Visible spectrophotometer Shimadzu. pH measurements were carried out using (Ascott Gerasle) pH – meter model 820 as well as Lege unicam sp<sup>3</sup> – 2001 Infra red spectrophotometer and C.H.N FA1108 Elemental analyzer.

## 2.1. Preparation of Solution:

Stock solution 1mg/mL of  $Zn^{2+}$  ions was prepared by dissolved 1gm from element in 15mL of dilute hydrochloric acid HCl 1:1 and then complete the solution to 1L of distilled water in volumetric flask, all other working solution were prepared by dilution with distilled water. Buffer solution pH = 5 for determination  $Zn^{2+}$  ions in aqueous phase was prepared by dissolved 50gm of un hydrous sodium acetate and 30gm of glacial acetic acid in distilled water by use 250 mL volumetric flask . Sodium thiosulphate solution 10% concentration by dissolved 10gm of sodium thiosulphate and complete to 100 mL distilled water by use volumetric flask. Stock solution of  $(1 \times 10^{-2} M)$  dithiazone was prepared by dissolved 0.05232gm of dithiazone in 10 mL carbontetrachloride CCl<sub>4</sub> by use volumetric flask, and other working solutions prepared by

dilution with CCl<sub>4</sub>. Stock solution of ligand 4-ClMePADI of 1×10<sup>-2</sup>M was prepared by dissolved 0.3885gm of ligand in 100 mL of chloroform by use volumetric flask, other working solutions of ligand prepared by dilution with chloroform.

#### **2.2. General Procedure:**

Extraction experiments to relay on take of aqueous phase contain fixed quantity of Zn<sup>2+</sup> ions to make at pH at optimum pH, after that adding 10mL of ligand solution at fixed concentration and shaking the two solution for suitable time, afterward separate the two layers and determine the remainder quantity of  $Zn^{2+}$  ions in aqueous phase and transferred quantity of  $Zn^{2+}$  ions into organic phase to form ion pair complex with ligand to determination the remainder quantity of Zn<sup>2+</sup> ions in aqueous phase follow spectrophotometric determination method [14], by taking the aqueous phase and to make pH (2-3) by adding 2mL of buffer solution, also 2mL of thiosulphate solution afterward shaking the solution with many portions of  $1 \times 10^{-4}$  M dithiazone solution until the last portion don't change its green color, collect the portions in 10mL volumetric flask shaking with 5mL dilute ammonium solution to remove un reacted dithiazone and complete the volume to 10mL by CCl<sub>4</sub>, at last determine the absorbance of this solution at  $\lambda_{max}$ =538 nm by using CCl<sub>4</sub> as blank solution, from the calibration curve figure (1) determine the remainder quantity of  $Zn^{2+}$  ions in aqueous phase. To determine  $Zn^{2+}$  ions in organic phase, shaking organic phase with three portions of nearly concentration hydrochloric acid and collects the aqueous phase and determines  $Zn^{2+}$  ions as in the previous method [14]. Afterward division the quantity of  $Zn^{2+}$  ions in organic phase on its quantity in aqueous phase to determine distribution ratio (D).

# 2.3. Preparation of Ligand (4-ClMePADI):

To prepare imidazole derivatives added 100 mL of glacial acetic acid to mixture of 4.2gm Benzil and 0.52gm of hexamethylemtetramine and 12gm of ammonium acetate, and reflex for 1 hour, after chilling added 400mL of distilled water, afterward precipitate imidazole derivative by addition of 0.88N ammonium hydroxide, after completed the precipitation filter the precipitate and wash it by distilled water, recrystalized the product in pyridine. For produce diazo compound or diazonium salt, prepare amine solution by dissolved 1.57gm of 4-chloro-2-methoxy aniline in 150mL ethanol, also prepare sodium nitrite solution by dissolved 2gm in 150mL of distilled water and added to it 15mL of dilute hydrochloric acid HCl 1:1 drop by drop, needly prepare alcoholic sodium hydroxide solution by dissolved quantity of NaOH in solvent of (15 mL alcohol + 10 mL distilled water), after that mixing the nitrite solution with alcoholic sodium hydroxide, afterward added this mixture drop by drop to the amine solution with chilling to lower than 5°C to produce diazonium compound, the last step to produce the ligand 4-CIMePADI was to solution of imidazole product added diazonium solution drop by drop with chilling to (-5°C), washing the precipitate with distilled water and recrystalized in (ethanol : water).

