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ONIUM SYSTEM APPLICATION FOR SEPARATION AND MICROAMOUNT DETERMINATION OF ZINC (II) BY USE METHYL STEARATE

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ABSTRACT

As sensitive application method of solvent extraction used onium system for extraction Zinc ion Zn^{2+} from acidic aqueous solution of HCl as oxonium species by used Methyl Stearate ester as sensitive extract ant dissolved in chloroform at 1×10^{-3}molar concentration, the study show extracted species giving maximum absorbance at wave length λ_{max} =275nm in presence 1M HCl with shaking time equal to 25 min. so that the study appear extraction efficiency differ with organic extract ant used whereas 2,4-Dimethyl -3- pentanone giving higher extraction efficiency ,electrolyte effect study show there is enhancement in extraction efficiency in presence electrolyte salt in aqueous solution as well as foundation 30% methanol in aqueous solution effect to increase extraction efficiency. Thermodynamic study appear the extraction behavior was endothermic giving maximum increasing in extraction at 40°C with thermodynamic data ΔH_{ex} =0.068 kJ.mol^{-1} and ΔG_{ex}= -53.95 kJ.mol^{-1} ΔS_{ex}= 172.58 J.mol^{-1}.K^{-1} .The study included also organic solvent effect and spectrophotometric determination of Zn^{2+} in different samples by used calibration curve appear good linearity from (1-10) ppm and molar absorptivity ε=7861.45L.mol^{-1}.cm^{-1}, RSD% (n=3)=0.00545 and standard deviation=0.0728, Sandal's sensitivity= 0.00832µg.cm^{-2}.

KEYWORDS: Extraction of Zn^{2+} Ion, Solvent Extraction Method, Onium System

INTRODUCTION

Shawket and Faris (2015) study the extraction of Zn^{2+} ion from aqueous solution as ion association complex with organic reagent AIBSNB by application CPE methodology in presence nonionic surfactant 1% TritonX-100 [Zn (AIBSNB)]$^{+}$;Cl^{-} coupled with spectrophotometric determination[1]. Ardeshir and Roghayeh (2014) by used of CPE methodology for extraction and determination of Aluminum (III) from aqueous solution after formation ion pair complex with (QUIN) in presence TritonX-114 and this study limited all optimum condition of extraction as well as appear detection limit 2.09 ng mL^{-1} and study many effective parameter on extraction[2]. Shawket with another worker studied extraction and spectrophotometric determination of different metal ions by application determination Cloud point extraction methodology [3-8]. Abdal-Azeem and Alaa (2016) by using micelle –mediated extraction for extraction studies of Sb(II), Sb(III) and determination in different sample after used complexing agent (DCHNAQ) and in presence (CTAB) with potassium iodide at pH=4.5[9]. Alexa and Katherinc (2015) by used of DPT and 3-amino-7-dimethylamino-2-methylphenazine as complexing agents for determination the iron in drinking water by application CPE methodology in presence TritonX-114 with using FAAS for determination [10].

EXPERIMENTAL

For spectrophotometric studies and absorbance measurements used Double beam UV-Vis. spectrophotometer,

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

All chemicals used received from well-known commercial company and used in experimental studies without any further purifications and by used distilled water for prepared all solutions, standard Zinc ion Zn^{2+} 1000µg/mL was prepared by dissolved 0.1 g of Zinc metal in 100 mL HCl solution (1:1), standard Methyl Stearate at 1×10^{-3} M prepared by dissolved 0.2985g in 100mL of chloroform by used volumetric flask. All solution needing to determination reminder quantity of Zn^{2+}ion in aqueous solution, after extraction by dithizone spectrophotometric method prepared according to procedure detailed in [11].

