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Research paper

Solvent Extraction Method for Separation and Determination of Zn (||) by Using of Imidazole Derivative

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Abstract

Solvent extraction as sensitive and effective method for separation, pre concentration and determination Zn^{+2} after converted the cation into ion pair complex by combination, coordinately with complexion agent 2-[(2-methylphenyl)azo]-4,5-diphenyl imidazol (MPADPI). Spectrophotometric study shows wave length for maximum absorbance of complication reagent equal to λ_{max}= 405nm but maximum absorbance wave length for ion pair complex extracted of Zn^{+2} equal to λ_{max}=535nm. The experimental studies for pin point the optimum conditions of extraction shows pH=10 in presence 50µg Zn^{+2} in 5mL with shaking time equal 10 min., by using slope analysis method and mole ratio method demonstrated the structure of the ion pair association complex was$[1:1]^{2+};2Cl^{-},[MPADPI\text{-}Zn]^{2+};2Cl^{-}$. The experimental study about organic solvent effect shows there was not any linear relation between dielectric constant of organic solvent and the values that means there was not any effect for polarity of organic solvent on extraction efficiency but there was un effect for organic solvent structure .Temperature effect study shows the extraction method was exothermic behavior with thermodynamic factor equal to ΔH_{ex}=-0.0255kJmol^{-1}, ΔG_{ex} =-19.4005 kJmol^{-1},ΔS_{ex}=69.78 J molK^{-1} and other studies involved synergism effect, methanol effect ,spectrophotometric determination of Zn^{+2} in different samples.

Keywords: *Zinc(II), Solvent extraction, ion pair, separation, spectrophotometric determination.*

1. Introduction

By using solvent extraction as sensitive and effective method for separation ion pair association complex of binding Zn^{2+} coordinately with complexation reagent MPADPI in order to determination Zinc(II) in different samples ,due to total features for solvent extraction method may used in wide spread application for separation the more of elements as cations or anions with different applications, there was many application in (2014) extracted Nickel(II) as chloroanion complex by DB18C6 and coupled with cloud with cloud point extraction method and in presence 0.25 NaCl and TritonX-100 and application this method for determination Zn(II) in different samples after pinpoint the optimum condition[1].The researcher(2012) extracted Pb^{2+} and Cd^{2+} and determined them in different samples by using two complexing agents 2- [(benzothiazolyl)azo]-4- benzylphenol (BTABP) and 2-[(3-bromophenyl) azo] 4,5-diphenyl imidazole (BPADPI) coupled with CP5 method with Troton x-100[2]. Gharabaghi and others (2013) by application solvent extraction extracted Ni and Zn from acidic solution by Di(2- ethylhexyl) phosphoric acid (Cyanex272),and pinpointed the optimum condition and application this method to extracted and determined these ions from waste water[3]. There was many application for solvent extraction to separation and determination metal elements as cations or as anions and applicable their methods for determination these elements in different samples after determination optimum condition[4-10].And in preferential research involved separation and extraction Lanthanum(III) by joined cloud point with salvation [11] .By application Onium method for separation and spectrophotometric determination of Co(II) joined with cloud point extraction methodology[12]. Extracted many metal ions by solvent extraction methods [13-19].

2. Experimental

For spectrophotometric studies and absorbance measurements was used double beamUv–Vis spectrophotometer and single beam Uv –Vis spectrophotometer, preparing stock solution of Zinc(II) 1000µg/mL by dissolved 0.286g in 100mL distilled water in presence1mL of HCl, and for determination Zn^{2+}in aqueous phase following Dithizone method[20].

3. Method supported

We are taking 5 mL aqueous solution contain 50 µg Zn^{2+}at pH =10 and added to it 5mL of 1x10^{-4}M (MPADPI) dissolved in chloroform and shaking for 10min and then separate the aqueous phase from the organic phase and measure the absorbance of ion complex formed in organic phase at λmax =535nm against blank preparing at the same manner without Zn^{2+}ion and the aqueous phase treated according to spectrophotometric dithizone method [20] to determine the remainder quantity of Zn^{2+} ion in aqueous phase and by subtraction the quantity from the total quantity of Zn^{2+} ion aqueous solution to determine the transfer quantity into organic phase to formation ion pairs complex the calculate distribution ratio D:

$$D = \frac{[Zn^{2+}]_{org.}}{[Zn^{2+}]_{aq.}}$$

By following Dithiazon method [20] on 5mL aqueous solutions contain rising quantity of Zn^{2+} ion the results calibration carve demonstrated in Figure(1)

