Research article

Determination and Extraction of Zinc (II) Via Cloud Point Methodology

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Abstract

This paper involved , extraction of Zn^{+2} ion from aqueous solution according to CPE method by using laboratory prepared new organic agent2-(4–amino–N–5–methylisoxazol–3-yl)BezenSulfonamideazo–1–Naphthol–Benzen(AIBSNB) as complexing agent at PH=9 and by using Triton X–100 as surfactant , the method need heating to 90C° for 15 minutes , and then the cloud point layer(CPL)was separated and dissolved in 5ml ethanol to measure the absorbance of complex extracted at λ_{max}=380nm .This research includes many studies such as thermodynamic , time of heating , interferences , effect of electrolyte salts , Stoichiometry Shows that the complex extracted is$[Zn(AIBSNB)]^{+}$;Cl⁻ or $[Zn(AIBSNB^{-}(Cl^{-})]$ synergism study shows participation one of TBP or MIBK in structure of complex extracted , this research appear Ɛ=13067 L mol^{-1} cm^{-1}, R.S.D=0.0068 , D.L=1.55×10^{-5} and Sandel's sensitivity=0.0005μg cm^{-2}.   **Copyright © IJACSR, all rights reserved.**

Key words: stoichiometry, method, DB18C6, Micelle, participation.

Introduction

CPE methodology is chosen as rapid sensitive method for extraction many of element cations from aqueous solution after formation complexes with selective organic reagents coupled with spectrophotometric method for determination metals in vital and environmental samples .The specific research use cloud point extraction method for separation and extraction Nickel (II) as chloroanion by using of crown ether DB18C6 combined with spectrophotometric determination [1].
Micelle–mediated was developed as versatile procedure for spectrophotometric determination of manganese . The method involves the formation of an ion association complex between manganese oxyanion MnO_4^{-} and brilliant

green in acidic solution and the complex was extracted into the surfactant Triton X–100 at optimum condition .The surfactant–rich phase which contains manganese complex mediated with solvent and the Mn content measured spectrophotometrically at maximum absorbance wave length λ_{max}=657nm[2].

A new trend in extraction and preconcentration of chromium (VI) using laboratory-made Azo dye reagent 2–[benzene thiazolylazo]–4–benzenenaphthol (BTABN) after cloud point extraction and its determination is spectrophotometically calculated .The method involves the reaction of $Cr_2O7–2$ with BTABN in acidic medium forming a hydrophobic ion association complex $[HBTABN]^+[HCr_2O_7]^-$ which is entrapped into micelle–mediating solvent (TritonX–100) and the Cr(VI) detected spectrophotometrically at λ_{max}=475nm [3].

CPE procedure is presented for preconcentration of lead (II) and cadmium(II) ions in various samples after the complexation by using 2–[(Benzothiazoyl)azo]–4–benzyl phenol (BTABP) with lead and2–[(3–Bromo phenyl)azo]–4,5–diphenylimidazole (BPADP) with cadmium ions are quantitatively extracted into Triton X–100 .The surfactant–rich phase which contains complex is mediated with 1,2–Dichloro ethane and the metal ion content measured spectrophotometrically at maximum absorbance wave length λ_{max}=393nm for Pb(II) and λ_{max}=516nm for Cd(II) [4]. According to CPE method ,the Nickel(II) is extracted by using 8– hydroxyquinoline as complexing agent and Triton X–100 , after limitation all optimum condition[5]. For preconcentration and spectrophotometric determination of pb(II) and Cu(II) using anew micelle phase separation with an anionic surfactant sodium dodecyl sulfate (SDS) , the procedure is based on the complex formation for pb(II) and Cu(II) with synthesized chelating agent N_1,N_2-diphenylhydrazine-1,2-dicarbothioamide (PHCT) the chemical variable affecting , the separation and determination procedure were optimized [6]. Extraction and preconcentration of Cobalt from different samples of water according to CPE method after complex formation with 4-Benzylmpiperidine dithioCarbamate as complexing agent andTriton X–100 is determination Co^{+2} by usesFAAS[7]. CPE methodology is used as selective method for extraction trace amount of silver from water and blood samples by using complexing agent Bis[1H-bezo[d];midazol-2yl]methyl sulfane at PH=8 and nonionic surfactant Triton X–114 [8]. CPE methodology is developed for separation and determination in serum sample for Cr(III) after complex formation with PAN by using nonionic surfactant Triton X-114 as well as for determination uses ETAAS [9]. Preconcentration and extraction Cr(III) from water samples by developed CPE method and complex formation with Brilliant Crystal blue (BCB) by using nonionic surfactant Triton X-114 as wellas for determination uses FAAS method [10]. Solvent extraction for selective separation of Palladium (II) form its acidic chloride solutions using 4-aroyl-3-phenyl-5-isoxazolones (HA) such as 3-phenyl-4-(4-fluorobenzoyl)-5-isoxazolone(HFBPI) , 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) and 3-phenyl(-4-(4-touoyl)-5-isoxazolone (HTPE) , the extraction strength of Pd(II) with HA were in the following order HFBPI > HPBI > HTPI . as well as HPBI is used for separate Pd(II) from Pt(II) , Ni(II) and Rh(III) metal ions and calculate this separation factors[11]. CPE method is developed for determination copper and lanthanide in water samples after complex with P–Sulfonato calix [4].Using arene and nonionic surfactant TritonX-100 ,involves limitation of all optimum conditions [12]. Used 3,5-dimethoxy-4-hydroxy benzaldehydeisonicotinoylhydrazon (DMHBIH) as analytical reagent for spectrophotometric determination of lead(II) and giving bright yellow complex , at pH=9 with molar absorptivity 1.82×10^4 l.mol^{-1}.cm^{-1} and sandell's sensitivity 0.01302μg/cm^2 , as well as the Stoichiometry studies show the complex extracted was 1:1[13]. Developed CPE method coupled with FAAS technique for extraction and determination of Zn(II) and Cd(II) in samples of blood , urine and water by using complexing agent $3,3^I,3^{II},3^{III}$–tetraindoly(tetraphthaloyl)dimethane in basic solution with DL=3.2 μg/L for Zn^{+2} and 10.7 μg/L for Cd^{+2}[14].