PRINCIPAL PROCEDURE

5mL aqueous solutions contain 50µg of Zn^{2+}ion and optimum concentration of hydrochloric acid HCl shaking these solutions for 5min. afterward added 5mL of organic solution of organic reagent Methyl stearate dissolved in chloroform at 1×10^{-3} M and shaking these two layers for optimum shaking time then separated there two layer and measure the absorbance of organic layer at λ_{max}=275nm against blank prepared at the same manner without Zn^{2+}ion,and aqueous solutions treated according to dithizone spectrophotometric method[11]and after return to calibration curve Figure (2) determine the remain quantity of Zn^{2+} ion in aqueous phase after extraction and by subtraction this quantity from the original quantity Zn^{2+}ion in aqueous solution determine the transfer quantity to the organic phase as oxonium species and then divided the transfer quantity on the remain quantity to calculate Distribution ratio (D)

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

And to be sure we are correct determined the transfer quantity of Zn^{2+}into organic phase as oxonium species depended on the stripping method for checking by shaking organic phase with two portion 5mL of 2M solution of NaOH to destroy the oxonium species and determined Zn^{2+} ion after stripping by dithizone method [11], it is found transfer quantity of Zn^{2+} calculated by stripping method was equal to the same quantity calculated by subtraction method.

RESULTS AND DISCUSSIONS

Spectrophotometric study for oxonium species extracted into organic layer show wave length for maximum absorbance was 275nm against blank prepared as the same manner without Zn^{2+}ion the result clear in the Figure(1)

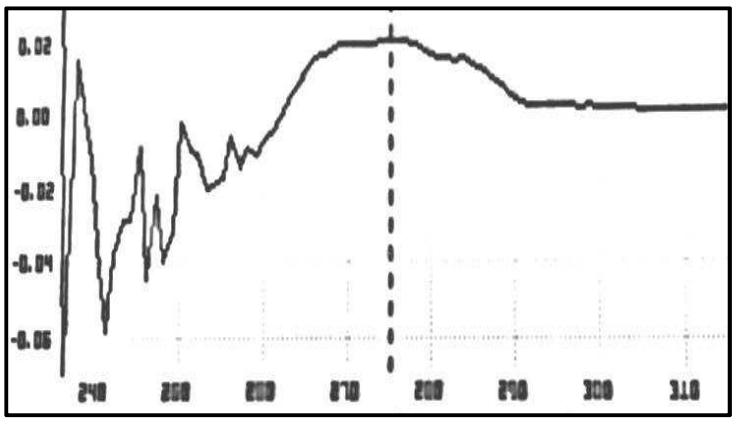

Figure 1: UV-Vis Spectrum of Oxonium Species

EFFECT OF HCL CONCENTRATION

Extraction 50µgZn^{2+} ion from 5ml aqueous solution contain different concentration of Hydrochloric acid HCl by 5mL organic solution of Methyl Stearate dissolved in chloroform at 1×10^{-3} M according to principal procedure and giving the result as in Figures (3,4 and 5):

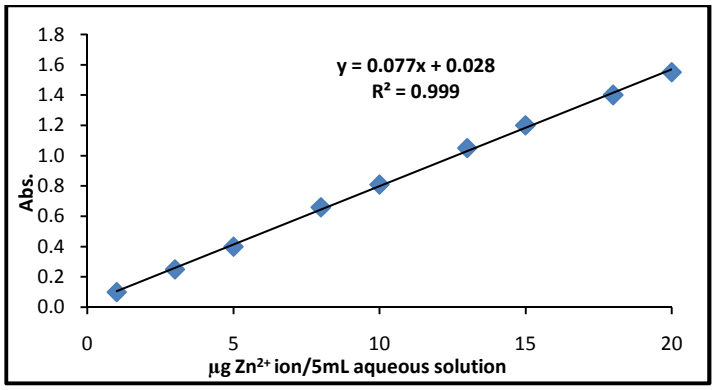

Figure 2: Calibration Curve for Determination Reminder Quantity ofZn^{2+}ions by Dithizone Spectrophotometric Method

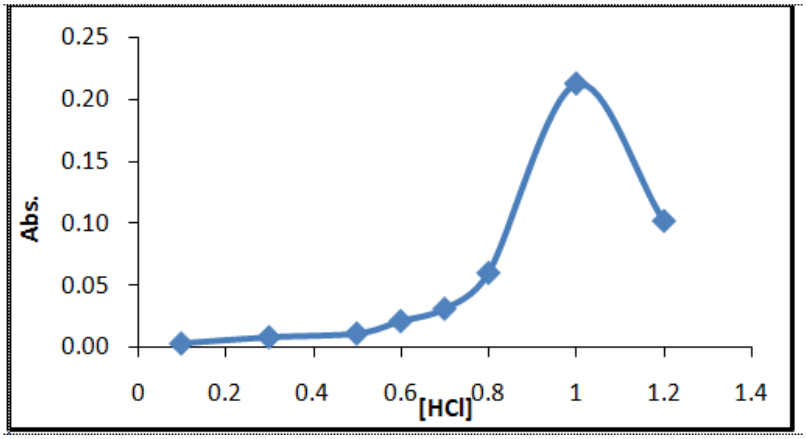

Figure 3: Effect of HCl Concentration on Prepared and Stability of Oxonium Species

