

## Extraction and Spectrophotometric Determination of $Zn^{2+}$ so $Cd^{2+}$ from Different Samples via Liquid Ion Exchange Method.

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### الخلاصة

من خلال أتباع تقنية فصل حساسة تم استخلاص والتقدير الطيفي لكل من اينيوني الخارصين والكاديوم في نماذج مختلفة بعد ان تم تحويل هذه الايونات الى معقدات ترابط اينيوني بأستخدام كاشف عضوي كعامل تعقيد وهو *4-[N-(5-methylisoxazol-3-yl)benzene sulfonamide azo-1-naphthol (NMIBAN)* الدراسة الطيفية أظهرت ان الطول الموجي لأعلى قمة امتصاص كانت عند  $\lambda_{max}=530\text{ nm}$  لمعقد الترابط الاينيوني للخارصين اما لمعقد الترابط الاينيوني لأيون الكاديوم كانت عند الطول الموجي  $\lambda_{max}=527\text{ nm}$  كذلك تم دراسة وتحديد الظروف المثلى للاستخلاص وقد أظهرت هذه الدراسة ان عملية الاستخلاص تحتاج الى  $1.5\text{ M}$  من حامض الهيدروكلوريك  $\text{HCl}$  لإستخلاص ايون الخارصين  $Zn^{2+}$  و  $1\text{ M}$  لأستخلاص ايون الكاديوم  $Cd^{2+}$  عند وجود  $100\mu\text{g}$  من كل ايون من هذه الايونات في  $5\text{ mL}$  من المحلول المائي وقد احتاجت هذه الطريقة الى زمن رج لمدة  $10\text{ min}$  للطورين في هزاز كهربائي وعندما يكون تركيز الكاشف العضوي  $(1 \times 10^{-4}\text{ M})$  اضافة الى دراسة مجموعة من العوامل المؤثرة على كفاءة الاستخلاص مثل وجود الالكتروليتات في المحلول المائي ودراسة المتداخلات وكذلك احتواء المحلول المائي على نسبة مئوية من الميثانول وقد تضمنت الدراسة ايضاً تأثير المذيب العضوي على كفاءة الاستخلاص ومن جانب آخر فقد أظهرت الدراسة الترموديناميكية لعملية الاستخلاص ان عملية الاستخلاص كانت ماصة للحرارة وقد تم حساب الدوال الترموديناميكية لكل ايون من الايونات قيد الدراسة مع أعداد وتقدير طيفي لهذه العناصر في نماذج مختلفة وفق تقنية الاستخلاص المتبعة.

### Abstract

By followed good sensitive separation method extracted  $Zn^{2+}$  and  $Cd^{2+}$  and determination Spectrophotometrically in different samples after converted metal ions into ion pair association complexes by used organic reagent as complexing agent 4-[N-(5-methylisoxazol-3-yl) benzene sulfonamide azo-1- naphthol (NMIBAN), the spectrophotometric study about ion pair complex extracted show wavelength for maximum absorbance was  $\lambda_{max}=530\text{ nm}$  for  $Zn^{2+}$  and  $\lambda_{max}= 527\text{ nm}$  for  $Cd^{2+}$ , as well as the study about pointed optimum condition for extraction, appear this extraction method needs  $1.5\text{ M}$  and  $1.0\text{ M}$  of  $\text{HCl}$  for  $Zn^{2+}$  and  $Cd^{2+}$  respectively in presence  $100\mu\text{g}$  of each ion  $Zn^{2+}$  or  $Cd^{2+}$  in  $5\text{ mL}$  aqueous solution with  $10\text{ min}$ . shaking time in electrostatic shaker by use  $1 \times 10^{-4}\text{ M}$  (NMIBAN), there is many effective parameters on extraction efficiency was studied such as presence electrolyte interferences, methanol in aqueous solution as well as organic solvent, from another side thermodynamic study show extraction method is endothermic in nature and calculated thermodynamic data in the research for each metal ion under study with spectrophotometric determination of each ion under study.

**Key word:** Zinc(II), Cadmium(II), liquid ion exchange method, solvent extraction.

## **Introduction :**

Using new complexing agent 2-(N-5- methylisoxazol-3-yl) benzene sulfonamide azo-1-Naphthol-Benzene (AIBSNB) for extraction Zn(II) via CPE methodology by use of Triton X-100 at pH=9 and 90°C for 15min. by determined all optimum conditions as well as studied all parameters effective on extraction efficiency<sup>[1]</sup>. By application cloud point method and used non-ionic surfactant Triton X-100 separated and determined Bismuth (III) by used complexing agent 4-[N-(5- method isoxazol -3-yl) benzene sulfonamide azo]-1,2-dihydroxy-9,10-anthracenedione at pH=9 and heating at 90°C for 20min. in electrostatic water bath and pointed all optimum conditions and studied all effective parameter<sup>[2]</sup>. Separation and spectrophotometric determination of Cr(VI) as  $\text{Cr}_2\text{O}_7^-$  and Mn(VII) as  $\text{MnO}_4^-$  from acidic media of HCl by used Janus green B after formation ion pair association complex in presence 1% TritonX-100 as a surfactant, in addition, to studying the optimum condition for extraction. This method applied for the spectrophotometric determination of Cr(VI) and Mn(VII) in different samples<sup>[3]</sup>. For extraction chloro anion complexes of  $\text{Cd}^{2+}$  as  $\text{CdCl}_4^-$  and  $\text{Hg}^{2+}$  as  $\text{HgCl}_4^-$  used different extractant according to liquid ion exchange methods such as  $\alpha$ -Naphthyl amine, 4-Amino benzoic acid, 2-[(4-Carboxy methyl phenyl) azo]-4,5-diphenyl imidazole and Cryptand C222. This study includes definition hydrochloric acid concentration in the aqueous phase and shaking with organic phase necessary for extraction as well as shaking time, organic solvent effect, interferences and alkaline salt effect<sup>[4]</sup>. Rhodamine 6G used as anion exchanger for extraction and spectrophotometric determination of  $\text{Hg}^{2+}$  and  $\text{Zn}^{2+}$  ions from HCl media after conversion metal ions into chloroanion complexes. The study includes limitation optimum condition for extraction; in addition to applications this method for determination analyte metal in different samples<sup>[5]</sup>.The Solvent extraction method of Cd(II) by using 2-[Benzothiazolylazo]-4-benzylphenol as an organic reagent, optimum pH of extraction was  $\text{pH}_{\text{ex}}=9$ , As well study all effective parameters on extraction efficiency<sup>[6]</sup>.

## **Experiment :**

Used spectrophotometer double beam UV-Vis. spectrophotometer, (Biochrom Libra S60) (UK) and single beam(UV.-Vis.)spectrophotometer,Shimadzu(UV.-100-02)(Japan)for spectrophotometric studies and absorbance measurements. For shaking used HY-4 vibrator with AD Just about speed multiple (Italy).