Materials and Method

Spectrophotometric studies is performed by double-beam UV–Vis spectrophotometric Shimadzu UV–1700 (Japan) . Absorbance measurements is made by single beam UV–Vis spectrophotometer TRIVP International Corp – TRUV 74,S Italy ,as well as all materials used as received without farther more purification .All solutions prepared by double distilled water , stock solution of Zn^{+2} 1mg/ml prepared by dissolving 0.1gm of metal in small portion of HNO_3 and diluted the solution to 100ml by distilled water in volumetric flask.Other working solutions prepared by dilution with distilled water , 5×10^{-3}M AMIBNB prepared by dissolving 0.242gm in 100ml distilled water by using volumetric flask .Azo derivative 2-(4-Amino-N-(5-methyl isoxaol-3-yl)benzene sulfonmide azo-1-naphtol benzene (AIBSNB) was prepared by dissolving (2.5g , 0.01mol) of (4-amino-N-(5-methyl isoxazol-3-yl)benzene sulfoamide) in amixture containing 4ml concentrated HCl and 25ml distilled water. After cooling this solution to 0C$^°$,1.4g of solution nitrite dissolved in 10ml distilled water was added with maintaining the temperature at 0C$^°$. The mixture was setaside for 15minets. To complete diazotization reaction , therefor the diazonium salt solution was poured drop by drop into a beaker containing (2.2g , 0.01mol) of 4-benzene naphthol and (1.2g) sodium hydroxide dissolved in 150ml ethyl alcohol at 0C$^°$. After complete the addition left all containsin the beaker for two hours , then 150ml of

cooled distilled water was added and maintained the pH of the solution at pH=6 , abrown precipitate appear after 24 hour . The solid precipitate was filtered off and washed with cooled water afterward crystallized twice from hot absolute ethanol and dried over CaCl$_2$.
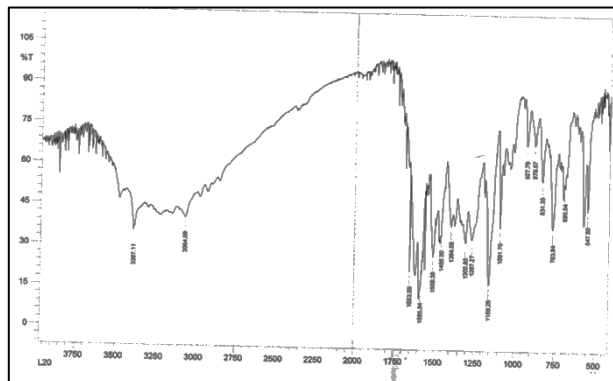
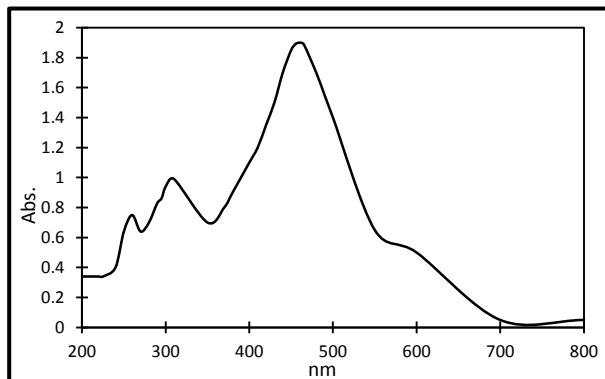Figure(1): IR-spectrum of organic reagent4-Amino-N-(5-methyl isoxazol-3yl) benzene sulfoamide azo-1-naphthol benzene

Figure (2) UV-Vis. spectrum of organic reagent4-Amino-N-(5-methyl isoxazol-3yl) benzene sulfoamide azo-1-naphthol benzene

Table (1):Spectral data of the AIBSNB reagent

peaks(nm)	Assignments
260	π-π* very small sensitive absorption.
310	π-π* middle sensitive absorption.
460	π-π* visible region high sensitive absorption.

a\ UV-Visible spectral peaks (nm).

