Liquid- Liquid extraction method for extraction Zn(II) and Cd(II) from aqueous solutions by two synthesized azo organic reagent.

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Abstract

2-[2-pyridil azo]-4-benzen naphthol [PABN] and 2-[(4-Hydroxy phenyl azo]-4,5-diphenyl imidazol [HPADPI] were Synthesized and used for the extraction of Zn(II) and Cd(II) from aqueous solutions. Effective factors on the extraction method was investigated stoichiometry shows the complex extracted was $[M^{+2}(PABN^{-}(Cl^{-})]$ and $[M^{+2}(HPADPI)]_2Cl^{-}$ when ($M^{2+}=Zn^{2+},Cd^{2+}$), Thermodynamic studies appeared complexation reaction for Zn^{2+},Cd^{2+} with both organic reagents was endothermic, in addition of another studies.
The research is apart of MSC thesis.

الخلاصة

2-(2-بريـديل ازو)-4-بنـزين نفثـول(PABN) ،2-[4-هيدروكسـيل فنيـل ازو] -5,4 – ثنـائي فنيـل اميدازول (HPADPI) حضـرت واسـتعملت لاسـتخلاص ايونـات Zn^{2+},Cd^{2+} مـن المحاليـل المائيـة . تمـت دراسة وتحديد العوامل المؤثرة على عملية الاستخلاص . دراسة تركيب المعقد المستخلص أثبتت إن التركيب هـو $[M^{+2}(PABN^{-}(Cl^{-})]$ ،$[M^{+2}(HPADPI)]2Cl^{-}$ حيـث ان($M^{2+}=Zn^{2+},Cd^{2+}$)،امـا الدراسـة الثرموديناميكية أثبتت إن تفاعل التعقيد للايونين الفلزيين مع الكاشفين العضويين كان ماصاً للحرارة، إضافة إلى دراسات أخرى.

Introduction

At present, there are a growing interests in studying complexes formed from azo derivatives as major ligands for metal ions by chemists .In this respect ,many authors have been synthesized various types of azo compounds for diverse purposes concerning the extraction, separation and spectrophotometric determinations of metal ions from different matrix. For example ,1-(5-Methyl-4-Imidazole azo)-2-Naphthol was prepared and used for spectrophotometric determination of Zinc(II) [1-2].New imidazol ligands were synthesized and used for extraction and spectrophotometric determination of cobalt (II), nickel(II) and copper(II) [3].Chromium in steel was determined spectrophotometricaly after its complexation with 4-[thiozolyl azo)-resorcinol (TAR)[4], extraction of Zn(II) and Ni(II) complexes with 1-octyl imidazol and 1-octyl-2-methyl imidazol [5]. Study by use 2-(2-benzimidazolyl azo)-4-acetoamidophenol by use complex formation with Fe(III),Co(II),Ni(II),Cu(II),Zn(II) and Cd(II) [6]. Complexation ability of Co(II),Zn(II)and Ni(II) with several imidazols and some methylated derivatives of 1,3,5-triamino-cisinoctol[7]. Study about examined the extraction of Fe(III), Co(II), Ni(II), and Cu(II) form aqueous media with thiourea monophosphazene (H_2MPZ) in chloroform at different temperature [8]. spectrophotometric determination of micro amounts of manganese (VII) by formation of ion association complex with crystal Niolet [9]. Extracted copper(II) and silver(II) from aqueous solutions by use 2-[(4Carboxy methyl phenyl)azo]-4,5-diphenyl imidazol and 2-[(3-MethylBenzen)azo]-4,5-diphenyl imidazol[10] . solvent extraction

method used for extraction Zn(II) and Cd(II) form sulphate media by 1-phenl-3-methyl-4-benzoylazol-5-one(HPMBP)[11]. 2-[(4-chloro-2-methoxy phenyl)azo]-4,5-diphenyl imidazol used for extraction Zn(II) ,Cd(II) and Hg(II)[12].

Experimental

***Instrument*s**

All spectrophotometric measurements and absorbance were registered by using a double beam (UV-Vis) spectrophotometer shimadz UV 1700 (Japan) and a Single beam (UV-Vis) spectrophotometer TRIUP international corp. TRUV 74,S (Italy), IR-Spectra for the complexes were recorded by using FTIR S 8400 (England).The determination of melting point 5063 Stuart Melting Point Apparatus (England),as well analytical unit 1108 C.H.N Element analyzer.

Materials

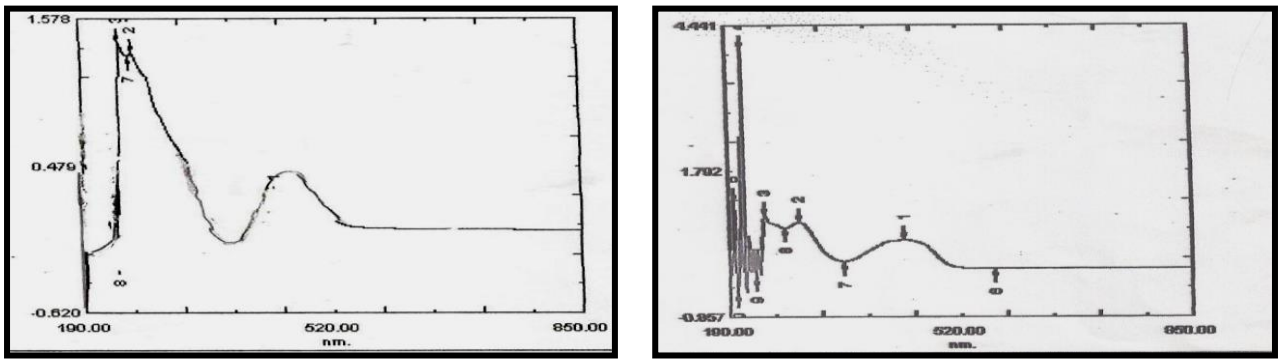
All chemicals used provided from Fluka and Merck such as Zinc chloride ,Cadmium chloride, 4-Di phenyl thio carbazone (dithizone), Amonia, chloroform,2-amino pyridine,4-amino phenol,4-benzen naphthol, benzil, Hexamethylenetetramine, tributylphosphate, methyl isobutyl ketone ,methanol.