All materials used as received from the commercial company without any more purifications as well as all solution prepared by used distilled water.

The organic reagent 4-[N-(5-methylisoxazol-3-yl) benzene sulfonamide azo-1- naphthol (NMIBAN) prepared as in study<sup>[7]</sup>, prepared solution of  $1 \times 10^{-3} \text{M}$  from the organic reagent (NMIBAN) by dissolved 0.0408g in 10mL of chloroform by used volumetric flask and all other working solution prepared by dilution with chloroform. Stock solution 1mg\ mL of  $\text{Zn}^{2+}$  prepared by dissolved 0.0210g of  $\text{ZnCl}_2$  in 10mL distilled water in presence 0.5mL of concentrated. HCl in a volumetric flask and other working solution prepared by dilution with distilled water. As well as stock solution of  $\text{Cd}^{2+}$  1mg\mL prepared by dissolved 0.0160g of  $\text{CdCl}_2$  in 10mL distilled water contains 0.5mL of concentrated. HCl in a volumetric flask.

### **Principal method :**

Prepared 5ml aqueous solution contain  $100 \mu\text{g}$  of  $\text{Zn}^{2+}$  or  $\text{Cd}^{2+}$  and optimum concentration of hydrochloric acid HCl added to each solution 5mL of organic reagent solution NMIBAN dissolved in chloroform at  $1 \times 10^{-4} \text{M}$  and shaking the solution in electrostatic shaker for optimum shaking time (10 min.), at later separate the organic phase from the aqueous phase afterward measure the absorbance of organic phase at wavelength of maximum absorbance which is  $\lambda_{\text{max}}=530 \text{ nm}$  for  $\text{Zn}^{2+}$  and  $527 \text{ nm}$  for  $\text{Cd}^{2+}$  against blank prepared in the same manner at absence metal ion, whereas aqueous phase treated according to spectrophotometric method (Dithizone method)<sup>[8]</sup> and by return to the calibration curve Figure (1) determined the remainder quantity of metal ion in aqueous phase then subtraction the remain metal ion from the original quantity was in aqueous solution to determine the transferred quantity of metal ion into organic phase to from ion pair association complex and from these quantities calculate the distribution ratio D:

$$D = \frac{[M^{2+}]_o}{[M^{2+}]_{aq.}} \quad \text{Where } M^{2+} = \text{Zn}^{2+}, \text{Cd}^{2+}$$

As well as we can be determined the transferred quantity of metal ion  $\text{Zn}^{2+}$  or  $\text{Cd}^{2+}$  by stripping method which is involved shaking the organic phase with moderate ammonium solution by two portions of 5mL and afterward determined the stripped quantity of metal ion by used Dithizone spectrophotometric method but when we are determined metal ion

transferred into organic phase by stripping method find the quantity determined in this method equal to same quantity determined by subtraction method and then we are followed subtraction method to determined transferred quantity of metal ion in all experiments because it is faster and easier.

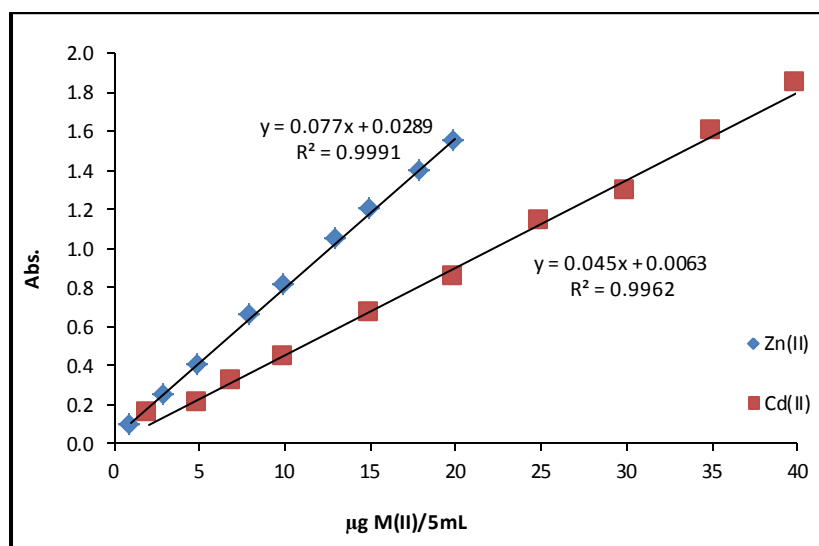
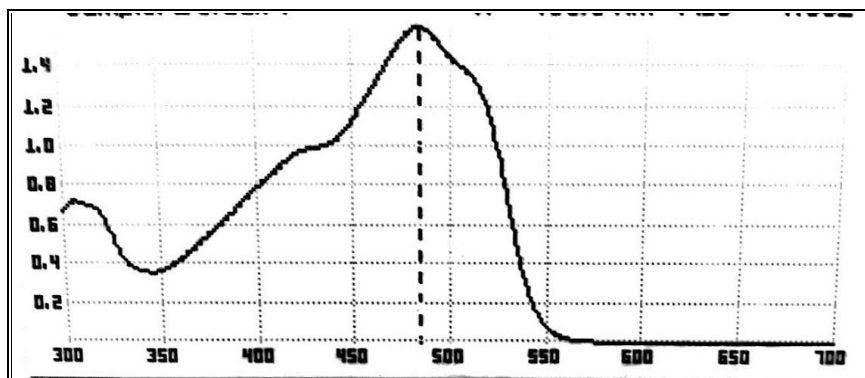


Figure 1: Calibration curve for determination Zn(II) and Cd(II) in aqueous solutions