Bands (cm^{-1})	Assignments
3387.11	phenolic OH stretching
3064	aromatioc CH stretching
1602, 1585	C=N stretching and bending
1508.38	for five member ring nitrogen
1456.30	for –N=N-
1159.26	for, S=O
763.84	for rings of naphtol

b\ IR spectral bands (cm^{-1})

Element	Theoratical results	Experimental results
% C	64.18	64.06
% H	4.56	4.45
% N	11.52	11.51
% O	13.15	13.13
%S	6.61	6.58
c/C.H.N study		

The UV-Spectrum and IR-Spectrum as well as the results obtained by C.H.N study as in figures 1,2 and Tables(1a,1b,1c) demoustrate the structure of azo ligand prepared suggested was .
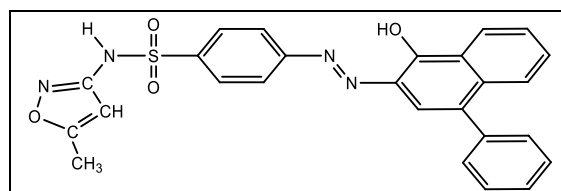

2-(4-Amino-N-5-methyl isoxazol-3-yl)benzene sulfoamide azo-1-naphthol benzene (AIBSNB).

10ml aqueous solution contain 50μg Zn^{+2} at PH=9 and 1×10^{-4}M AIBSNB and 0.5ml of 1% Triton X–100 .Heating the solution in Electrostatic water bath to 90C° for 15minutes till the appearance of cloud point layer.This layer isseparated from aqueous solution and dissolved CPL in 5ml ethanol and the absorbance is measured at λ_{max}=380nm against blank prepared at the same manner without Zn^{+2} ion . Aqueous solution is treated according to spectrophotometric determination methods (Dithzone Method)[15] .After returning to calibration curve infigure(2) to determine remainder quantity of Zn^{+2} in aqueous solution after extraction and subtraction this quantity of Zn^{+2} from the original quantity. The determined Zn^{+2}istransferred to CPL as complex .And from these two quantities the distribution ratio D is calculated .Of stripping method , shaking ethanolic solution of CPL with three portion of 5ml from 1:1 HCl , and determined by dithizone method the stripped quantity to the acidic aqueous solution , worth mentioning the transfered Zn^{+2} determined by stripping equal to the same quantity determined by subtraction , then to rely on subtraction method in all experiments because easyer and faster afterward calculate distribution ratio (D) .

Results and Discussion

Absorptio UV–Vis spectrum in Figure (3) shows maximum absorption for ion pair complex extracted into cloud point at λ_{max}=380nm.
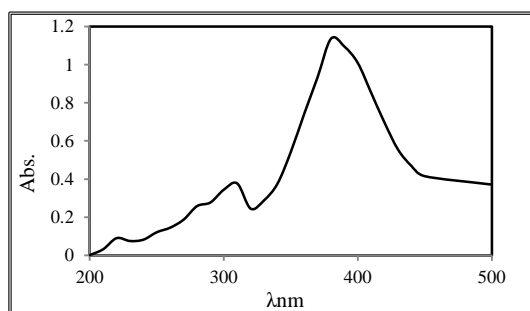

Figure(3):absorption UV–Vis spectrum for ion pair complex extracted to cloud point

Effect of acidic function

Extracted Zn^{+2} from aqueous solution 10ml in volume according to CPE method contains 50μg Zn^{+2} at different pH(5 – 12)as ion pair complex formed between $Zn^{+2}$and AIBSNB 1.85×10^{-3}Mand 0.5ml from 1%Triton X–100 .Then the solution heated at 90C° in Electrostatic water bath for 15minutes and later , the CPL is separated from aqueous solution . CPL is dissolved in 5ml ethanol and the absorbance is measured against blank prepared at the same manner without Zn^{+2}ion.But the aqueous solution is treated according to Dithizone spectrophotometric method and D–Value is determined at each pH as explained in experimental after return to calibrationcurve Figure (4) .The results are as in figures 5,6
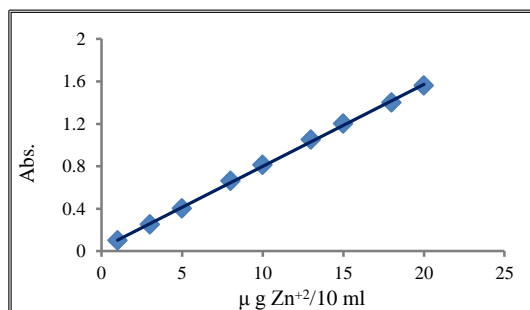
Figure(4): calibration curve for determination Zn^{+2} in aqueous solution according to dithizone method
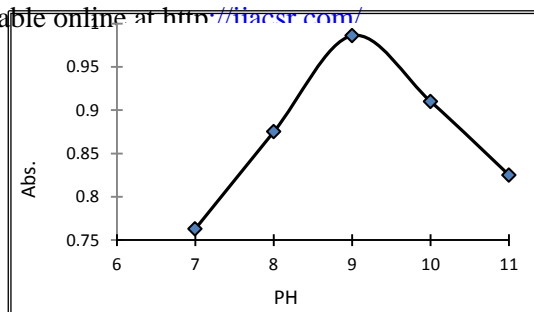
Figure(5)* :*effect of PH on complex formation
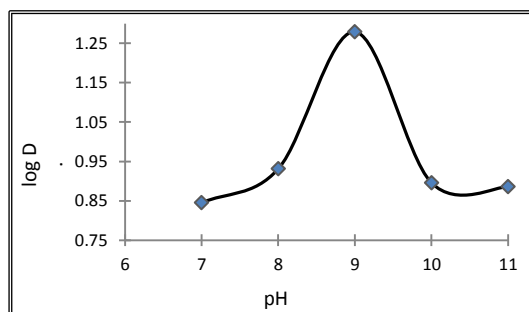
Figure(6):*Distribution ratio change as a function of PH