#### **2.4. Spectrophotometric Studies:**

For detect the structure of ligand prepared (4-CIMePADI) by spectrophotometric studies, UV – Visible spectra shows three peaks, one at (233 nm) for electronic transition  $(\pi - \pi^*)$  for imidazole ring [15], the second at 299 nm for electronic. Transition  $(\pi - \pi^*)$  for benzene ring, the third peak at (442 nm) for Internal charge transfer  $(n - \pi^*)$  this results identify with previous studies. Infra red spectra shows many peaks for stretching vibration for functional groups, strong peak at 3350 cm<sup>-1</sup> for(N–H) group in imidazole ring [15], there weak peaks appear at positions 3050 cm<sup>-1</sup>, 2995 cm<sup>-1</sup>, 2885 cm<sup>-1</sup> to (C–H) aliphatic, aromatic and etheric [15,16], in position 1600 cm<sup>-1</sup> appear strong peak for (C=N) to imidazole ring, imidazole group shows two middle peak at 1450cm<sup>-1</sup>, 1480cm<sup>-1</sup> but the peak appear at (700 cm<sup>-1</sup>) belong to (C–Cl) group. Elements analysis shows the percentage of elements in ligand molecule identify with theoretical (C = 67.95%) (H = 4.37%), (N = 14.4%).



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#### **3. Results and discussion:**

#### **3.1. Effect of pH:**

Extraction of (50µg)  $Zn^{2+}$  ions (7.6 × 10<sup>-5</sup> M) in 1 mL aqueous phase at different pH (3 – 10) by 10mL of ligand solution (1×10<sup>-2</sup> M) 4-ClMePADI dissolved in chloroform at room temperature after shaking two phases for suitable time, separate aqueous phase from organic phase and determine distribution ratio (D) according to previous method illustrated in general procedure. The results in table (1) and figure (2) demonstrate the optimum pH<sub>ex</sub> for extraction of  $Zn^{2+}$  ions from aqueous phase was  $(pH_{ex}=8)$ , and the pH values lower than optimum value effect to protonated ligand molecule and minimizing the extraction ability and decrease distribution ratio (D), but pH value rather than optimum value effect to produce many stable species for  $Zn^{2+}$  ions such as  $Zn(OH)_3^-$ ,  $Zn(OH)_4^{2-}$  [17] which is stable in aqueous phase and can not be extracted, as well as giving ion pair complex contain (OH<sup>-</sup>) as anion more soluble in aqueous phase and effect to decrease distribution ratio (D) also.

pН	3	4	5	6	7	8	10
D	1.66	5.25	13.28	22.38	39.0	49.0	13.29
%E	62.4%	84%	93%	95.7%	97.5%	98%	93%

Table (1): Effect of pH on the extraction of  $Zn^{2+}$  ions



Figure (1): Calibration curve for extraction of Zn<sup>2+</sup> ions





#### **<u>3.2 Effect of Metal Ion Concentration:</u>**

Extraction different concentrations of  $Zn^{2+}$  ions in (10mL) aqueous phase at (pH = 8) was carried out by (10mL) of ligand solution (4-ClMePADI) dissolved in chloroform at (1×10<sup>-4</sup> M) concentration after shaking the two layers for a suitable time separate aqueous phase form organic phase and then determine the quantity of  $Zn^{2+}$  ions in each phase after that calculate distribution ratio (D) and percentage of extraction (E) according to previous method as in the general procedure. The results in table (2) and figure (3) illustrated 80 µg (1.223×10<sup>-4</sup> M)  $Zn^{2+}$ ions was the optimum concentration value which is giving higher distribution ratio (D) and percentage of extraction (E), according to thermodynamic equilibrium for complexation reaction as distinct below:

according to above equilibrium the concentration of  $Zn^{2+}$  ions less than optimum value don't allow to reach the equilibrium but concentration higher than optimum value effect to decrease distribution ratio (D) by reason of dominate the dissociation equilibria according to lechateier principle. And then all concentration less or more than optimum value giving decrease in distribution ratio (D) and percentage of extraction (E), from other hand optimum value giving good and strong complexation binding to produce more stable ion pair complex may be contact ion pair (tight ion pair) or solvent separated ion pair (loose ion pair).

μgZn <sup>2+</sup>	10	20	30	40	50	60	70	80	90	100
D	0.15	0.39	1.99	4.56	8.34	12.59	16.22	19	6.31	4
%E	13.04%	28.05%	66.55%	82.01%	89.29%	92.64%	94.19%	95.06%	86.32%	80%

Table (2): Effect of Zn<sup>2+</sup> ion concentration of extraction method



Figure (4): Effect of  $Zn^{2+}$  ions concentration on the extraction method

# **3.3 Effect of Shaking Time:**

To study the effect of kinetic side on the extraction of ion pair association complex for  $Zn^{2+}$  ions. Extracted 80µg (1.223 ×10<sup>-4</sup> M)  $Zn^{2+}$  ions in 10mL aqueous phase at pH = 8 by 10mL of (1× 10<sup>-4</sup> M) ligand solution 4-ClMePADI dissolved in chloroform, after shaking the two layers for different time (10→25 min.). Separated two layers and determine the quantity of remainder  $Zn^{2+}$  ions in aqueous phase and in organic phase to form the complex by application method in general procedure, and then determine distribution ratio (D) and percentage of extraction (E). The results in Table (3) and Figure (4) shows the suitable shaking time for extraction  $Zn^{2+}$  ions which is giving higher distribution ratio (D) was 15 min., this time allow to reach the equilibrium and produce stable ion pair complex, shaking time less than optimum value not allow to reach equilibrium and minimizing distribution ratio (D) as well as shaking time more than optimum value effect to dominate the dissociation equilibrium and decrease distribution ratio (D).