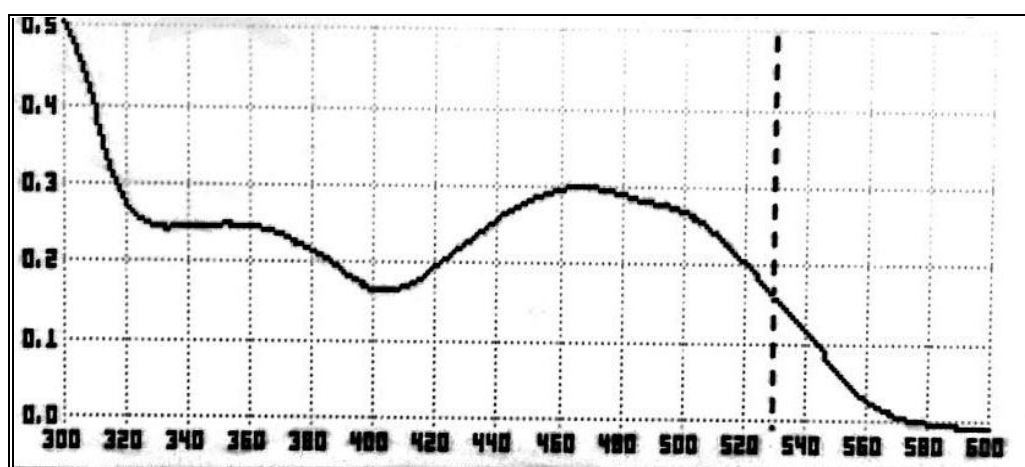
## Results and discussion

### Spectrophotometric study

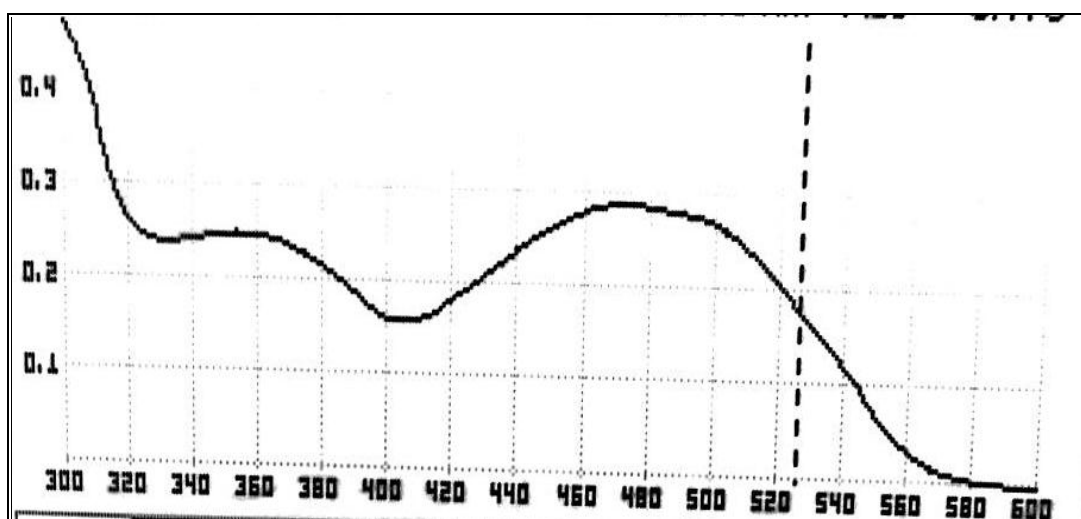
To definition the wavelength of ion pair association complexes extracted to the organic phase for each ion under study prepared aqueous solution 5mL in volume contain 100µg of  $Zn^{2+}$  or  $Cd^{2+}$  with 0.5M of hydrochloric acid HCl afterward added 5mL of NMIBAN solution dissolved in chloroform at  $1 \times 10^{-4}$  M for each solution and shaking these solution for 10min. in electrostatic shaker at later separate organic phase from aqueous phase and perform spectrophotometric study for the organic phase against blank prepared in the same manner in absence metal ion. The results were in Figure 2.



a) spectrum of organic reagent NMIBAN



b) spectrum of ion association complex of  $Zn^{2+}$



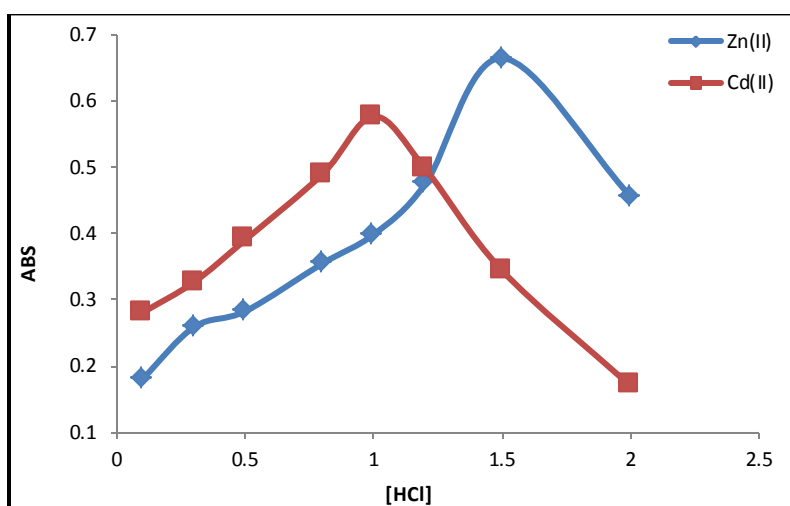
c) spectrum of ion association complex of  $Cd^{2+}$

Figure 2: Spectrophotometric study

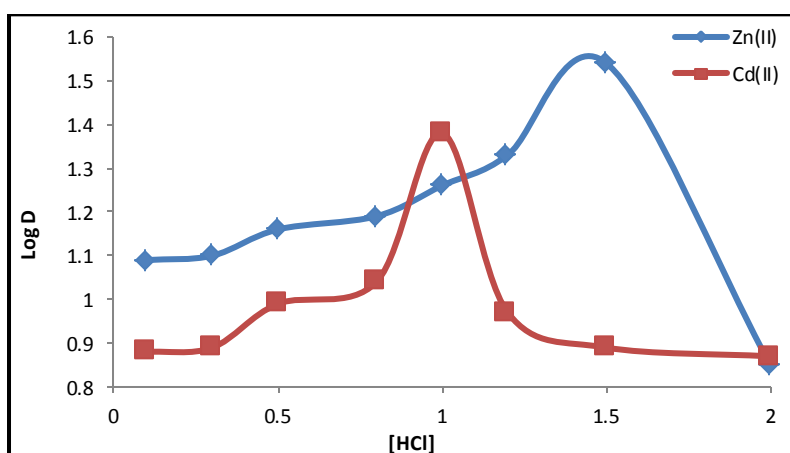
The study shows the wavelength for maximum absorbance for NMIBAN was 485nm and ion pair association complex for  $Zn^{2+}$  was 530nm and for  $Cd^{2+}$  was 527nm.