General procedure

Aqueous solution 5ml in volume contain limited concentration of metal cation (Zn(II), Cd (II) at optimum pH shaking with 5ml of chloroform solution for PABN, HPADP,after complete shaking separate aqueous solution from organic phase and determine remainder quantity of metal cation in aqueous solution by spectrophotometric method (dithizone method)[13], at later calculate distribution ratio(D) for each ion.

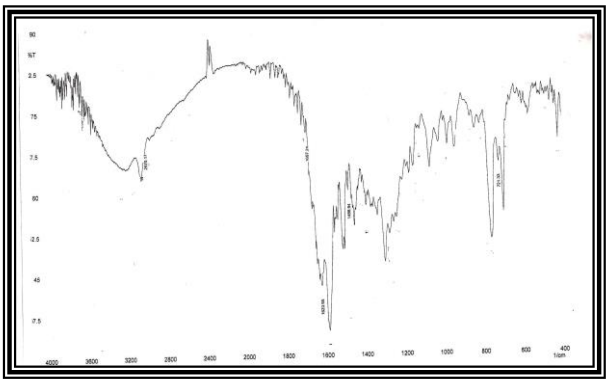
Results and Discussion

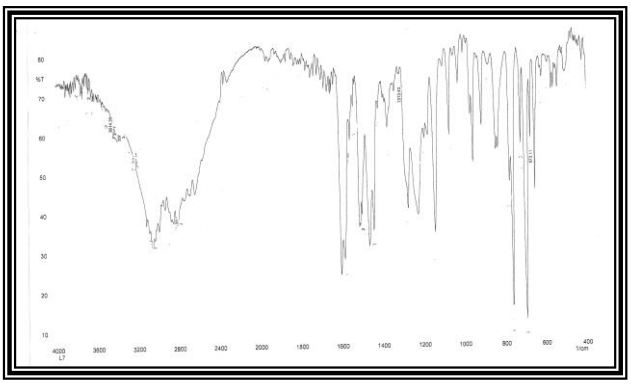
PABN& HPADP ligands were synthesized and used for extraction and spectrophotometric determination of Zinc(II), and Cadmium(II), as shown in UV-VIS and IR spectrums Fig(1) to Fig(6)[14].



A *B*

Fig (1):UV-Vis spectra for(A): PABN(1×10^{-4}M) &(B): HPADPI(1×10^{-4}M) in chloroform

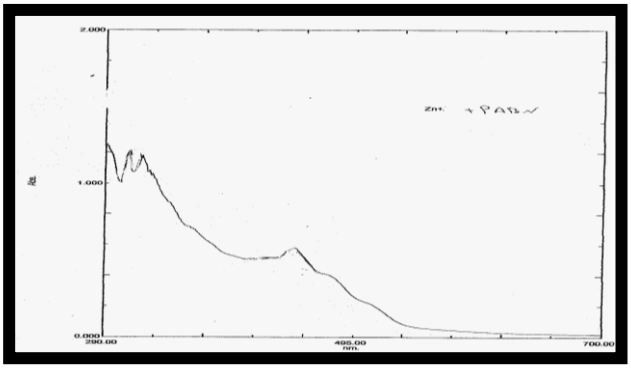




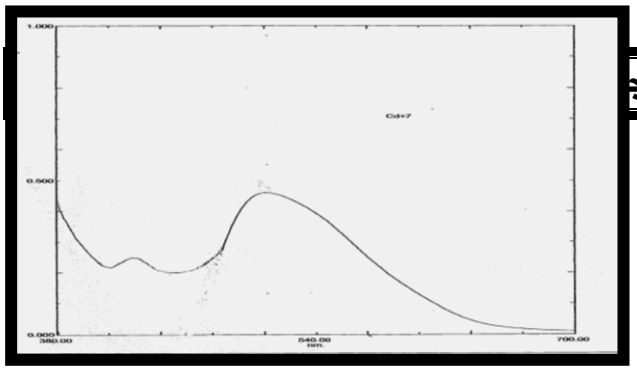
A B

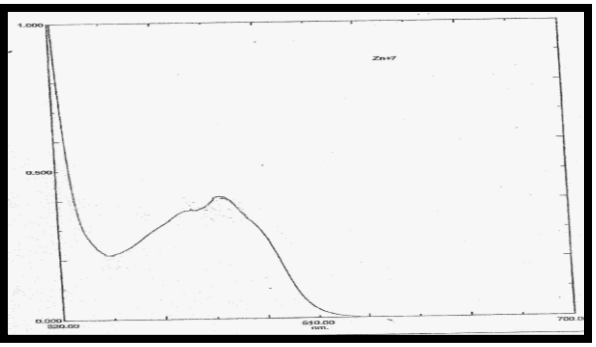
Fig (2):IR-Spectrum for (A: PABN) and (B: HPADPI) ligands

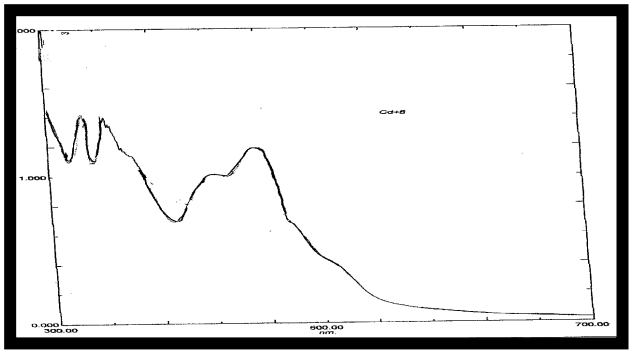
A



Fig(3) : UV-Vis spectra for Zinc(II) complex with (A): ($Zn^{+2}(PABN^{-})(Cl^{-})$) & B($Cd^{+2}(PABN^{-})(Cl^{-})$)