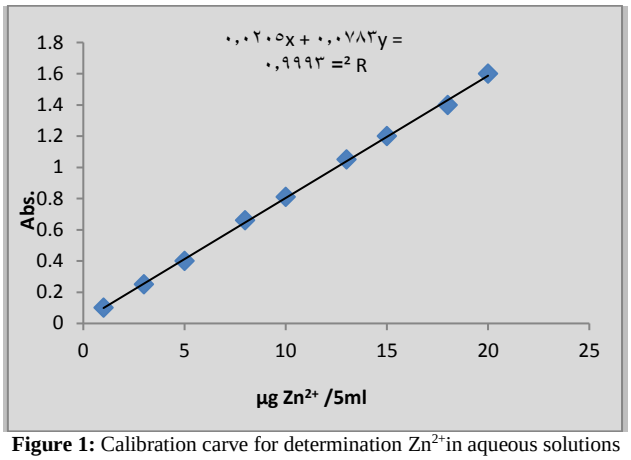
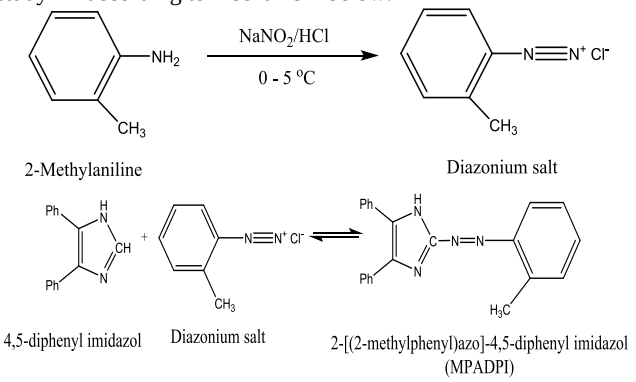


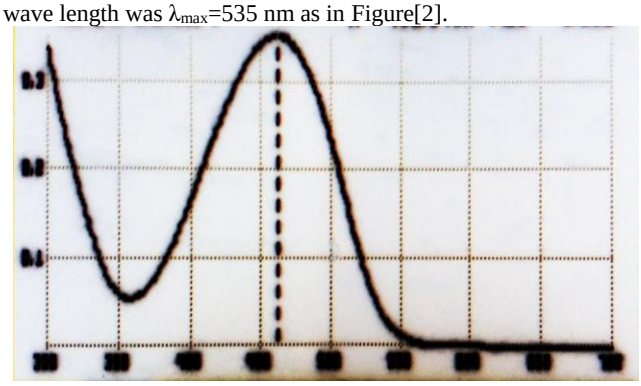
Figure 1: Calibration carve for determination Zn^{2+}in aqueous solutions

4. Results and discussion

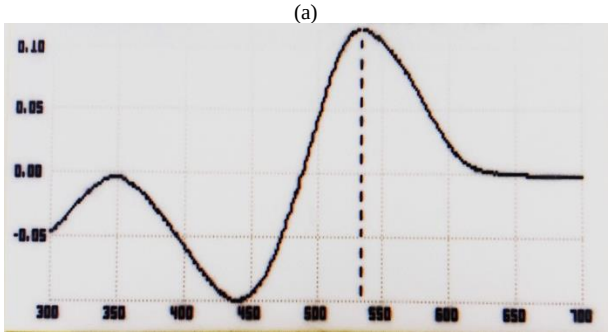
After preparing organic reagent MPADPI according to previous study [21] according to mechanism below:



UV-Vis spectrum of this organic reagent dissolved in chloroform demonstrate the wave length of maximum absorbance for this reagent was λ_{max}=405nm but the ion pair complex with Zn^{2+} shows in its UV-Vis spectrum the maximum absorbance appear at wave length was λ_{max}=535 nm as in Figure[2].



(a)



(b)

Figure 2: UV –Vis spectra
A- for organic reagent MPADPI.
B- for ion pair association complex between Zn^{2+} and organic reagent MPADPI.