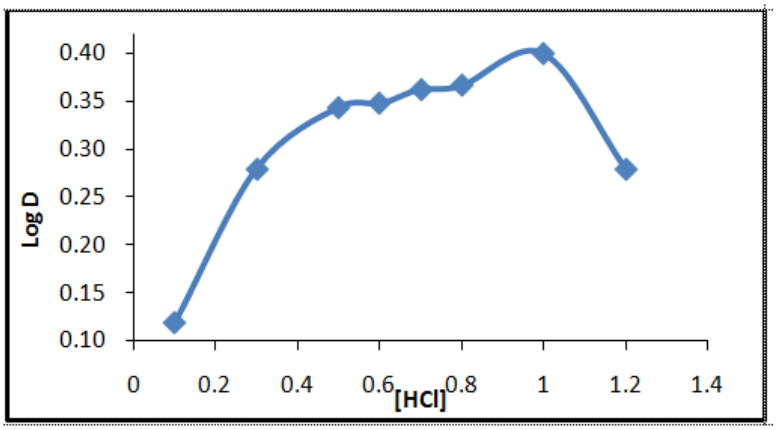

Figure 4: Effect of HCl Concentration on Extraction Efficiency and D-Values

The results show 1M HCl was optimum concentration of HCl giving higher absorbance and D value that is mean at this concentration of HCl reached to favorable extraction efficiency because at this concentration of HCl reached best

thermodynamic equilibrium for formation and extraction oxonium species, any concentration of HCl less than optimum value not allow to reached thermodynamic equilibrium also concentration of HCl more than optimum value giving decrease in absorbance and D-values by effect of increase in the rate of backward reaction and decrease in oxonium species formation according to mass action law.

CHANGE METAL ION CONCENTRATION EFFECT

Extracted different microgram of Zn^{2+} ion in 5mL aqueous solutions contain 1M HCl by application principal procedure the results was as in Figures (5 and 6)

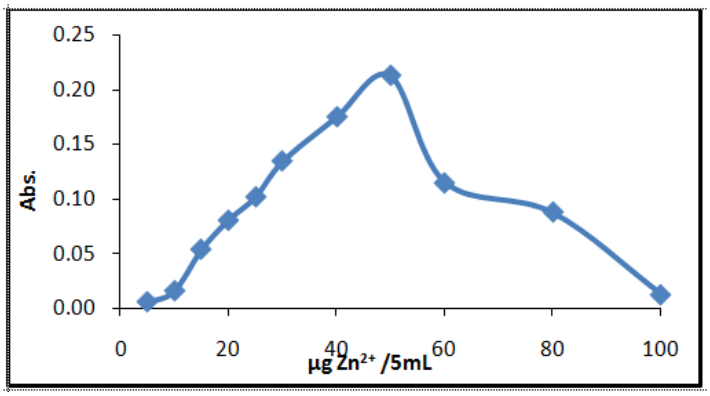

Figure 5: Effect of Metal Ion Concentration on Formation Oxonium Species

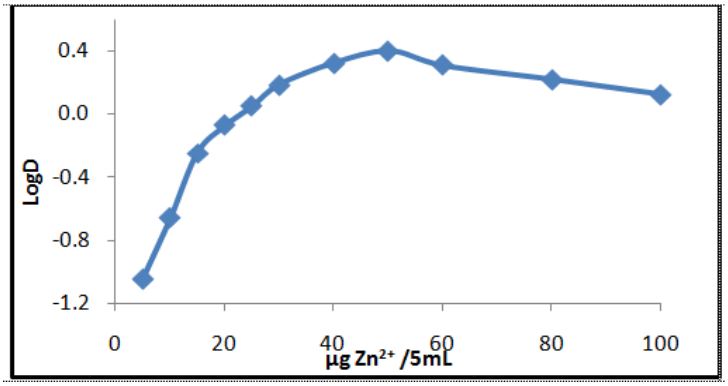

Figure 6: Effect of metal Ion Concentration on Extraction Efficiency

The result show 50µg Zn^{2+} /5mL was the optimum value for metal ion concentration which is giving best thermodynamic equilibrium for formation of oxonium extracted species as equilibrium relations below:

$$Zn^{2+} + 4H^{+} + 4Cl^{-} \underset{\text{Solution}}{\overset{\text{Aqueous}}{\rightleftharpoons}} H(H_2O)_4^{+}; HZnCl_4^{-}$$

$$(H(H_2O)_4^{+}; HZnCl_4^{-})_{aq.} + 3S \overset{\text{Extraction}}{\rightleftharpoons} (H(H_2O)S_3^{+}; HZnCl_4^{-})_{org.}$$

Oxonium species

Whereas: S is Methyl stearate ester

Any concentration of metal ion Zn^{+2} in aqueous solution less than optimum value not allow to reach

thermodynamic equilibrium for formation acidic hallow complex and decrease in the oxonium species formed appear decline in the absorbance and D-values ,as well as any concentration of Zn^{+2} ion in aqueous phase more than optimum value effect to decrease extraction efficiency also by effect of mass action law which is causes to increase in dissociation direction of acidic hallow complex and increase in oxonium species also.

SHAKING TIME EFFECT

According to principal procedure detailed in experimental part extracted 50µg Zn^{+2} in 5mL aqueous solution by different time of shaking for the two layers and the results was as in Figures (7 and 8):

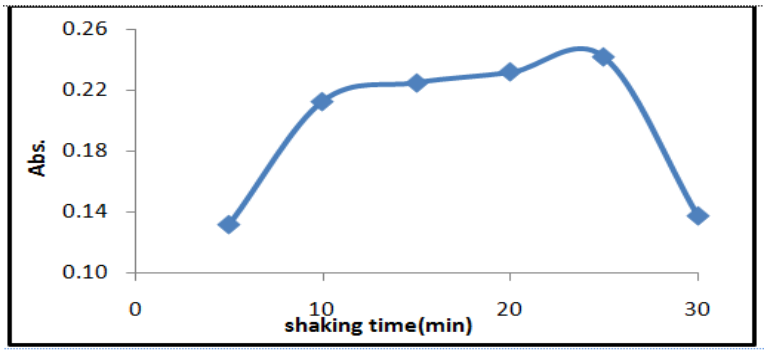

Figure 7: Shaking time Effect on Oxouium Species Formation

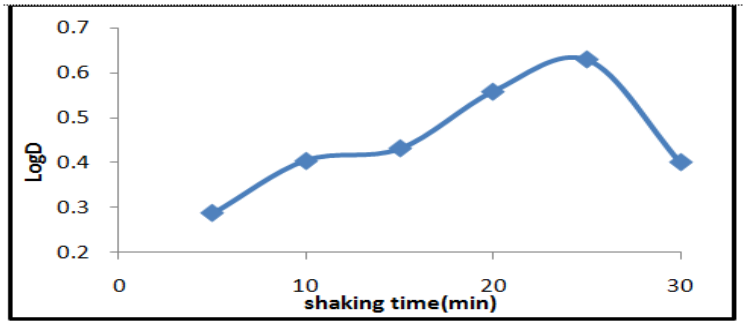

Figure 8: effect Shaking Time on Extraction Efficiency

The results show 25min. was the optimum shaking time which is help to reached batter thermodynamic equilibrium to giving higher concentration of oxonium species with higher absorbance and D-values whereas shaking time represented the kinetic energy for formation oxonium species in view of the fact that onium extraction method is an application of solvent extraction system which is depend on thermodynamic laws in origin and second effective is kinetic laws. Any shaking time less than optimum value not enough to reach thermodynamic and kinetic equilibrium to form oxonium extracted species, but shaking time more than optimum effect to decrease extraction efficiency too by reason of increase rate of dissociation equilibrium by increasing kinetic energy over than needed for general equilibrium to formation and extraction oxonium species.