The results show optimum value is pH=9 , at this acidic function reach to the favorite thermodynamic equilibrium for complex formation and extraction .Any pH value less than optimum is not suitable for extraction giving decreasing ion pair complex formation and extraction efficiency. But each pH–value more than optimum effect to decline extractability of Zn^{+2} because increasing of hydroxyl ion (OH^-) in aqueous solution play to bind the Zn^{+2} ions and formed stable compound not extracted such as $Zn(OH)_2$, $Zn(OH)_3^-$, $Zn(OH)_4^{-2}$ .Hydroxyl ions (OH^-) participate as anion in ion pair association complex which in effect to increases back reaction of equilibrium–dissociation.

Effect of Zn^{+2} concentration

10ml aqueous solution contains 50μg Zn^{+2} at PH=9 , 1.85×10^{-3}M (AIBSNB) and 0.5ml from 1%Triton X–100 .Heating the solution to 90C° in electrostatic water bath for 15minutes until formation CPL . CPL is separated and dissolved in 5ml ethanol and absorbance is measured at 380nm against blank prepared at the same manner without Zn^{+2} ion .Aqueous phase is treated according to Dithizone spectrophotometric method and D–Value is determinedat each concentration of Zn^{+2} as detailled in experimental part .The results are as in figures 7,8 .
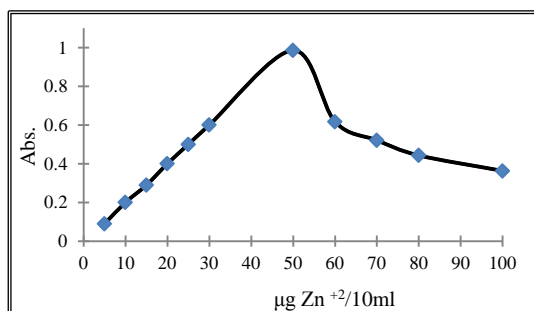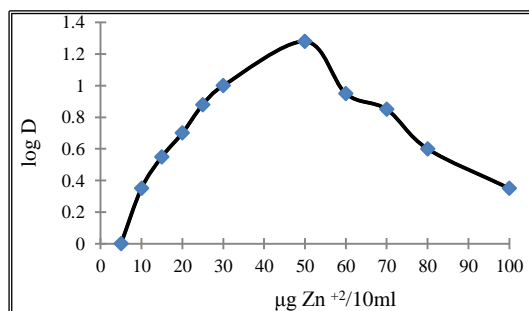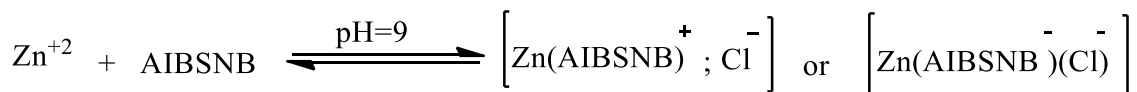

Figure (7):*effect of Zn^{+2} concentration on complex formation

Figure(8): D α f [Zn^{+2}]

The results proof that the concentration of Zn^{+2} is a thermodynamic data effect on formation and stability of the complex so that the extraction efficiency, and optimum concentration50μg Zn^{+2} are enough to reach thermodynamic equilibria .

$$Zn^{+2} \; + \; AIBSNB \; \underset{\longleftarrow}{\overset{pH=9}{\longrightarrow}} \; \left[Zn(AIBSNB)^+ \; ; \; \overset{-}{Cl} \right] \; or \; \left[Zn(AIBSNB^-)(\overset{-}{Cl}) \right]$$