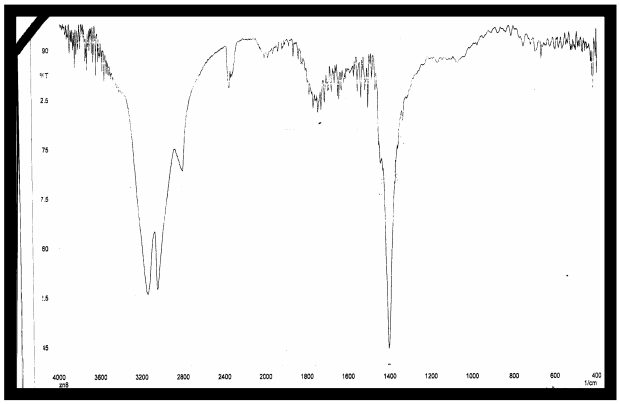


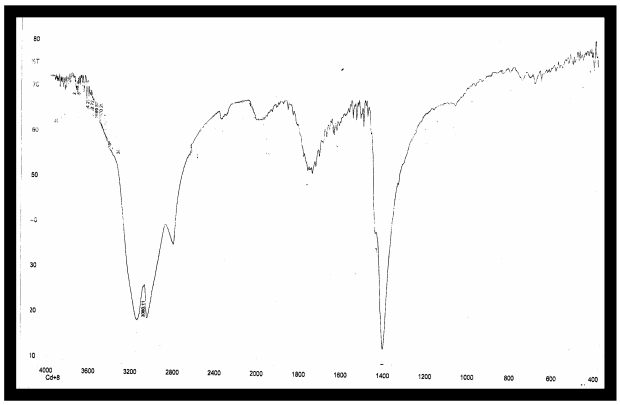




A **B**

Fig(4) : UV-Vis spectra for Zinc(II) complex with (A): (Zn^{2+}(HPADPI)(Cl^-)&B(Cd (HPADPI)$^{+2}$2Cl^-)

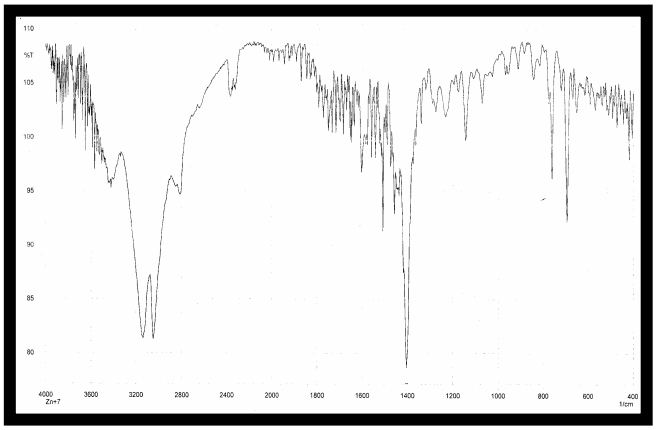


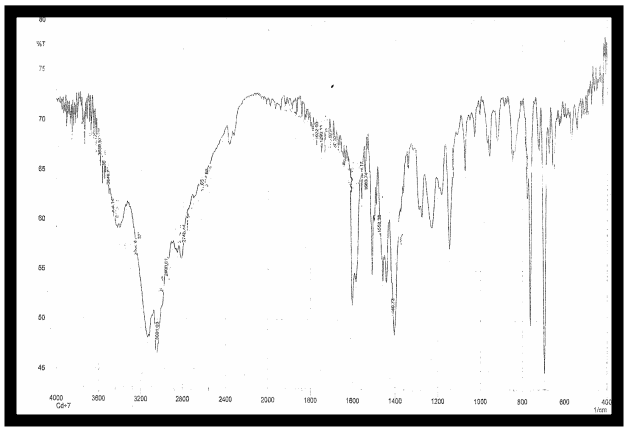


A

B

Fig(5):FT IR- Spectrum for PABN complex with A:Zinc(II) and B:Cadmuin(II)





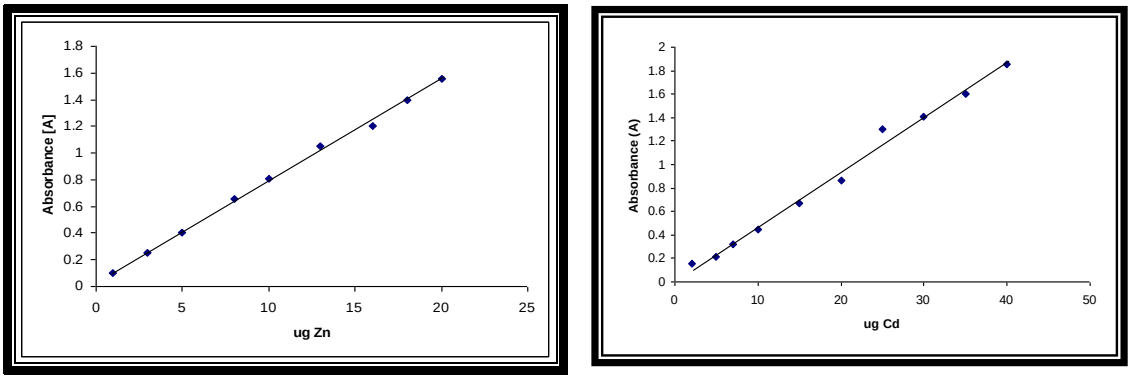
A B

Fig(6): FTIR-Spectrum for HPADPI complex with A: Zinc(II) and B: Cadmium(II)

The study of C.H.N shows the percentage of C=75.243% ,H=4.329%, N=12.860%, O=5.06% identify with theoretical values C=77.5%, H=4.615, N=12.923%, O=4.923% for PABN but for HPADPI is C.H.N results shows the percentage of C=76.041%, H=5.264%, N=16.041%, O=5.08% identify with theoretical values C=74.12%, H=4.706 N=16.47,O=4.706%.