VARIATION ORGANIC REAGENT CONCENTRATION EFFECT

By following the principal procedure which is detailed previously extracted 50µg Zn^{2+} in 5mL aqueous solutions at all optimum conditions with different concentrations of organic reagent Methyl stearate ester the results were as in Figures (9 and10):

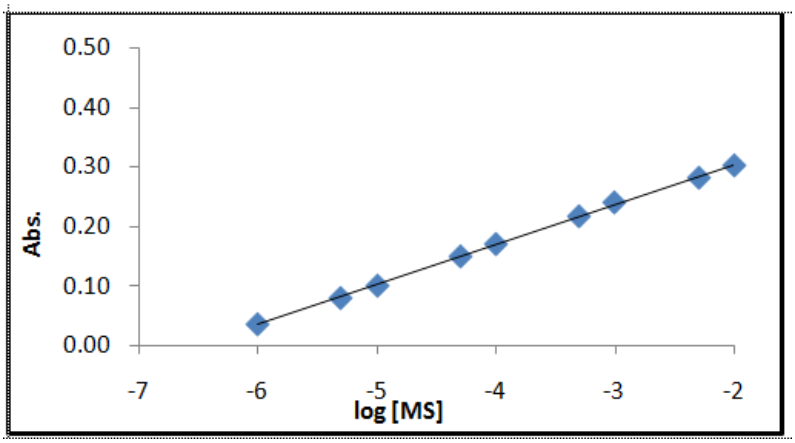

Figure 9: Oxonium Species Formation Change as a Function of Methyl Stearate Concentration

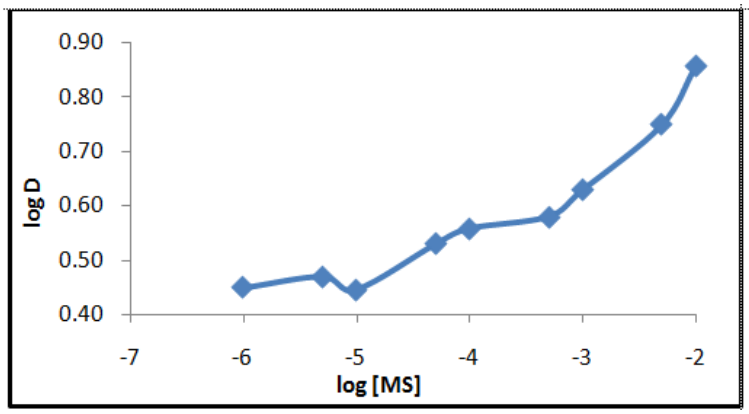

Figure 10: D-Value Increase with Methyl Stearate Concentration Increase

The results show extraction efficiency behave as a function to Methyl stearate concentration and giving increasing straight line or nearly straight line relation whereas increasing concentration of organic reagent Methyl stearate mean increase the opportunities of substitution of ester molecules instead of water molecules in hydrated proton and complete substitution three molecules to extracted to organic phase as oxonium species because substitution of Methyl Stearate submitted to thermodynamic equilibrium.

KIND OF ORGANIC REAGENT EFFECT

Extracted 50µg Zn^{2+} in 5mL aqueous solutions at optimum conditions according to principal procedure by used of different kind of organic reagent the results were as in Table(1):

Table 1: Effect of Different Organic Reagent

Organic Reagent	*Abs. at λ_{max}=275nm*	*D*
Methyl stearate	0.242	4.263
**2,4-DMP*	0.155	3.770
Butanone	0.388	5.500
***MIBK*	0.325	4.850
Acetophenone	0.460	6.130

***2, 4-DMP 2, 4-Dimethyl-pentan-3-one, **MIBK Methyl isobutyl ketone**

The results show Acetophenone appear higher extraction efficiency that is mean any organic reagent to write

down enhancement in extraction efficiency it is the favorable to substituted water molecules in hydrated proton as cation and increase the rate of oxonium species formation and extraction.