4.1. Effect of pH

Aqueous solutions 5mL in volume contain 50µg Zn^{2+} and different pH at the range (4-11) , then added to each solution 5mL of organic reagent solution MPADPI dissolved in chloroform at $1x10^{-4}$and then shaking these solution for 10 minute afterward separation organic phase from aqueous phase ,then measure the absorbance of the organic phase at λ_{max}=535nm against blank prepared at the same manner without Zn^{2+},but the aqueous phase treated according to dithizone method and return to calibration curve to determined Distribution ratio D at each pH value the results were as in Figures 3,4:

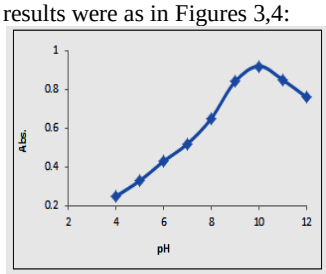
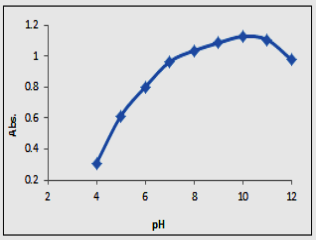


Figure (3): Effect of pH on the formation and stability of ion pair complex.

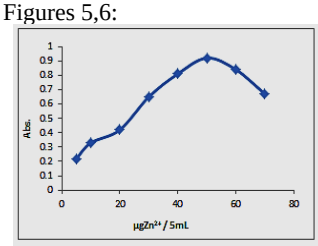


Figure(4) : Effect of pH on the Extraction efficiency .

The result demonstrate pH=10 was the optimum value which is giving higher extraction efficiency because at this pH giving best binding between organic reagent MPADPI with Zn^{2+}ion and more stable, any pH less than optimum value it is not suitable for formation complex, so pH value more than optimum give decline in extraction efficiency and complex formation by effect increasing OH^- ion in aqueous solution which is prevent the complex formation.

4.2. Effect of metal ion concentration

Preparing a series of aqueous solutions 5mL in volume contain rising quantity of Zn^{2+} ion at pH =10 and added to each one 5mL of BPADPI dissolved in chloroform at $1x10^{-4}$ M and shaking for 10 min , then separated aqueous phase from organic and complete the experimental as the general method the results were as in Figures 5,6:



Figure(5): Effect of metal ion concentration on the formation of ion pair complex.

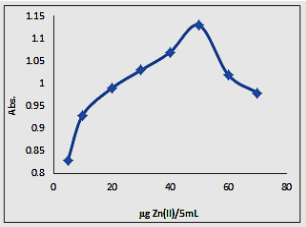


Figure (6) Effect of metal ion concentration on extraction efficiency and D values

The experimental study show 50µg was the optimum concentration of Zn^{2+} ion in 5mL aqueous solution to give higher absorbance and D value that is mean at this concentration reach to maximum efficiency for formation of ion pair complex and extraction ,whereas the concentration of metal ion is eon of the thermodynamic factor then optimum value help to give better the thermodynamic equilibrium and any concentration less than optimum not suitable to reach the best equilibrium ,so concentration more than optimum giving decrease in extraction efficiency according to mass active law .

4.3. Variation shaking time

5mL aqueous solutions contain 50µg Zn^{2+}at pH=10 added to each one 5mL of $1x10^{-4}$ BPADPI dissolved in chloroform and shaking these solutions for different shaking time afterward separate the aqueous phase from the organic and complete the work as in the general method . The results were as in Figures 7,8:

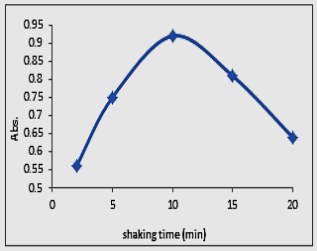
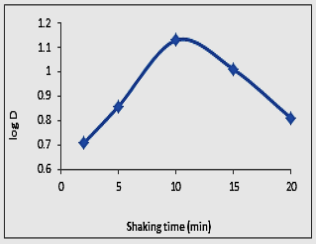


Figure (7) : Effect of shaking from ion complex formation

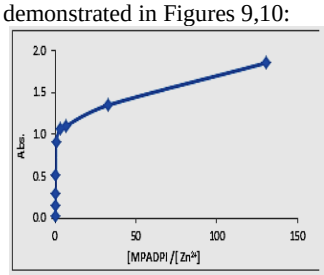


Figure(8) : effect of variation shaking time on extraction efficiency

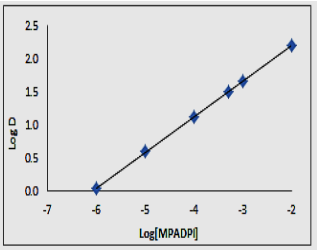
Shaking time represent kinetic law effect on indirect extraction method. The results value for shaking time giving higher extraction efficiency and help to reach best equilibrium for formation ion pair association complex, any shaking time less than optimum not suitable for extraction so that shaking time more than optimum value.