Any concentration of Zn^{+2} Lessthanoptimum 50μg Zn^{+2} does not allow to reach thermodynamic equilibria and to decrease effect complex formation and stability and extraction according to CPE method . Of concentrations more than optimum effect to decreases the efficiency of extraction by effects of mass action law and lechatelier principle .
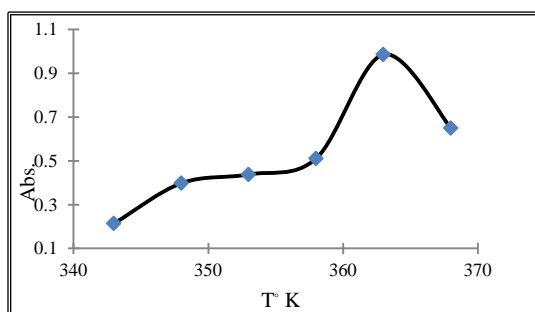
Effect of Triton X–100 Volume

By using different Volume of 1%Triton X–100 , the extracted Zn^{+2} ion from 10ml aqueous solution contains 50μg Zn^{+2}, 1.85×10^{-3}M (AIBSNB) at PH=9,heating the solution to 90C° for 15minutes until cloud point layer formation .Separation CPL from aqueous solution and dissolved in 5ml ethanol .The absorbanceis measured at 380nm against

blank prepared at the same manner without Zn^{+2} ion . The aqueous solution is treated accordingto Dithizone spectrophotometric method [15] And calculated the distribution ratio D as detailled in experimental. the results are as in figures 9,10 .

The results demonstrated there is an optimum Triton X–100 Volume gives the best CPL which was 0.5ml which is represented to critical micelle concentration giving higher density and smaller Volume for CPL . To give best extraction for Zn^{+2} complex with higher absorbance and D , any volume less than optimum 0.5ml is not allowed to formation CPL and not enough to extract effect to decrease absorbance and D–Value .Any volume more than 0.5ml effectsto decline absorbance and D–Value because this Volume effectsincrease diffusion of Triton X–100 in aqueous solution .

Effect of Temperature

10ml aqueous solution contains 50μg Zn^{+2}, 1.85×10^{-3}M (AIBSNB) at PH=9, 0.5ml from 1% Triton X–100 and heating this solution to different Temperatures $70C^{°}$–$95C^{°}$ for 15minutes .After that,the CPL is separated and dissolved in 5 ml ethanol . The absorbance is measured at λ=380nm against blank prepared at the same manner without Zn^{+2} ion .Aqueous solution is treated according to Dithizone spectrophotometric method [15] and calculated the distribution ratio after returning to calibration curve figure(4) .The results are as in figures 11,12

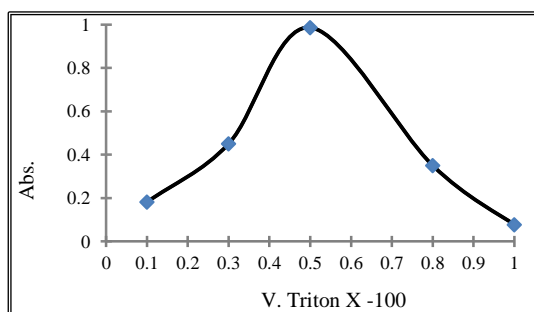*Figure(11): effect of temperature onextraction efficiency*
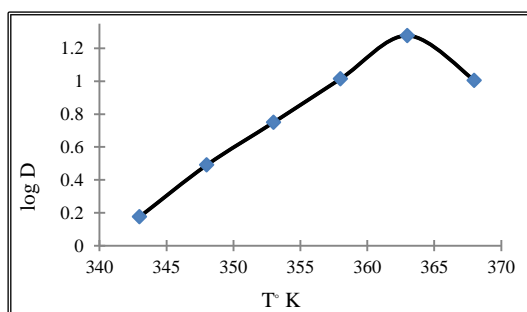
Figure(12): D = F(T° K)

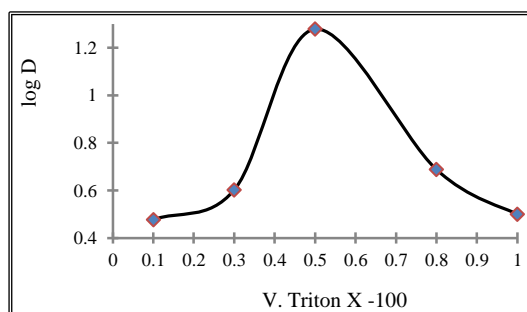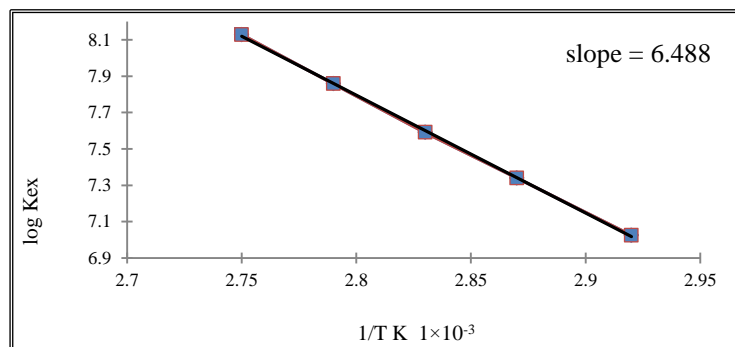*Figure (9):effect Triton X–100 Volume on extraction efficiency*