### Variation of HCl concentration

5mL aqueous solution prepared contain 100 $\mu$ g of each metal ion alone with different concentration of hydrochloric acid HCl and 5mL of (NMIBAN) solution dissolved in chloroform at  $1 \times 10^{-4}$  and shaking these solution at 15min, at later separated organic phase from aqueous phase and treated with these two phase according to the principal method the results were as in the **Figures 3 and 4**:

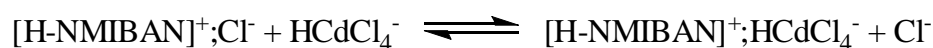
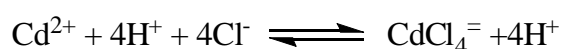
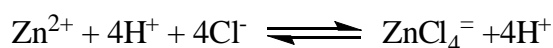


**Figure 3:** HCl concentration effect on ion pair complex formation and stability.



**Figure 4:** D values change as a function of HCl concentration

The results shows optimum value of HCl concentration was 1.5M for Zn<sup>2+</sup> and 1.0M for Cd<sup>2+</sup> at this optimum concentration of HCl reach to the favorable thermodynamic equilibrium for extraction because at this concentration reach to the best rate of formation of halo anion complex for each metal ion ZnCl<sub>4</sub><sup>-</sup> and CdCl<sub>4</sub><sup>-</sup> as well as the best rate for formation ion exchanger so that rate of ion exchange behavior as in equilibria below:



Any concentration of HCl less than optimum value not suitable to reach favorable thermodynamic equilibrium then giving a decrease in anion metal complex concentration ZnCl<sub>4</sub><sup>-</sup> and CdCl<sub>4</sub><sup>-</sup> as well as ion exchanger so that decline in ion exchange behavior that is a mean decline in extraction efficiency. So the concentration of HCl more than optimum value giving decreasing in extraction efficiency also by the effect of a deviation in thermodynamic equilibrium of formation anion metal complex and ion exchanger with an increase in the rate of the backward direction of equilibrium which is a mean increase in the rate of dissociation by the effect of mass action law.

### **Variation of metal ion concentration**

5mL aqueous solution contains rising quantity of Zn<sup>2+</sup> or Cd<sup>2+</sup> and 1.5M or 1.0M of HCl respectively added for each solution 5mL of NMIBAN solution dissolved in chloroform at 1×10<sup>-4</sup> M shaking this solution for 15min. in an electrostatic shaker and then separated the two layers and treated with these layers according to the principal method detailed previously. The results were as in **Figures 5 and 6**:

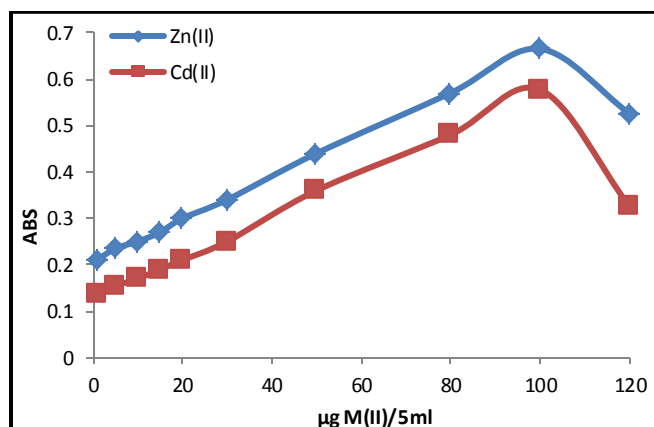


Figure 5: change ion pair complex formation and stability with variation metal ion concentration.

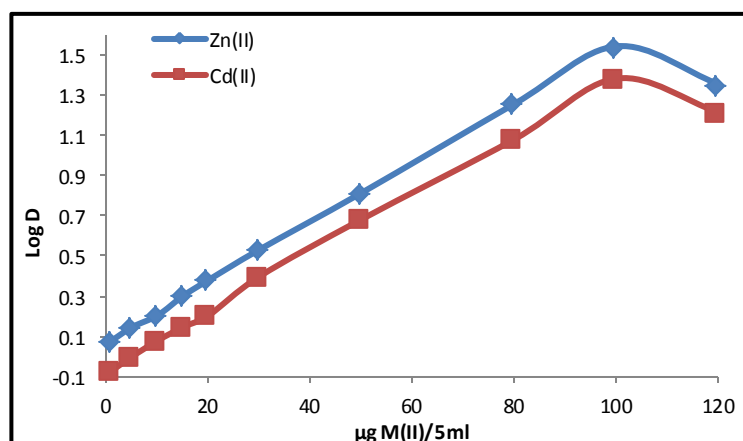


Figure 6: change D values as a function of changing metal ion concentration

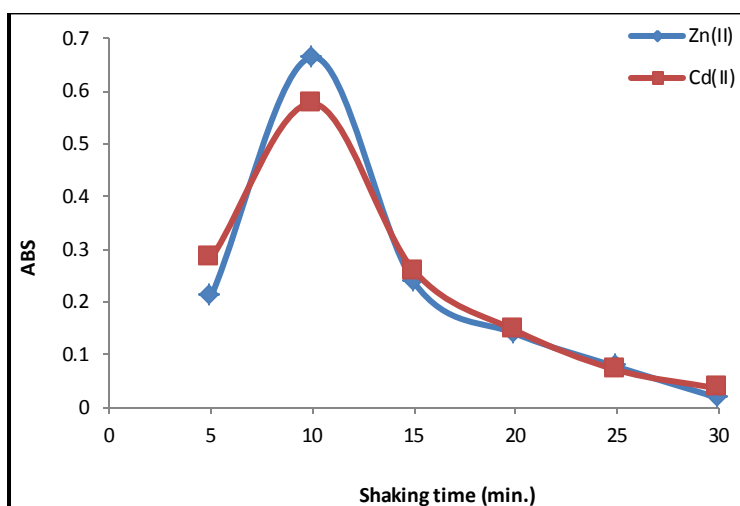
The results demonstrated increasing extraction efficiency as increasing in absorbance and D-value with raising the concentration of metal ion in the aqueous solution until reached optimum value of concentration  $100\mu\text{g M}^{2+} / 5\text{mL}$  at this concentration we are reached to the higher extraction efficiency for both ions under study whereas this result reflect at  $100\mu\text{g}$  of metal ion reach the favorable equilibrium for extraction that is mean giving best concentration of chloro anion complex  $\text{ZnCl}_4^-$  or  $\text{CdCl}_4^-$  by increase the rate of formation in the equilibrium relation as well as increase the rate of exchange behavior and transferring to the organic phase but any concentration of metal ion less than optimum not allow to reach favorable equilibrium and giving increase in dissociation equilibrium and decline in the extraction efficiency from



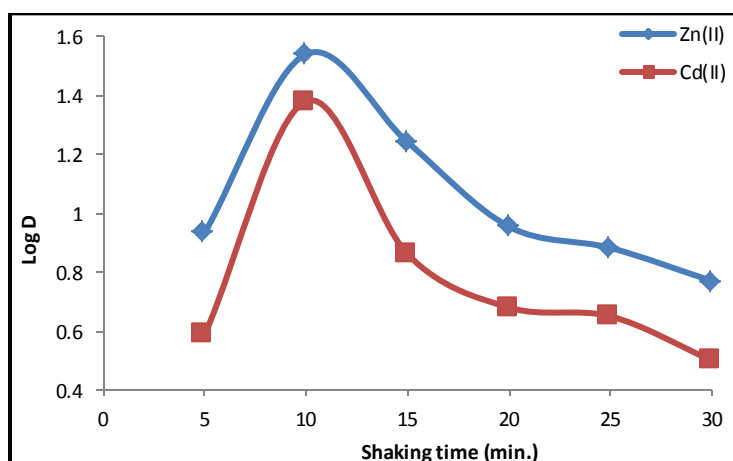
other side the increasing of metal ion concentration more than optimum concentration overshadowed about increasing in extraction efficiency by effect of mass action law.