4.4. Stoichiometry

By using mole ratio and slope analysis method for determination more probable structure of ion pair complex extracted the results demonstrated in Figures 9,10:

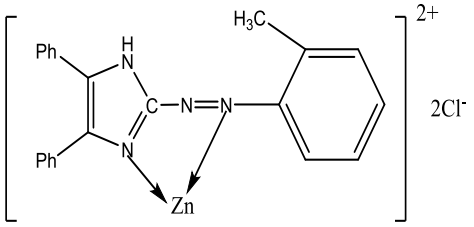


Figure(9): mole ratio method



Figure(10):Slope analysis method

The results appear structure of ion pair complex extracted was $[1:1]^{2+}$ anion



4.5. Organic solvent effect

A series of aqueous solution 5mL in volume contain 50µg Zn^{2+} at pH=10 added to each one 5mL of $1x10^{-4}$ M solution of BPADPI dissolved in different organic solvents and shaking them for 10minutes the results were as in Table (1):

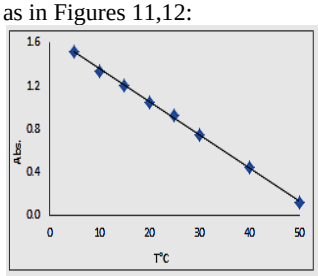
Table 1: Effect of Different Organic Solvents

Organic solvents	Dielectric constant	Abs. at λ_{max}=535nm	D
Nitrobenzene	35.49	1.14	16.52
1,2-Dichloroethane	10.650	1.55	22.63
DiChloromethane	9.080	1.23	17.53
Chlororbenzene	5.708	0.83	10.44
Chloroform	4.806	0.92	13.44
Benzene	2.804	0.42	4.85
Toluene	2.438	0.16	2.84

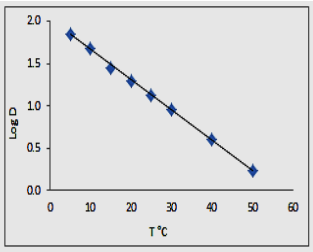
The results shows there was not any linear relation between dielectric constant of the solvents and distribution ratio for extraction that is mean there was not any effect of polarity of organic solvent on extraction efficiency as well as the results appears there is un effect for organic solvent structure on extraction efficiency and this demonstrate the participation of organic solvent in the formation of ion pair complex extracted and its stability.

4.6. Thermodynamic study

Aqueous solution 5mL in volume contain 50µg Zn^{2+} at pH=10 added to each solution 5mL of $1x10^{-4}$ MBPADPI dissolved in chloroform and shaking these solution for 10min the results were as in Figures 11,12:



Figure(11):Effect of temperature on the formation of ion pair complex



Figure(12):Effect of temperature on the extraction efficiency and D values

Calculate extraction constant Kex according to relation below

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

And draw log Kex against 1/TK the results as in Figure (13):

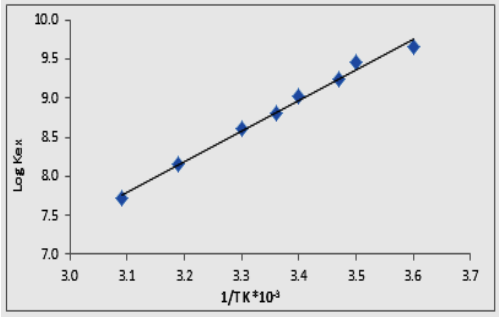


Figure (13): Extraction constant Kex as a function to T K

From the slope of the relation above and relation below calculated thermodynamic data of extrication:

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

ΔG_{ex} = -RT lnK_{ex}

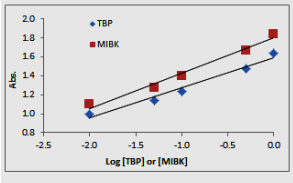
$\Delta G_{ex} = \Delta H_{ex} - T\Delta S_{ex}$

ΔH_{ex}	KJ/molΔG_{ex}	KJ/molΔS_{ex}	$Jmol^{-1}K^{-1}$
-0.0275	-19.4005	69.7800	

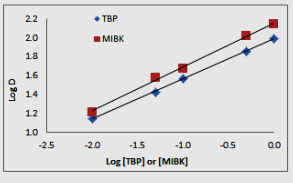
The results appear extraction method was exothermic relation, so the high value of entropy ΔS_{ex} demonstrates the method of extraction is entropic in region.