Figure (10): D = f (Triton X–100) ml

From D–Value and by application relation below the extraction constant K_{ex} iscalculated.

$$K_{ex} = \frac{D}{[Zn^{+2}][AIBSNB]}$$

After plot $logK_{ex}$ against 1/T K   slope is determinedfor straight line obtained . Figure (13) determines thermodynamic data of extraction .

Figure(13): *log K_{ex}= f(1/T K)*

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

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

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

$\Delta H_{ex} = 0.1242$ K J mol^{-1}

$\Delta G_{ex} = -56.483$ K J mol^{-1}

$\Delta S_{ex} = 155.94$ J mol^{-1} K^{-1}

The results appeared from extraction according to CPE methodology the thermodynamic behavior was endothermic relation . Large Value of ΔS_{ex} demonstrates that the method is intropic in region.

Effect of heating time

Returning to extraction method at optimum for all parameters except time of heating , the solution was heated in electrostatic water bath at 90C° for different time (2–30minutes) . Each solution the cloud point layer is separated from aqueous solution and dissolved in 5ml ethanol and the absorbance is measured at 380nm against blank prepared at the same manner without Zn^{+2} ion .The aqueous phase is treated according to Dithizon spectrophotometric method[15] the results are as in figure 14,15.
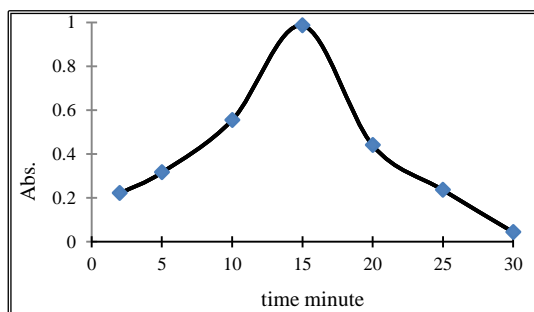
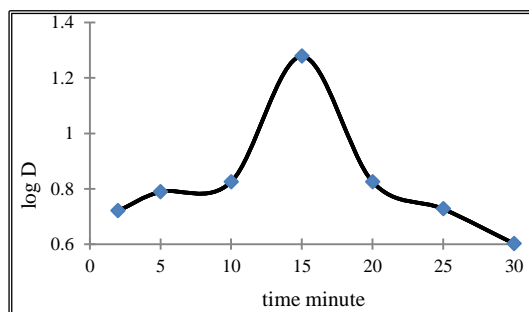**Figure(14):***effect of heating time*
On efficiency

Figure (15): *D α F(time of heating)*

The results in Figure 12,13 show the optimum time of heating is 15minutes.In this time complex formation reaches the best thermodynamic equilibria and favorable extraction Zn^{+2} as ion pair complex by CPE Method . But any Value of heating time less than optimum Value is not suitable and not enough to reach thermodynamic

equilibria.The extraction is not efficient and the absorbance and D–Value is decreased . So , any heating time more than the optimum effect to increases diffusion of micelles in aqueous solution and decreases the density of CPL . as well increases its Volume that means moving away from efficient of extraction and decrease absorbance and D–Value.

Stoichiometry

By using four spectrophotometric methods to know the more probable structure of complex extraction into micelles aggregation layer which are slope analysis , mole ratio , continuous variation method , slope ratio .The results are as in Figure (16–19)
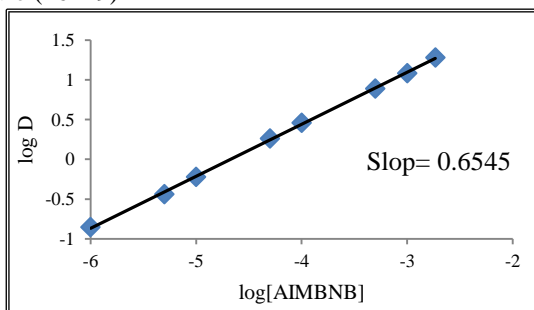

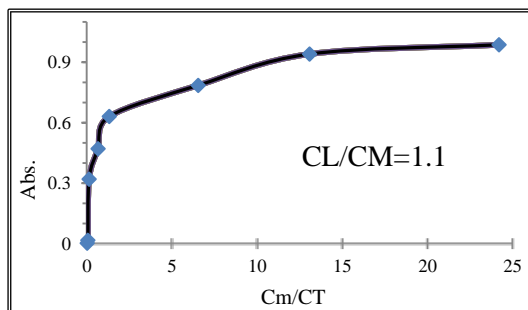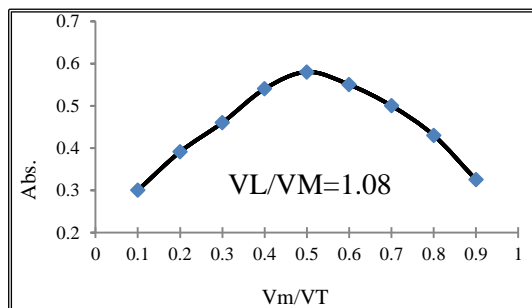*Figure (16): Slope analysis method*