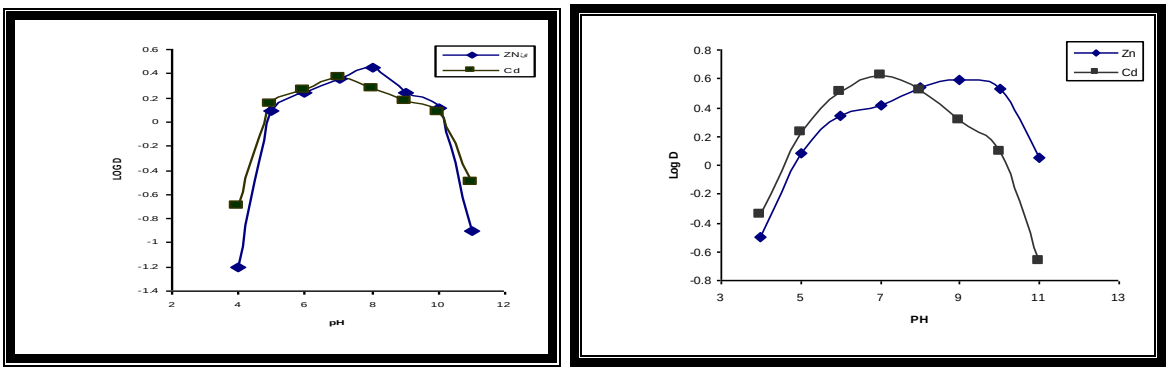
Effect of pH

Extraction of 50 µgZn^{2+}/5ml and 50 µgCd^{2+}/5ml by the two ligands at different pH(1-14) as in general procedure and calculate D value at each pH ,Figures(7,8) shows optimum pH_{ex} for $Zn^{2+}$was pH_{ex}=8 and 9 with PABN & HPADPI respectably but Cd^{2+} was pH_{ex}=7 with both ligands.



A B

Fig(7) Calibration Curves of Dithizone method for A:Zn(II) and B: Cd(II)



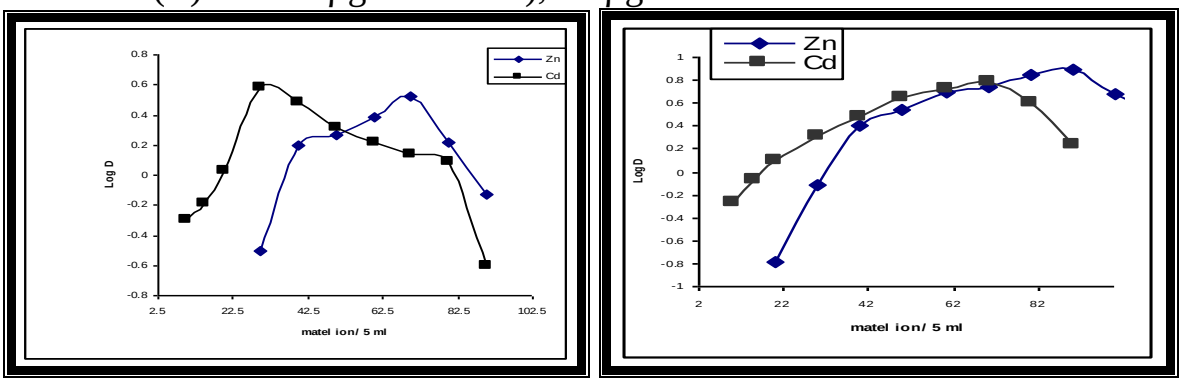
A B

Fig(8) :effect of pH (A) PABN,(B) HPADPI with Zn(II) &Cd(II) ions

Acidic media not suitable for extraction because effect to protonated ligand molecule and decline extraction and distribution ratio (D), also pH more than optimum value not as well suitable for extraction because dissociation of complex and formation stable species' of metal cation.

Effect of metal ion concentration

aqueous solutions 5ml in volume contain (10 µg-90 µg) Zn(II) or Cd(II) extracted by PABN or HPADPI after calculate distribution ratio (D). The results in Figure(9) shows optimum concentration of Zn(II) was 70 µg with PABN, 80 µg with HPADPI but Cd(II) was 30 µg with PAB), 70 µg with HPADPI.



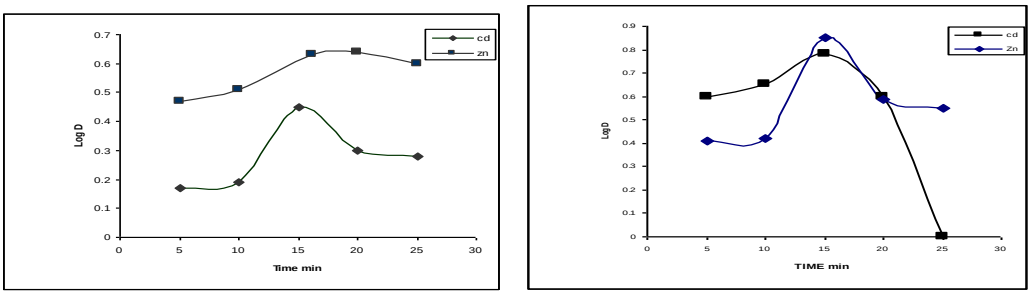
A B

Fig (9) Effect of metal ions concentration with(A): PABN and B: HPADPI

According to thermodynamic equilibrium for complexation reaction ,concentration of metal cation play major rule for formation and stability of complex extracted.

Effect of shaking time

Beside thermodynamic there is un effect for kinetic energy on extraction method. 5ml aqueous solution contain optimum quantity of each ion at optimum pH_{ex} extracted with 5ml ligand solution (1×10^{-4} M) dissolved in chloroform at different shaking time (5-25) minutes. Figure (10)shows 20min forZn(II) and 15min for Cd(II) with PABN, but 15min suitable for extraction Zn(II) and Cd(II) with HPADPI.