4.7. Synergism effect

Series of aqueous solutions at 5mL in volume contain 100µg Zn^{2+}at pH= 10 added to each solution 5mL of organic solution of BPADPI dissolved in chloroform at $1x10^{-4}$ M in presence different concentrations MIBK or TBP in organic phase and shaking these solutions for 15 min. and then separated the aqueous phase from the organic phase and complex the experiment as in the general method the results were as in Figures 14,15:



Figure(14): Increasing ion pair complex formation by increasing concentration of MIBK or TBP



Figure(15): Increasing extraction efficiency and D values with increasing concentration of MIBK or TBP

In presence MIBK and TRP in organic phase whereas these compounds replace the water molecules bonding in the empty

coordination position of Zn^{2+} in the complex and increasing the hydrophobicity of the ion pair complex and increase the partitioning to the organic phase.

4.8. Effect of methanol

Aqueous solution 5mL in volume contain 100µg of Zn^{2+} ion at pH =10 and in the presence rising percentage of method added to each solution 5mL of BPADPI dissolved in chloroform at $1x10^{-4}$ M and shake these solutions for 15min. then separated the organic phase from the aqueous phase and complex the work as in the general method . The results were as in Figures 16,17:

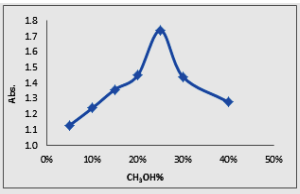


Figure (16): Effect of increasing methanol percentage on ion pair complex formation

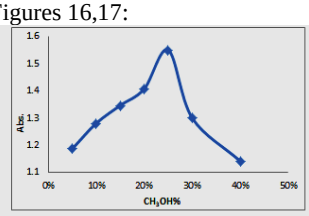


Figure (17): Effect of increasing methanol percentage on extraction efficiency

The results demonstrate presence methanol in the aqueous solution with Zn^{2+} ion effect to increase the extraction efficiency and the optimum percentage of methanol was 25%, because the presence methanol decreases the dielectric constant and polarity of aqueous phase and destroy the hydration shell of the metal ion and partition the ion pair complex to the organic phase.

4.9. Spectrophotometric determination

By application this method of extraction at optimum conditions and in order to determination Zn^{2+} in different samples preparing calibration carve as in the Figure (18)

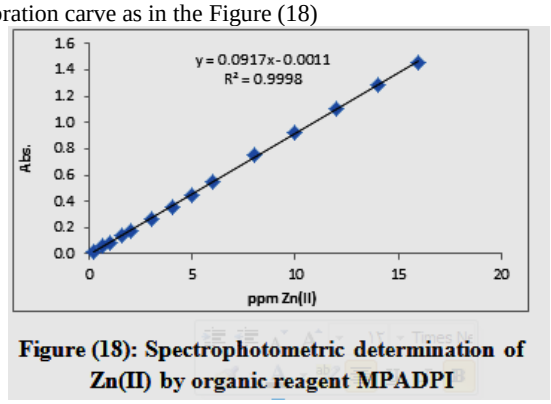


Figure (18): Spectrophotometric determination of Zn(II) by organic reagent MPADPI

Parameters	Values
λ_{max}	535nm
RSD	0.882
Sandell's Sensitivity	1.091×10^{-7} µg.cm^{-2}
Molar absorbtivity	5.994×10^{3}
Detection limit	2.40×10^{-4} M

And after determination Zn^{2+} in different samples the results were as in Table (2):

Table 2: Applications

Samples	ppm Zn(II)
Agriculture soil (Kufa city)	1.5
Agriculture soil(mishkhab city)	2.5
Euphrates river (Kufa city)	0.122
Euphrates river(mishkhab city)	0.143
Vegetables	0.225
Sheep meat	0.254
Beef	0.316
Chickens	0.165

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