EFFECT OF ELECTROLYTE SALTS PRESENCE

By followed principal procedure for extracted 50µg Zn^{2+} in 5mL aqueous solutions in presence different electrolyte salts of first, second and third groups of periodic table, the results were as in Table (2):

Table 2: Electrolyte salts effect on extraction efficiency of Zn^{2+} ion

Electrolyte salts	*Abs. at λ_{max}=275nm*	*D*
LiCl	0.614	8.800
NaCl	0.534	6.690
KCl	0.461	5.840
NH_4Cl	0.314	5.570
$MgCl_2$	0.582	6.780
$CaCl_2$	0.408	5.250
$BaCl_2$	0.307	4.740
$AlCl_3$	0.514	6.05

The results show increase absorbance and D-values in presence of electrolytesalts in aqueous solutions because this electrolyte salts effect to destroy the hydration shell of metal ion Zn^{2+} and increase formation of acidic halow complex $H(H_2O)_4^+$;$HZnCl_4^-$ as well as increase the rate of thermodynamic equilibrium for substitution water molecules in hydrated proton and increase formation and partition oxonium species into organic phase in addition to increase stability of extracted species $H(H_2O)S_3^+$;$HZnCl_4^-$.

INTERFERENCES EFFECTS

Extracted 50µg Zn^{2+} in 5mL aqueous solutions according to principal procedure in presence interferences metal cations in aqueous solutions the results were as in Table (3):

Table 3: Effect of Interferences Some Metal Cations

Interferences	*Abs. at λ_{max}=275nm*	*D*
Ni^{2+}	0.115	1.630
Fe^{2+}	0.138	2.260
Hg^{2+}	0.123	2.050
Co^{2+}	0.107	1.120

The results show decline extraction efficiency in presence metal cation under study that is mean these cations giving interferences with extraction of Zn^{2+} which is demonstrate participation of these metal cations in the formation of acidic hallow complexes in acidic aqueous solutions and giving oxonium species after inter Methyl stearate molecules in its structure and this result tell us must be used masking agents when we are extraction and determination Zn^{2+}in environmental and vital samples.

EFFECT OF METHANOL CONCENTRATION

Extracted 50µg Zn^{2+} in 5mL aqueous solutions at optimum conditions according to general method detailed in principal procedure and in presence different percentage of methanol in aqueous solutions the results were as in Figures (11 and 12):

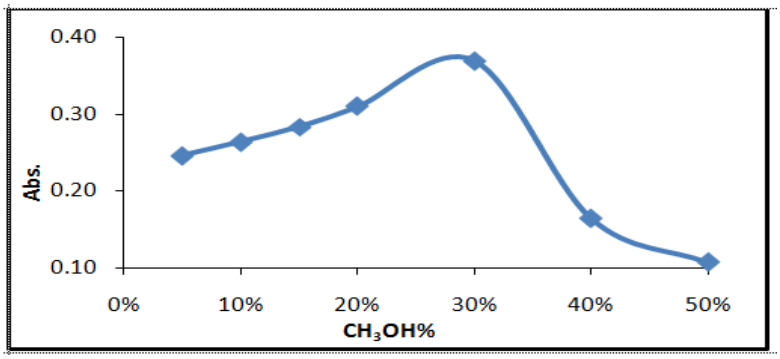

Figure11: Effect of Methanol Concentration on Formation and Extraction Oxonium Species