A B

Fig (10) Effect of shaking time on extraction of Zn(II) & Cd(II) by A:(PABN) andB:(HPADPI)

Effect of organic solvent

Extraction metal cations from 5ml aqueous phase according to general procedure by 5ml ligands solution at (1×10^{-4} M) dissolved in different organic solvents. The results at Tables(1,2) shows there is not any linear relation between dielectric constant (ε) and distribution ratio (D),but there is an effect for organic solvent structures on distribution ratio (D).

Table (1) Effect of organic solvents on extraction of Zn(II) extraction

Organic solvent	Dielectric constant ε	PABN					HPADPI				
		D	ΔG_T KJ mol	K_A *mol* $*10^4$ *L*	K_{ex} $*10^8$	$-\Delta G_{ex}$ K.J.mol	D	ΔG_T KJ mol	K_A 10^4 *mol L*	K_{ex} $*10^8$	ΔG_{ex}*K.J - mol*
Nitro Benzene	*.47035*	*1.65*	.0420	1.231	1.272	45.20	*.146*	042.0	2.669	13.960	51.02
Amyl Alcohol	*.80015*	*1.66*	.1370	1.248	1.287	45.24	*.8012*	.1370	5.120	60.680	54.57
1،2-DCE	*.65010*	*1.95*	.2190	1.392	3.802	47.86	*.256*	.2190	2.717	14.465	51.10
DCM	*.0809*	*1.89*	.2690	1.410	3.465	47.64	*.506*	.2690	2.731	15.640	51.28
Chloro Benzene	*.7085*	*2.15*	.4390	1.472	2.159	46.53	*.345*	.4390	2.301	10.560	50.34
Chloroform	*.8064*	*4.34*	.5280	2.553	8.801	49.97	*.417*	.5280	3.060	20.000	51.92

Benzene	*.8042*	*2.01*	.9300	1.435	1.887	46.16	*.416*	.9300	2.601	13.96	51.02
Toluene	*.4382*	*1.71*	.0801	1.266	1.366	45.38	*.037*	.0801	2.929	18.300	51.67
Carbon tetra chloride	*.3802*	*1.89*	.8901	3.480	3.465	47.64	*.008*	.8901	3.278	23.000	52.29

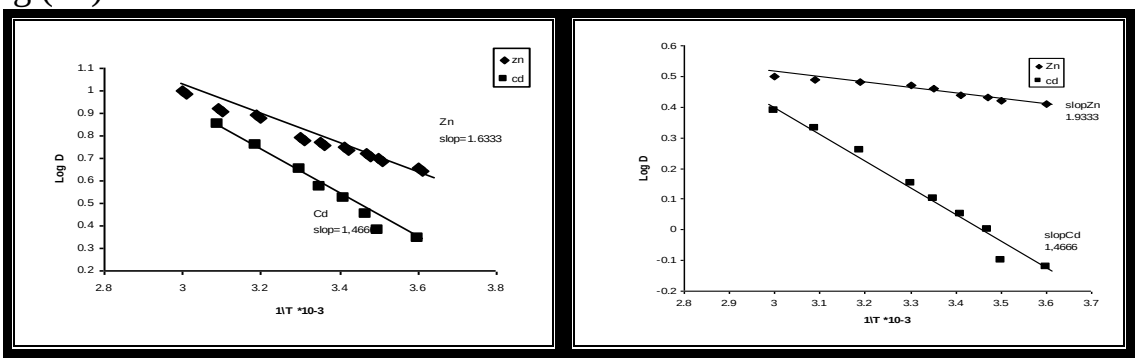
Table (2) Effect of organic solvents on extraction of Cd(II)

Organic solvent	Dielectric constant ε	PABN					HPADPI				
		D	$-\Delta G_T$ K.J. mol	K_A *mol L* 10^4 *	**10* K_{ex} ^{8}	ΔG_e $_x$*k.J. mol*	D	ΔG_T K.J. mol	K_A 10^4 *	K_{ex} **10* ^{8}	$-\Delta G_{ex}$ K.Jmol
Nitro Benzene	*.47035*	*.581*	*2.85*	*2.85*	*2.85*	*2.85*	*852.*	*2.85*	1.803	1.803	1.803
Amyl Alcohol	*.80015*	*.501*	*1.85*	*1.85*	*1.85*	*1.85*	*851.*	*1.85*	2.312	2.312	2.312
1،2-DCE	*.65010*	*.381*	*3.12*	*3.12*	*3.12*	*3.12*	*123.*	*3.12*	3.319	3.319	3.319
DCM	*9.080*	*.301*	*2.26*	*2.26*	*2.26*	*2.26*	*262.*	*2.26*	2.977	2.977	2.977
Chloro Benzene	*5.708*	*.141*	*1.85*	*1.85*	*1.85*	*1.85*	*851.*	*1.85*	2.312	2.312	2.312
Chloroform	*4.806*	*.622*	*6.14*	*6.14*	*6.14*	*6.14*	*146.*	*6.14*	5.738	5.738	5.738
Benzene	*2.804*	*.980*	*2.04*	*2.04*	*2.04*	*2.04*	*042.*	*2.04*	2.457	2.457	2.457
Toluene	*2.438*	*.021*	*3.21*	*3.21*	*3.21*	*3.21*	*213.*	*3.21*	3.378	3.378	3.378
Carbon tetra chloride	*2.380*	*.870*	*1.67*	*1.67*	*1.67*	*1.67*	*671.*	*1.67*	2.168	2.168	2.168

Effect of Temperature

Extraction metal cations from 5ml aqueous phase according to general procedure by 5ml ligands solution at (1×10^{-4} M) dissolved in chloroform at different temperature (5-60)C after separate organic phase from aqueous phase, determine remain Zn(II) and Cd(II) in aqueous phase and transferred quantity to organic phase

and calculate distribution ratio (D) at each temperature and plot log D against 1/T K get Fig (11).



A B

Fig (11):Temperature effect on distribution ratio(D);A(PABN),B(HPADPI)

After calculate extraction constant K_{ex} according to relation below, plot log K_{ex} vis1/T K get Fig (12).