### Effect of shaking time

Prepared 5mL aqueous solution each one contains 100 $\mu$ g of Zn<sup>2+</sup> or Cd<sup>2+</sup> in presence 1.5 M or 1M of HCl previously than added 5mL of NMIBAN solution dissolved in chloroform at 1 $\times$ 10<sup>-4</sup> M afterward shaker at later separated the organic phase from the aqueous phase and followed principal method for treating each phase. The results were as in **Figures 7 and 8**.



**Figure 7:** formation and stability of ion pair complex with shaking time change

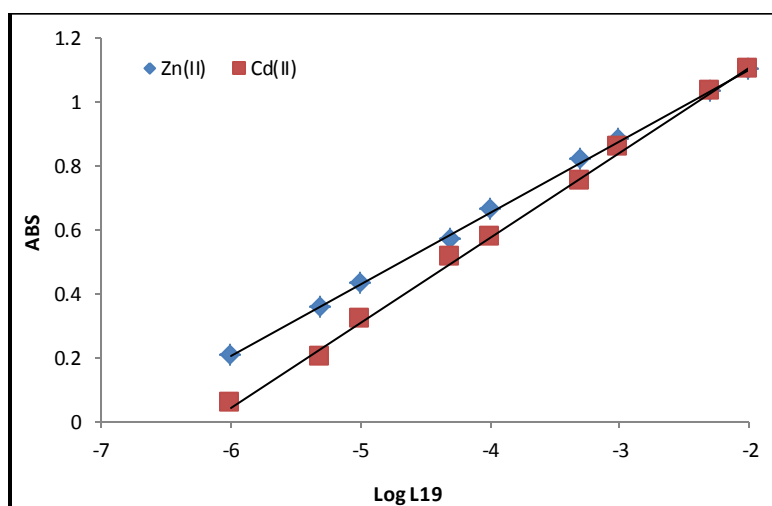


**Figure 8:** extraction efficiency change as a function for shaking time

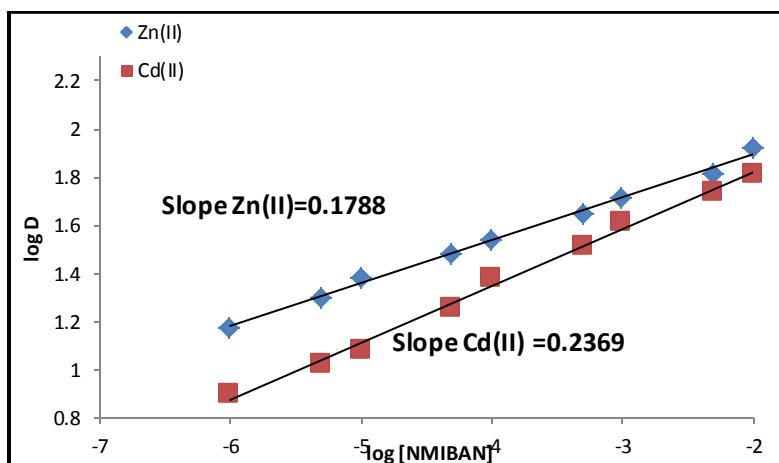
The results shows optimum shaking time for both metal ions was 10min at this time which is represent the kinetic side of extraction method at this time reached the best equilibrium for extraction and giving higher concentration of chloro anion complex and ion exchanger by increasing the forward direction of equilibrium and this shaking time was agreeable for giving maximum extraction efficiency so that any shaking time less than optimum not suitable to reach favorable equilibrium and effect to decrease extraction efficiency .From other hand any increasing in shaking time more than giving decline extraction efficiency as consequence for increasing the backward direction of equilibrium and giving increasing in dissociation by increasing the kinetic energy and diffusion behavior.

### Variation of NMIBAN

Prepared 5mL aqueous solution contain 100 $\mu$ g of Zn<sup>2+</sup> or Cd<sup>2+</sup> with 1.5 M and 1M HCl respectively added to each solution 5mL of NMIBAN solution dissolved in chloroform at rising concentration and shaking these solution in electro station shaker for 10 min and separated the two phases them treated them two layers according to principal method the result were as in **Figures 9 and 10:**



**Figure 9:** ion pair complex formation and stability of with change NMIBAN concentration

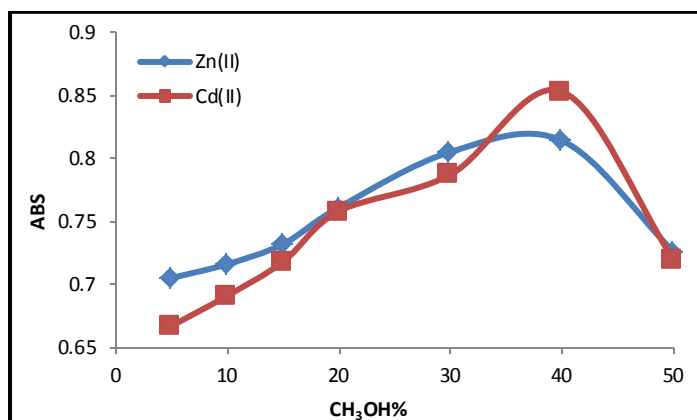


**Figure 10:** effect of NMIBAN concentration on extraction efficiency and D-value

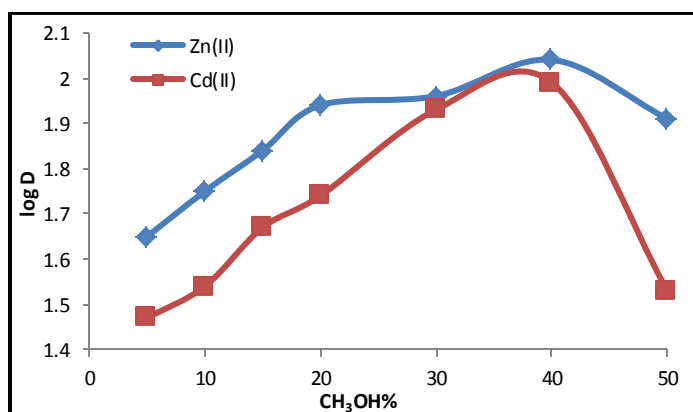
The results appear there in a linear relation for extraction efficiency and rising concentration of organic reagent NMIBAN which emphasize thermodynamic behavior of extraction depend on organic reagent concentration to formation ion pair association complex for each metal ion overshadowed on the increasing of ion exchanger formation with rising concentration of NMIBAN and increase the rate of ion exchange and stability of ion pair association complex formed.