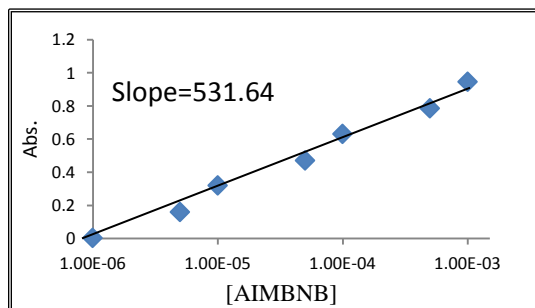*Figure (17): Mole ratio Method*

Figure(18): Job Method

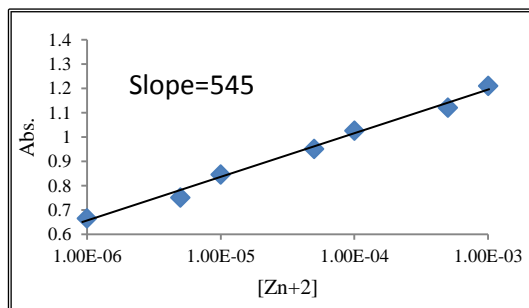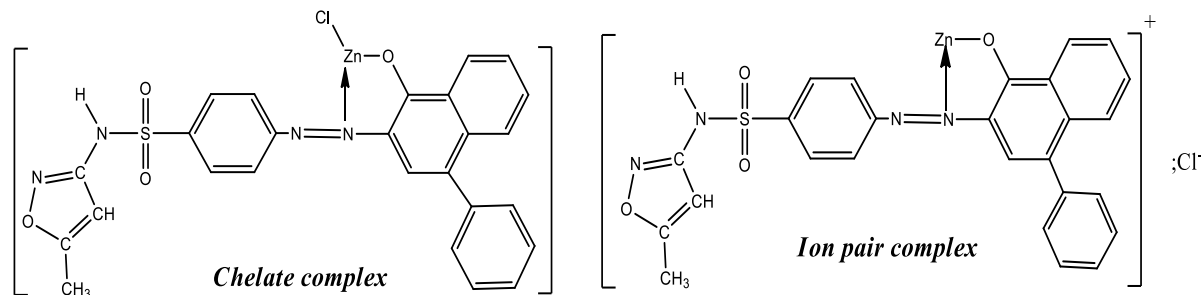*Figure (19-a): Slope ratio method change organic reagent concentration*

Figure (19-b): Slope ratio method change metal ion concentration

$$\text{Slope ratio} = \frac{531.64}{545} = 0.975$$

All these methods show the more probable structure of complex extracted was 1:1 Zn^{+2} : AIBSNB

Effect of electrolyte salts

Extraction Zn^{+2} ion from 10ml aqueous solution according to cloud point extraction methodology at optimum condition and in presence of some electrolyte salts after heating and separating cloud point layer and the absorbance of ethanolic solution of cloud point was measured and the distribution ratio D with each electrolyte salt was calculated.The results shown in Table (2).

Table(2): effect of electrolyte salts on extraction efficiency in CPE method

Electrolyte Salts	absorbance ethanolic CPL $\lambda=380$ nm	D
LiCl	1.22	49
NaCl	1.14	39
KCl	1.08	36.04
NH_4Cl	0.992	24.5
$MgCl_2$	1.15	45
$CaCl_2$	1.06	39
$SrCl_2$	0.995	27.6
$AlCl_3$	1.01	21.22

The results show the presence of electrolyte salt in aqueous solution of extraction effect increases extraction efficiency because the increasing of dehydration of cloud point layer helpsin destroying the hydration shell of metal cation which helps to increase the probabilityof complexation and partition to cloud point layer . Moreover this effect increases with decreasing ionic diameter and increasingcharge density . whereas Li^+ is the smallest ionic diameter and larger charge density and has the largest effect to destroy the hydration shell of Zn^{+2} and increasesdehydration for cloud point layer formation to give higher absorbance and distribution ratio D.