Time (min)	5	10	12	15	17	20	25
D	N.E	8.5	12.59	19	13.8	7.4	4.3
%E	N.E	84.5%	92.64%	95%	93.24%	88.1%	81.1%

Table (3): Effect of shaking time on extraction of  $Zn^{2+}$  ions



Figure (3): Effect of shaking time on the extraction of Zn<sup>2+</sup> ions

# **3.4 Effect of Organic Solvent:**

According the sensitivity of solvent extraction method and ion pair association complex produced to the organic solvent used in this method, Extracted 80  $\mu$ g (1.223×10<sup>-4</sup> M) Zn<sup>+2</sup> ions in 10mL aqueous phase at pH=8 by 10mL of organic solution contain ligand 4-CIMePADI dissolved in different organic solvents differ in dielectric constant at (1×10<sup>-3</sup> M) concentration, after shaking the two layers for 15 min., separate the organic phase from aqueous phase and determine the remainder quantity of Zn<sup>2+</sup> ions in aqueous phase and in the organic phase to determine the distribution ratio (D) and percentage of extraction (E) according to the previous method as distinct in general procedure. The results in table (4) demonstrate there is no linear, relation between dielectric constant ( $\varepsilon$ ) for organic solvents used and distribution ratio, but there is un effect for the structure of organic solvent on the extraction method and the ion pair complex stability throw the participation of organic solvent in the structure of ion pair complex extracted as contact ion pair (tight ion pair) or solvent separated ion pair (loose ion pair), from other hand this results reflect the priority of carbon tetra chloride organic solvent in extraction of Zn<sup>2+</sup> ions which is giving higher distribution ratio (D) and percentage of extraction (E).

Organic solvent	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Br	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	CCl <sub>4</sub>
3	9.08	5.708	5.40	2.804	2.438	2.38
D	43.40	43.40	35.40	31.00	35.40	79.00
%E	97.7%	97.7%	97.3%	96.9%	97.3%	98.75%

Table (4): Effect of organic solvent of extraction of  $Zn^{2+}$  ions

# 3.5.1. Slope analysis method:

Extraction 80  $\mu$ g (1.223×10<sup>-4</sup> M) Zn<sup>2+</sup> ions in 10mL aqueous phase at pH = 8, with different concentration of ligand solution 4-ClMePADI dissolved in chloroform at 10 mL volume, after shaking the two layers for 15 min separate this two layers and determine the remainder Zn<sup>2+</sup> ions in aqueous phase and the transferred Zn<sup>2+</sup> ions into organic phase and then determine distribution ratio (D) according to method as obvious in general procedure. The results in Table (5) and Figure (5) demonstrate the more probable structure of ion pair complex extracted was (1:2) (Metal:Ligand) [Zn(4-ClMePADI)<sub>2</sub>]<sup>2+</sup>(Cl<sup>5</sup>)<sub>2</sub>.

[4-ClMePADI]	D / CHCl <sub>3</sub>	Slope
$8 \times 10^{-3}$	794.3	
$6 \times 10^{-3}$	501.2	
$5 \times 10^{-3}$	425.3	
$4 \times 10^{-3}$	251.2	
$3 \times 10^{-3}$	98.6	1.8
$1 \times 10^{-3}$	17.8	
$6 \times 10^{-4}$	8.3	
$4 \times 10^{-4}$	3.2	
$1 \times 10^{-4}$	2.2	

Table (5) slope analysis for extraction of  $Zn^{2+}$ ions





### 3.5.2. Mole Ratio Method:

To be sure of structure for complex extraction, extracted  $80\mu g (1.223 \times 10^{-4} M) Zn^{2+}$ ions in 10mL aqueous phase at pH = 8, with 10mL of different concentration  $(3x10^{-4}M - 1x10^{-2}M)$  for ligand 4-ClMePADI dissolved in chloroform, after shaking these two phases for 15min. separate this two phase, and determine the absorbance of organic phase at  $\lambda = 537$  nm by use ligand solution as blank, after that plot absorbance values (A) vis mole ratio  $C_L/C_M$ , the results in table (6) and figure (5) illustrate the more probable structure of ion pair complex extracted into organic phase was (1:2) (Metal : Ligand) [Zn(4-ClMePADI)\_2]^{2+}(Cl\_0)\_2 which is identify with the result in slope analysis method.