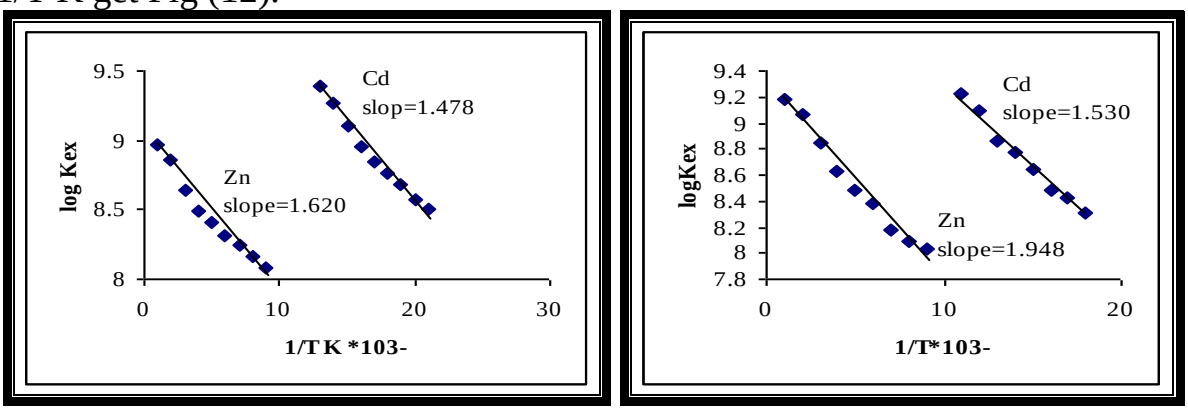


Fig (12) : Temperature effect on extraction constant K_{ex}: A(PABN),B(HPADPI)

$$Kex=\frac{D}{[cation]_{aq}[ligand]_{og}}$$

From the slope of straight line in Fig (12) enthalpy ΔH_{ex} was determined as :

$$Solpe=\frac{-\Delta Hex}{2.303R}$$

Free energy of extraction ΔG_{ex} and entropy ΔS_{ex} were calculated according to as in relation below :

$$\Delta Gex=-RTLnKex$$

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

Table (3) The thermodynamic values (ΔSex ,ΔGex ,ΔHex)

ions	PABN	HPADPI

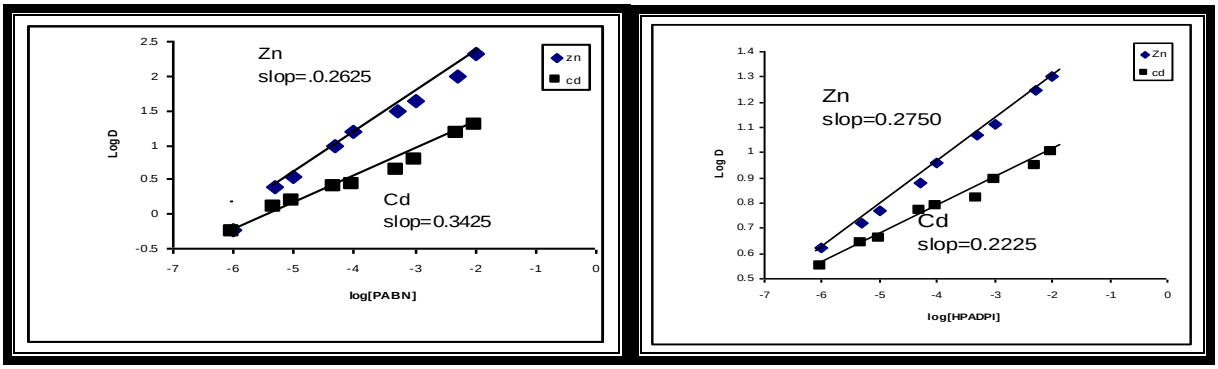
	Δ Hex kJmol -	Δ Gex kJ - mol-	Δ*Sex* J mol-K1-	Δ Hex kJ mol -	-ΔG_{ex} *K J* *m*ol-	Δ*Sex* J mol-K1-
Zn	*0.0372*	*58 .18*	*174.73*	*0.0309*	*56.47*	*169.390*
Cd	*0.0293*	*56.68*	*175.50*	*0.0282*	*58.90*	*176.90*

The results have that shows the reaction between PABN and HPADPI with Zn(II) and Cd(II) was endothermic (Table 3).

Stereochemistry

Slope analysis method

Extraction metal cations from 5ml aqueous phase according to general procedure by 5ml ligands solution dissolved in chloroform at different concentration (1×10^{-6}-5×10^{-4}M), sequentially separate the two layers after separate organic phase from aqueous phase, determine remain Zn(II) and Cd(II) in aqueous phase and transferred quantity to organic phase and calculate distribution ratio (D) at each concentration of ligand, afterward plot log D against log[ligand] get the graph in Fig (13).



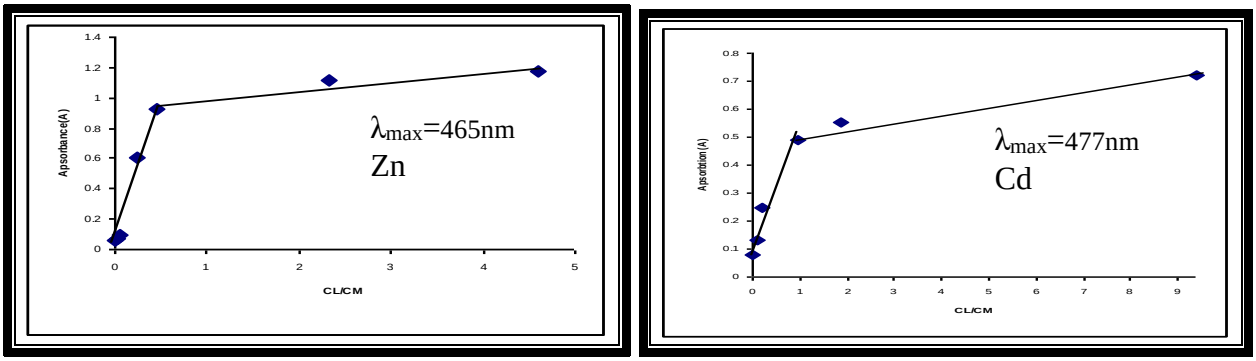
A B

Fig (13) The slope analysis method for A:PABN and B: HPADPI

The slope of straight lines in Figure(13) demonstrate the complex extracted was 1:1 metal :ligand