Effect of interferences

After the Zn^{+2} ion was extracted from aqueous solution according to CPE methodology at optimum condition in presence of chloride salts of Copper (II) ,Cadmium(II), Nickel(II) and chromium(III) , the absorbance of ethanolic solution of cloud point layer was later measured and D–Values of extraction is calculated .The results are as in Table(3)

Table(3): interference effect on extraction efficiency

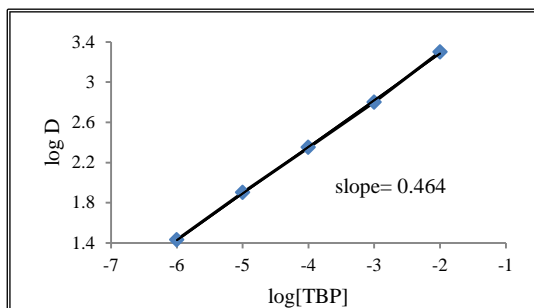| Interferences	Absorbance Ethanolic CPL at λ=380nm	D
$CuCl_2$	0.867	14.385
$CdCl_2$	0.570	7
$NiCl_2$	0.872	17.18
$CrCl_3$	1.082	21.22

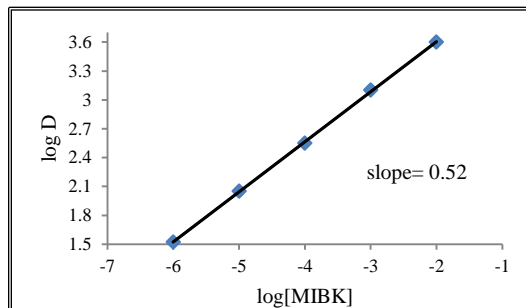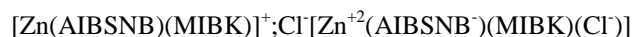*Figure (20): synergism effect with TBP*

Figure (21): synergism effect with MIBK

The results show higher interference given with Cd(II) which participate Zn^{+2} in large degree to form complex with organic reagent but Cu(II) and Ni(II) gives small interferences .As a result of that , Cr(III) shows no interferences and no tendency to interact with organic reagent but behave in aqueous solution as electrolyte salt effect to enhance extraction efficiently .

Synergism

Extracted Zn^{+2} from aqueous solution at optimum conditions and in presence Tributyl phosphate (TBP) or Methyl isobutyl Ketone (MIBK) in aqueous solution , after heating and separate cloud point layer dissolved in 5ml ethanol and measure the absorbance at λ=380nm against blank prepared at the same manner without Zn^{+2} ion ,and calculate D for extraction . the results was as in Figures 20,21.

The results show presence TBP or MIBK in aqueous solution effect to enhance extraction efficiency because these compound sharing in the structure of complex formation increases complex partition to cloud point layer and the results show that there is one molecules of TBP or MIBK sharing in complex .

$[Zn(AIBSNB)(TBP)]^+;Cl^-$ $[Zn^{+2}(AIBSNB^-)(TBP)(Cl^-)]$

$[Zn(AIBSNB)(MIBK)]^+;Cl^-[Zn^{+2}(AIBSNB^-)(MIBK)(Cl^-)]$

curve of spectrophotometric Determination of Zn^{+2} in different samples .
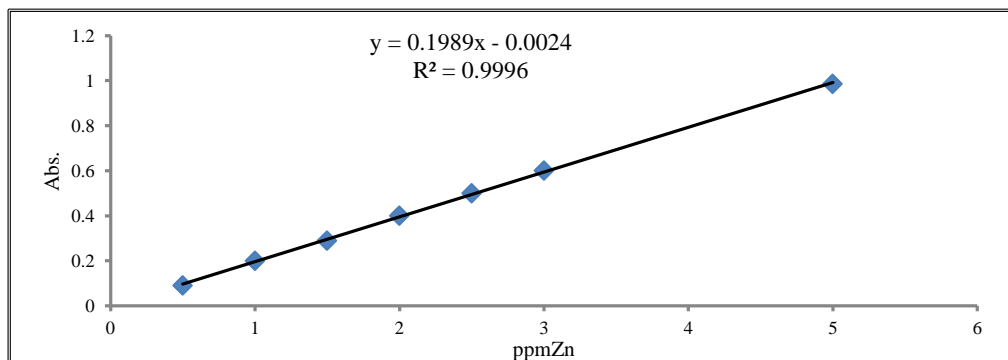
Spectrophotometric Determination

Calibration

Figure (22): Calibration curve of Zn^{+2}

Detection limit= 0.00015mol /L , RSD = 0.0068 % , Sandel'ssensitivits = 0.0005 mg cm^{-2} ,$\mathcal{E}$ = 13067 L mol^{-1}cm^{-1}

The application

The samples	ppmZn^{+2}
Alshawati soil	82
LepidiumSp.Al.mighkhab	212
I Agrecalture soil	75
Chickens liver	110
Celery	111
Al.mishkabunagricalture soil	135
Chickens meat	186
Lakes fish	240
Leek	120
Wadi Al Salam soil	112
Native beef	350
Fish of weast of faremis	316

Conclusion

The results show presence TBP or MIBK in aqueous solution effect to enhance extraction efficiency because these compound sharing in the structure of complex formation increases complex partition to cloud point layer and the results show that there is one molecules of TBP or MIBK sharing in complex .

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