### **Effect of methanol**

Prepared many aqueous solution 5mL in volume contain  $100\mu\text{g}$  of  $\text{Zn}^{2+}$  or  $\text{Cd}^{2+}$  with 1.5 M and 1M HCl respectively and rising percentage of methanol  $\text{CH}_3\text{OH}$  then added to each solution 5mL of  $1 \times 10^{-4}$  M NMIBAN dissolved in chloroform and shaking in electro station shaker for 10minutes then separated the organic phase from the aqueous phase and followed principal method to treated with this two- phases the results were as in Figures 11 and 12 :



**Figure 11:** Effect of methanol percentage on formation and stability of ion pair complexes extracted.



**Figure 12:** Change extraction efficiency and D values by rising percentage of methanol

The results shows there is an increasing in extraction efficiency in presence methanol in aqueous solution and this increasing rising with increasing percentage of CH<sub>3</sub>OH to reach maximum rising at 40% methanol and then decline .this rising in efficiency of extraction produce as a result of effect methanol in aqueous solution which is effect to decrease the dielectric constant and polarity of aqueous solution which cause to destroy the hydration shell of metal ion to increasing formation and stability of chloro metal anion ZnCl<sub>4</sub><sup>=</sup> and CdCl<sub>4</sub><sup>=</sup> with increasing in ion exchange rate and stability of ion pair association complex so that increasing partitioning to the organic phase. But the increase in methanol percentage more than optimum value effect to decrease polarity of aqueous solution very much and increase

partitioning of ion pair association complex to the aqueous solution and decrease extraction efficiency.

### Electrolyte effect

Prepared 5mL aqueous solution contain 100 $\mu$ g of Zn<sup>2+</sup> or Cd<sup>2+</sup> in presence 1.5 M and 1M HCl in the solution respectively and 0.1 M from different electrolytes, shaking this solution for 5min then added to each one 5mL of (NMIBAN) solution dissolved in chloroform at 1 $\times$ 10<sup>-4</sup>M so that shaking in electro station shaker for 10 min afterward separate organic phase from aqueous phase and complete the working according to principal method detailed previously the results were as in **Table 1**.

**Table 1:** Electrolyte effect on extraction efficiency of Zn<sup>2+</sup> or Cd<sup>2+</sup>

<i>Electrolytes</i>	<i>Zn(II)</i>		<i>Cd(II)</i>	
	<i>ABS at <math>\lambda_{max}=530nm</math></i>	<i>D</i>	<i>ABS at <math>\lambda_{max}=527nm</math></i>	<i>D</i>
<i>LiCl</i>	0.819	99.00	0.777	65.67
<i>NaCl</i>	0.787	71.44	0.731	49.00
<i>KCl</i>	0.762	55.82	0.685	36.74
<i>NH<sub>4</sub>Cl</i>	0.688	42.86	0.61	27.57
<i>MgCl<sub>2</sub></i>	0.795	83.75	0.764	43.44
<i>CaCl<sub>2</sub></i>	0.774	67.49	0.695	34.09
<i>BaCl<sub>2</sub></i>	0.733	59.97	0.633	31.26
<i>AlCl<sub>3</sub></i>	0.786	90.74	0.782	32.89

The results appear enhancement in extraction efficiency with presence electrolyte salts in aqueous phase because the electrolyte effect to destroy the hydration shell of metal ion by withdrawing water molecules and increase the chance of formation and stability ion pair association complexes but this behavior show the increasing of extraction efficiency differ by different electrolyte and with the different in ionic diameter and charge density of metal cation in electrolyte and the results demonstrate LiCl giving higher extraction efficiency because Li<sup>+</sup> has smaller ionic radius and higher charge density with larger hydration shell that

is mean could be withdrawing more water molecules from hydration shell of  $Zn^{2+}$  or  $Cd^{2+}$  and increase formation and stability of  $ZnCl_4^-$  and  $CdCl_4^-$  as well as ion pair association complex extracted so that for other electrolytes according to this rule.

### **Effect of interferences**

5mL aqueous solution prepared each solution contain  $100\mu g$   $Zn^{2+}$  or  $Cd^{2+}$  with 1.5 M and 1M HCl respectively in presence 0.1 M of different interferences in these solution added to each solution 5mL of  $1 \times 10^{-4} M$  NMIBAN solution dissolved in chloroform, shaking this solution for 10min in electro station shaker and complete the studying according to principal method and results were as in **Table 2**.

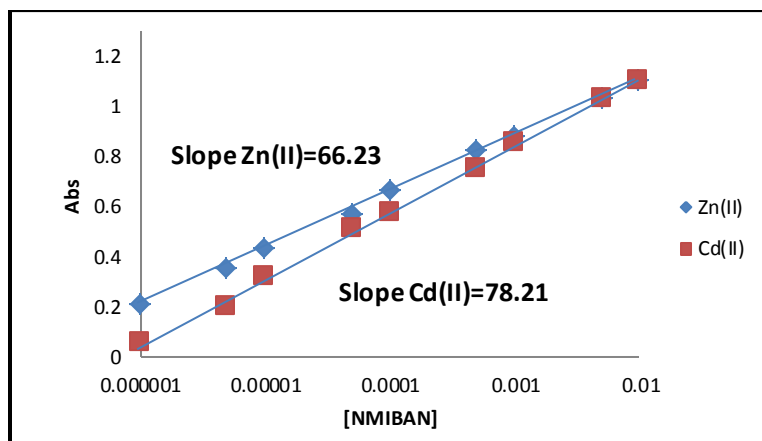
**Table 2:** Effect of interferences on extraction efficiency of  $Zn^{2+}$  or  $Cd^{2+}$ .

Interferences	Zn		Cd	
	<i>ABS at <math>\lambda_{max}=530nm</math></i>	<i>D</i>	<i>ABS at <math>\lambda_{max}=527nm</math></i>	<i>D</i>
<i>Co<sup>+2</sup></i>	0.153	19.41	0.187	8.62
<i>Ni<sup>+2</sup></i>	0.168	21.22	0.203	9.42
<i>Fe<sup>+3</sup></i>	0.186	23.39	0.262	11.82
<i>Hg<sup>+2</sup></i>	0.215	26.78	0.227	10.63

The results appear there is a large interference for the foreign metal ion in aqueous solution by participation. these ions with metal ions under study  $Zn^{2+}$  and  $Cd^{2+}$  in The formation of ion pair association complexes extracted into organic phase , the formation of then complexes effect to decrease HCl and organic reagent NMIBAN less than optimum concentration which causes not reach to favorite thermodynamic equilibrium for formation chloro anion complex and ion pair association complexes as well as decrease in stability of complexes that is mean decrease in extraction efficiency .but this effect differs from ion to another according to behavior of each ion is aqueous phase and ability of formation complexes .