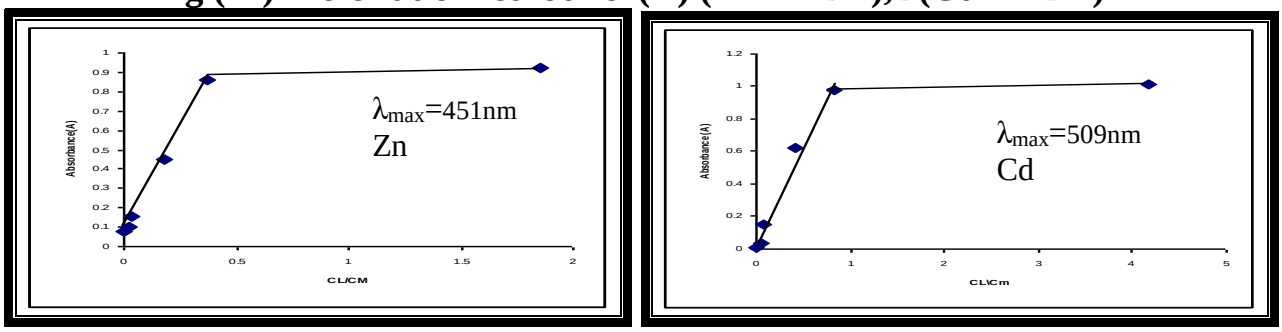
Mole ratio method

Extraction metal cations from 5ml aqueous phase according to general procedure by 5ml ligands solution dissolved in chloroform at different concentration (1×10^{-6}-$5\times10^{-}$4M), sequentially separate the two layers , afterward plot absorbance vis CL/CM get the graph fig (14,15) A&B



A B

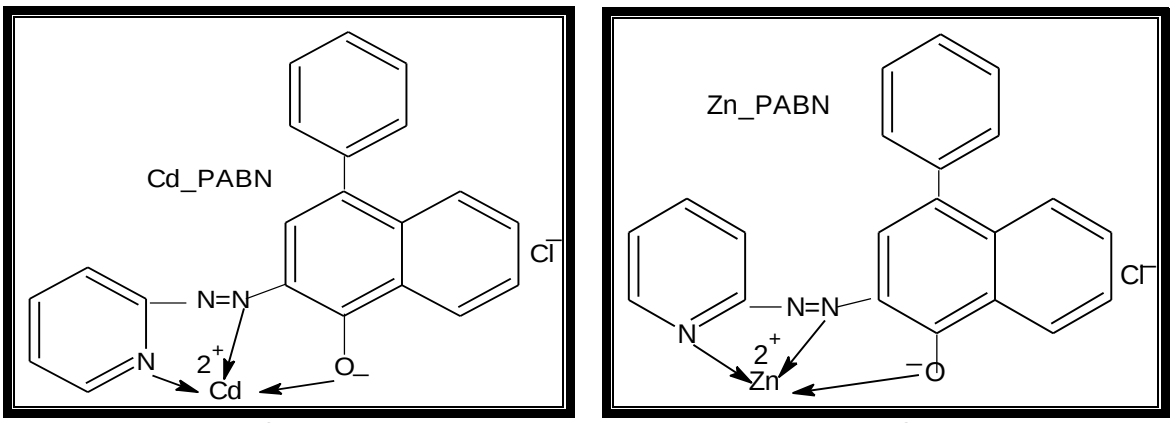
***F*ig (14) Mole ratio method for(A) (Zn-PABN),B(Cd-PABN)**



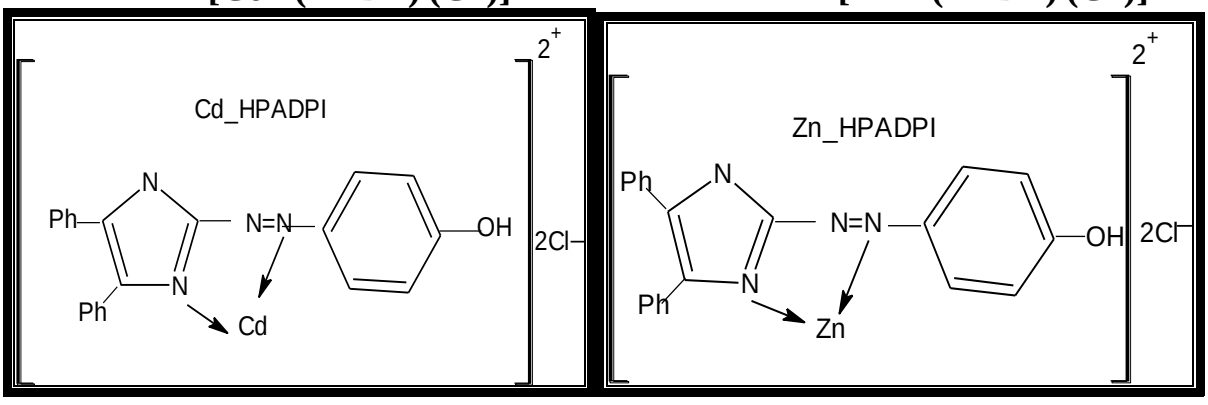
A B

***F*ig (15) Mole ratio method for(A) (Zn- HPADPI),B(Cd-HPADPI) ,**

The graph in Fig (14,15) shows the complex extracted was 1:1 metal : ligand, so we can suggest the following structures of the complexes as shown below :