Table (6) Mole ratio method for extraction of  $Zn^{2+}$  ions.

C <sub>L</sub> /C <sub>M</sub>	8.13	6.5	4.88	3.25	1.5	0.49	0.33
Α	0.69	0.66	0.59	0.53	0.35	0.09	0.04



Figure (5): Mole ratio method for extraction of  $Zn^{2+}$  ions

# 3.5.3. Continueous Variation Method (job method):-

Mixing different volume to maximum volume 10mL from the same concentration  $(1 \times 10^{-4} \text{ M})$  of aqueous phase contain  $\text{Zn}^{2+}$  ions and organic phase contain ligand 4-ClMePADI dissolved in chloroform at pH=8 after shaking the two layers for 15min. separate these two layers and determine absorbance of organic phase at  $\lambda = 537$  nm by un ligand solution as blank, the results in table (7) and figure (6) shows the more probable structure of ion pair complex extracted to the organic phase was (1: 2) (Metal : Ligand) [Zn(4-ClMePADI)\_2]^{2+}(Cl^{3})\_2 which is identify with the results in slope analysis and mole ratio method.

V <sub>M</sub> mL	1	2	3	4	5	6	7	8	9
V <sub>L</sub> mL	9	8	7	6	5	4	3	2	1
A	0.075	0.32	0.56	0.7	0.64	0.56	0.48	0.41	0.25

Table (7): Continueous Variation method for extraction Zn<sup>2+</sup> ions



Figure (6): Continueous variation method for extraction Zn<sup>2+</sup> ions



# **3.6.** Temperature Effect:

To demonstrate the thermodynamic side of the extraction method of  $Zn^{2+}$  ions as ion association complex extracted 80 µg ( $1.23 \times 10^{-4}$  M)  $Zn^{2+}$  ions in 10mL aqueous phase at pH=8 by 10mL of organic phase contain ligand 4-ClMePADI dissolved in chloroform at ( $1 \times 10^{-4}$  M)

concentration, and at different temperature (5–40±1°C), after shaking the two layers for 15 min separate these two layers and determine the remainder  $Zn^{2+}$  ions in aqueous phase and  $Zn^{2+}$ ions transfer to the organic phase to form ion pair complex, and then determine distribution ratio (D) at each temperature according to the previous method in general procedure. The results in table (8) and figure (7) show the complexation reaction between  $Zn^{2+}$  ions and ligand (4-CIMePADI) was Endothermic reaction.

T ℃	ΤK	1 / T K	D	$K_{ex} \times 10^7$
5	278	3.6	4.46	3.98
10	283	3.5	10.96	8.91
20	293	3.4	18.19	14.8
30	303	3.3	27.54	22.4
40	313	3.1	66.06	53.7

Table (8): Temperature effect on the extraction of  $Zn^{2+}$  ions



**Figure (7) : Temperature Effect for Extraction of Zn**<sup>2+</sup>**Ions** 

The above values of extraction constant  $K_{ex}$  in Table (8) evaluated by the mathematic relation below

$$K_{ex} = \frac{D}{\left[Zn^{2+}\right]_{aq} \left[4 - ClMePADI\right]_{org.}}$$

Afterward plot log K<sub>ex</sub> vis 1/T °K and from the slope of straight line determine the enthalpy of extraction  $\Delta H_{ex}$ , and other data of thermodynamic  $\Delta S_{ex}$ ,  $\Delta G_{ex}$  evaluated form the relations below:

Slope = 
$$-\frac{\Delta H_{ex}}{2.303R}$$
  
 $\Delta G_{ex} = -RTlnK_{ex}$   
 $\Delta G_{ex} = \Delta H_{ex} - T\Delta S_{ex}$ 

The results shows the enthalpy of extraction was ( $\Delta H_{ex} = 0.0424 \text{ KJ mole}^{-1}$ ) and Gibbs free energy was ( $\Delta G_{ex} = -51.15 \text{ kJ mole}^{-1}$ ) as well the entropy was ( $\Delta S_{ex} = 163.55 \text{ JK}^{-1} \text{ mole}^{-1}$ ) from these results appear the effect of charge density of  $Zn^{2+}$  ions for precision the association of  $Zn^{2+}$ ions with ligand molecule and the increase of temperature increase this precision and giving sandwich structure form of ion pair complex extracted (1 : 2) [18], the value of  $\Delta H_{ex}$  make sure of sandwich structure of complex extracted as well as the high value of entropy shows the complexation reaction is entropic in region.



Figure (8): UV – Visible spectrum for ligand 4-ClMePADI



Figure (8): Infra red spectrum for ligand 4-ClMePADI

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