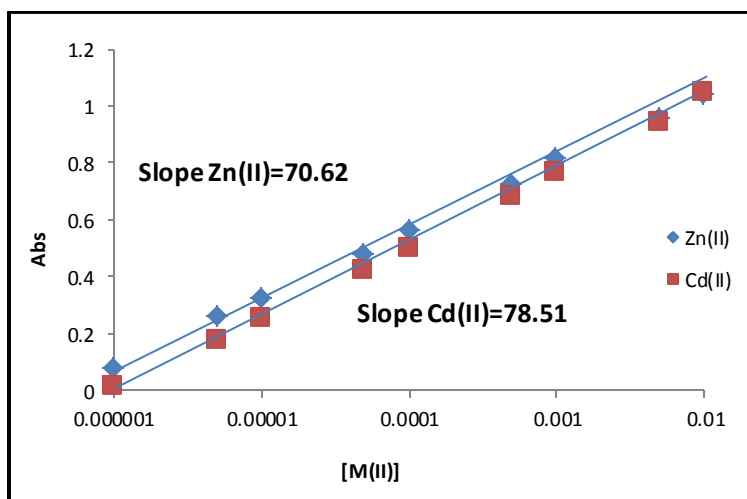
**Stoichiometry:**

For knowledge more probable structure of ion pair association complexes extracted for  $Zn^{2+}$  and  $Cd^{2+}$  by performed two spectrophotometric methods slope analysis method and slope ratio method and the results were as in Figures 13, 14 and 15:



*Slope ratio method*

**Figure 13:** Complex formation =F [NMIBAN]



*Slope ratio method*

**Figure 14:** Complex formation =f [ $M^{2+}$ ]

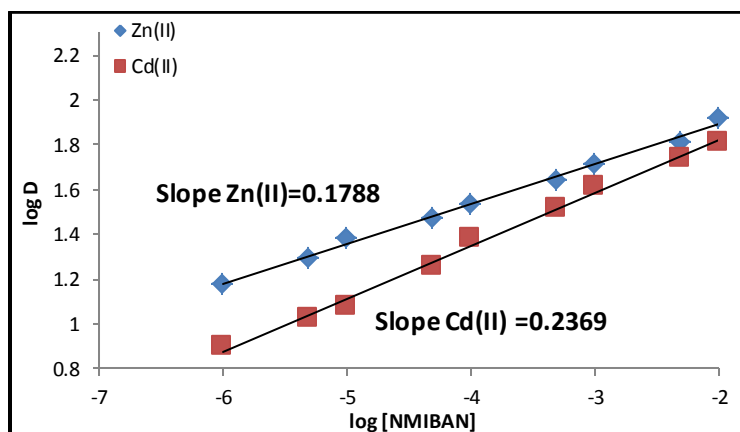
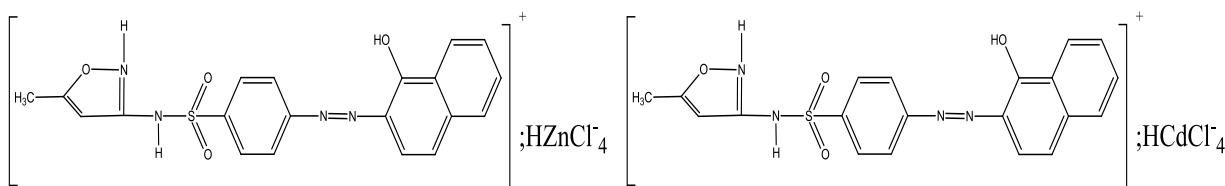


Figure 15: D =F [NMIBAN]

The results demonstrated the ion pair association complexes for both metal ion from the slope ratio and slope analysis method were (1:1) cation : anion  $[\text{H-NMIBAN}]^+$ ;  $\text{HZnCl}_4$  and  $[\text{H-NMIBAN}]^+$ ;  $\text{HCdCl}_4$



### Variation of organic solvent

5mL aqueous solution contain  $100\mu\text{g}$  from  $\text{Zn}^{2+}$  or  $\text{Cd}^{2+}$  with 1.5 M and 1M HCl respectively shaking this solution for 5min then added to each solution 5mL of NMIBAN solution dissolved in chloroform , for 10min in electro station shaker and complete the study on two phases after separated according to principal method the results were as in **Table 3**.



Table 3: Effect of organic solvent

Organic Solvent	Dielectric constant ( $\epsilon_r$ )	Zn			Cd		
		$\lambda_{max}$	ABS	D	$\lambda_{max}$	ABS	D
<i>Nitrobenzene</i>	35.74	459	0.825	17.41	462	0.231	10.31
<i>Amyl alcohol</i>	15.8	464	0.778	16.20	465	0.162	18.80
<i>50%NB+50%T</i>	15.6	414	0.429	12.30	505	0.170	7.21
<i>30%NB+70%T</i>	10.65	455	0.240	15.50	415	0.507	8.65
<i>1,2-Dichloroethane</i>	10.65	335	0.744	8.720	510	0.174	17.40
<i>Dichloromethane</i>	9.08	444	0.94	19.60	447	0.573	20.23
<i>Bromobenzene</i>	5.4	449	0.181	6.22	449	0.220	7.77
<i>Chloroform</i>	4.806	530	0.665	34.71	527	0.577	24.00
<i>50%NB+95%T</i>	3.4	392	0.627	17.41	564	0.150	19.26
<i>Benzene</i>	2.804	452	0.175	4.55	565	0.136	4.51
<i>Toluene</i>	2.438	416	0.398	10.60	563	0.004	6.36

\* *Nitrobenzene (NB)* , *Toluene (T)*

The results shows there is not any linear relation between dielectric constant for organic solvent and distribution ratio of extraction that is mean there is not any effect of polarity of organic solvent but there is an effect for organic solvent structure on extraction efficiency that is applicability predict participation of organic solvent in The formation and stability of ion pair association complexes extracted by giving contact ion pair or loose ion pair.