$[Cd^{+2}(PABN)^{-}(Cl^{-})]$ **$[Zn^{+2}(PABN)^{-}(Cl^{-})]$**

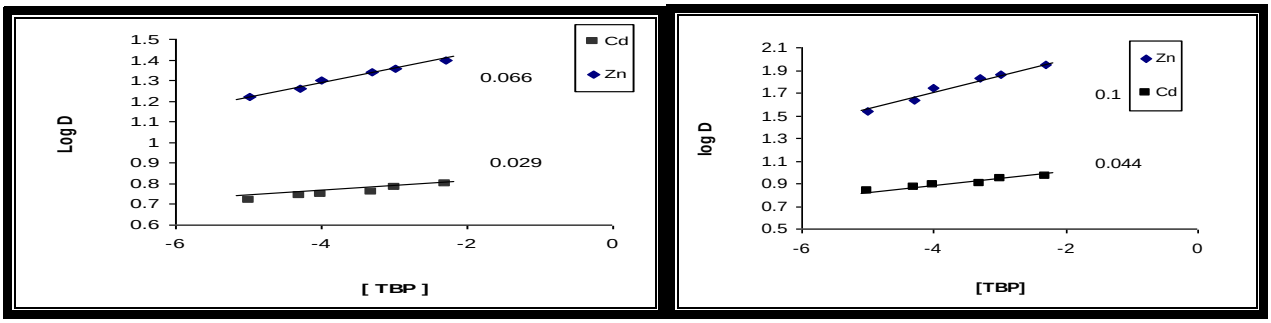


$[Cd(HPADPI)]^{+2}2Cl^{-}$ **[Zn (HPADPI)]$^{+2}$2Cl^{-}**

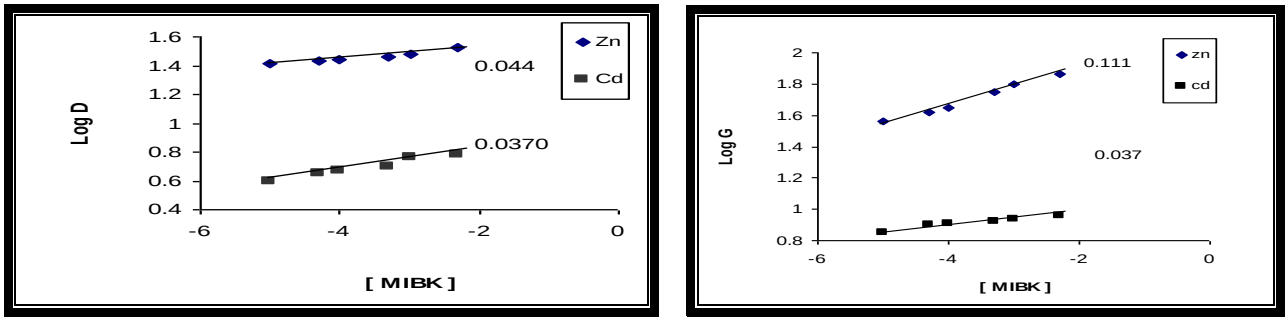
Synergism effect

Extraction metal cations from 5ml aqueous phase according to general procedure by 5ml ligands solution at (1×10^{-4} M) dissolved in chloroform contain different concentration of Tributyl phosphate (TBP) or methyl iso butyl ketone (MIBK) (1×10^{-5}-1×10^{-2}M), then separate the two layers and used spectrophotometric

method [14]for determination distribution ratio(D),afterward plot log D vis log [TBP] or log[MIBK] graphs were constrated Fig (16)



A B



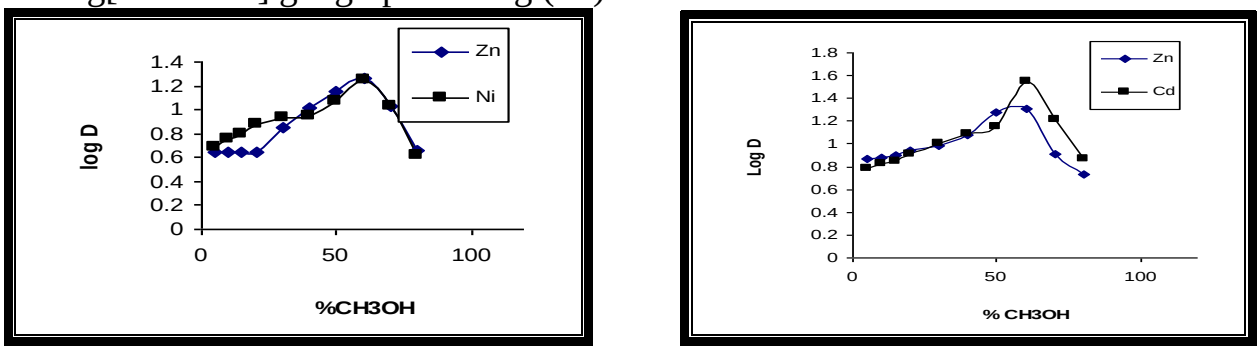
A B

Fig (18) :Synergism effect for TBP &MIBP on distribution ratio (D)A (PABN),B(HPADPI)

The results were show that the existence of TBP or MIBK with ligand in organic solution affect increasing distribution ratio(D) with concentration increase. The slope of straight line was show there is one molecule of TBP or MIBK participate in the complex.

Methanol effect

Extraction metal cations from 5ml aqueous phase according to general procedure by 5ml ligands solution at (1×10^{-4} M) dissolved in chloroform contain different different quantity of methanol for determination of distribution ratio(D), plot log D vis log[methanol] get graphs in Fig (17).



A B

Fig (17) effect of methanol distribution ratio (D): A(PABN),B(HPADPI)

The result shows existence of methanol in aqueous phase effect to rising distribution ratio (D) by reason of destroyed hydration shell of Zn(II) and Cd(II ions

and perform free ion which binding with ligand to produce more stable complex and increase distribution ratio (D) as well optimum quantity of methanol was (60%) with PABN and HPADPI.

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