### Thermodynamic Studys

Prepared 5mL aqueous solution each one contain 100 $\mu$ g from Zn<sup>2+</sup> or Cd<sup>2+</sup> with 1.5 M and 1M HCl respectively shaking these solution for 5min then added to each solution 5mL of 1 $\times$ 10<sup>-4</sup>M NMIBAN dissolved in chloroform, and shaking for 10min in shaker water with regulator at different temperature, afterward separate the two phases and complete the study on these phase as in principal method the results were as in **Figure 16 and 17**:

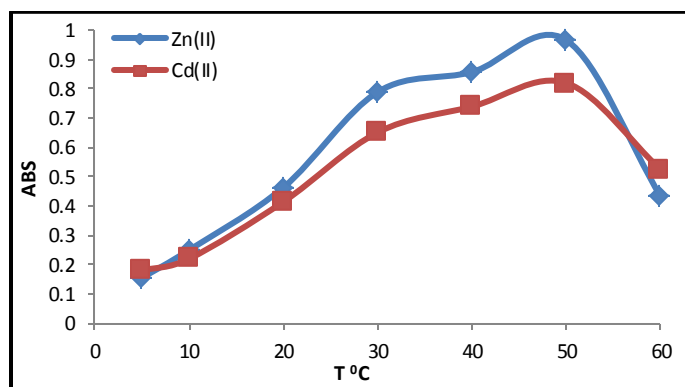


Figure 16: Effect of temperature on ion pair complexes formation and stability

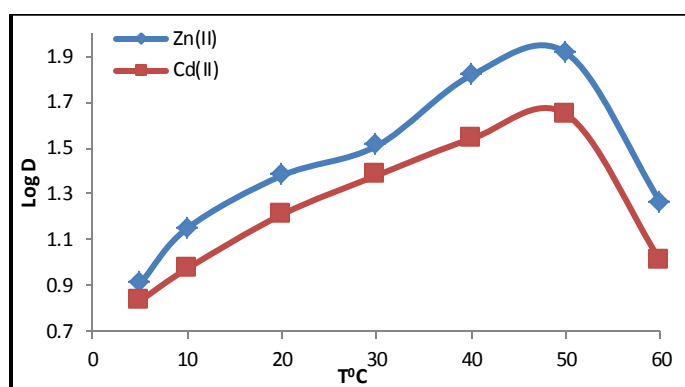


Figure 17: D=F(T°C)

After calculating extraction stability  $K_{ex}$  at each temperature the results were as in Figure 18.

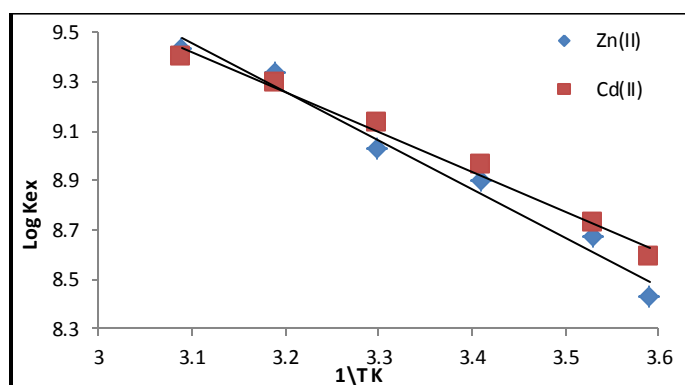


Figure 18:  $K_{ex} = f(T, K)$

From the slope of the straight linear in Figure 18 and application relation below calculate the thermodynamic data<sup>[9]</sup> of extraction and results were as in Table 4:

$$slope = \frac{-\Delta H_{ex}}{2.303R}$$

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

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

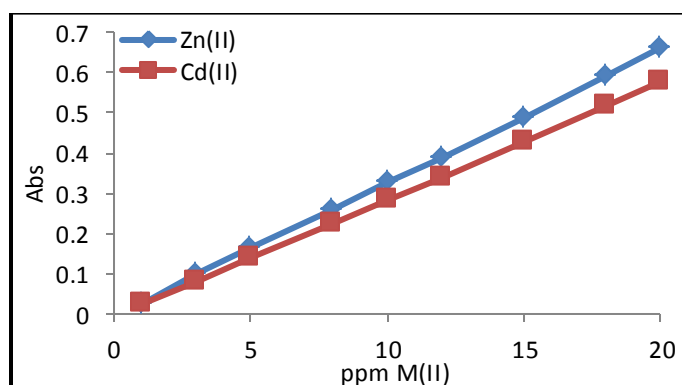
**Table 4:** Thermodynamic data for extraction Zn<sup>2+</sup> and Cd<sup>2+</sup>

	$\Delta H_{ex} \text{ KJ.mol}$	$\Delta G_{ex} \text{ KJ/mol}$	$\Delta S_{ex} \text{ J/mol/K}$
Zn(II)	0.0375	-58.309	180.639
Cd(II)	0.0312	-58.11	180.00

The study shows extraction was endothermic behavior as well as the small value of  $\Delta H_{ex}$  sure the good approaching of ion in complexes so that large positive value of  $\Delta S_{ex}$  mean the extraction method was entropic in region.

### Spectrophotometric Determination

For determination micro amount of Zn<sup>2+</sup> or Cd<sup>2+</sup> in different sample by application the study in title prepared calibration curve by followed liquid ion exchange method according to principal method for differed aqueous solution cation rising quantity of Zn<sup>2+</sup> or Cd<sup>2+</sup> the results were as in **Figure 19**:



**Figure 19:** Calibration curve for spectrophotometric determination Zn<sup>2+</sup> or Cd<sup>2+</sup>

After application the method as in principal method for different sample<sup>[10]</sup> and return to calibration curve determination ppm of each metal ion under study these results were demonstrated in Table 5

**Table 5:** Spectrophotometric determination of Zn(II) and Cd(II) in different samples

<i>Sample</i>	<i>Zn(II)</i>		<i>Cd(II)</i>	
	<i>Method</i>	<i>AAS</i>	<i>Method</i>	<i>AAS</i>
<i>Cow meat (Beef)</i>	27.41	27.24	1.68	1.71
<i>Chicken livers</i>	26.94	27.00	1.62	1.65
<i>Farms Fish</i>	34.22	34.54	1.53	1.51
<i>River Fish</i>	27.3	27.41	1.09	1.07
<i>Radish</i>	44.52	44.10	0.70	0.66
<i>Tomato</i>	31.08	32.12	0.97	0.98
<i>Spinach</i>	36.66	38.72	0.067	0.07
<i>Lettuce</i>	22.60	23.11	0.085	0.082
<i>Banana</i>	3.92	3.65	0.064	0.066
<i>Strawberry</i>	5.05	4.97	0.031	0.032
<i>Al-Mishikhab (Agriculture soil)</i>	135.40	133.52	0.044	0.042
<i>Al-Mishikhab (Non-Agriculture soil)</i>	80.62	81.71	0.014	0.015
<i>Old holy city soil</i>	111.06	111.00	0.021	0.023
<i>Tap water</i>	1.60	1.47	0.043	0.041
<i>Drinking water (Al-Ataba)</i>	4.02	3.94	0.32	0.29
<i>Euphrates river</i>	1.42	1.41	0.04	0.048

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