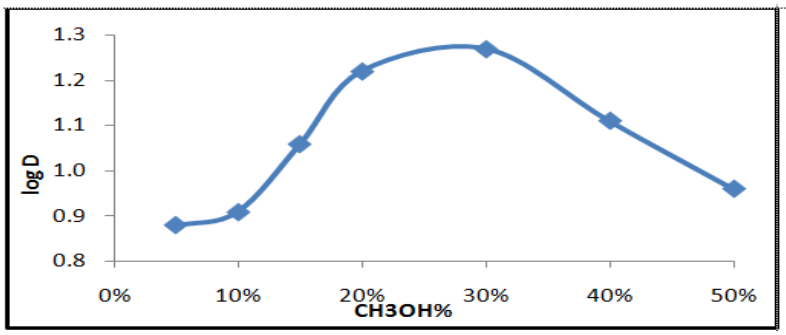

Figure 12: Effect of Methanol Concentration on Extraction Efficiency

The results show 30%CH_3OH was optimum concentration of methanol giving higher extraction efficiency where the enhancement in extraction appear from 5% to 30% and the decrease at 40% and 50% the increasing of extraction by effect of methanol because the methanol effect to decrease dielectric constant and polarity of aqueous solution and this decreasing cause more destroyed of the hydration shell of Zn^{2+}cation and increasing in the formation of acidic halow complex and oxonium species until reached maximum formation at 30%CH_3OH but at 40% and 50% of methanol effect to decrease extraction activity because at this percentage of methanol cause very great decreasing in dielectric constant and polarity of aqueous solution effect to transfer large quantity of Methyl Stearate from chloroform to aqueous solution and decrease formation and extraction of oxonium species.

TEMPERATURE EFFECT

By followed principal procedure extracted 50µg Zn^{2+} in 5mL aqueous solutions at optimum condition and different temperature the results were as in Figures (13 and 14):

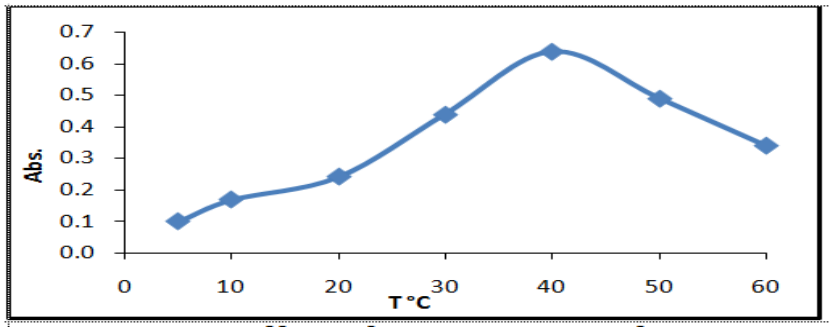

Figure 13: Effect of Temperature on Formation Oxonium Species

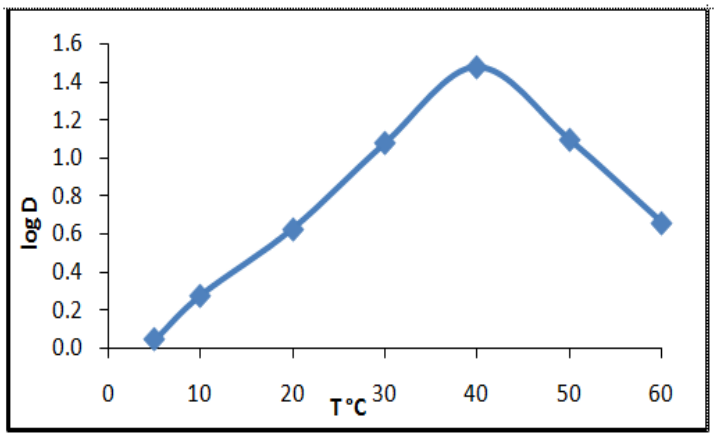

Figure 14: Effect of Temperature on Extraction Efficiency

And then calculated extraction constant K_{ex} at each temperature according to mathematical relation below:

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

The results illustrates in Figure (15):

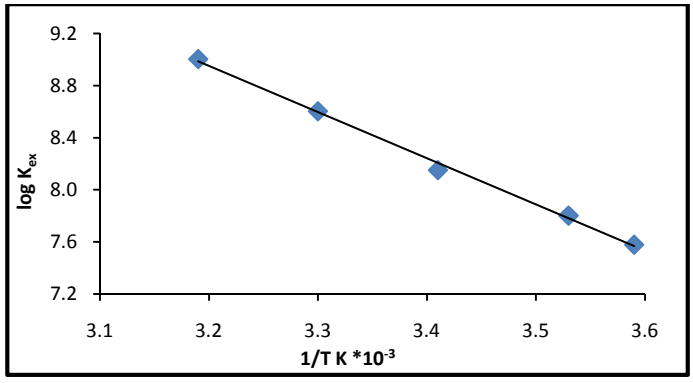

Figure 15: Change Kex as a Function for T K

And then calculated thermodynamic data as below

$slope = \frac{-\Delta H_{ex}}{2.303\,R}$	ΔH_{ex}=0.068 kJmol^{-1}
ΔG_{ex} = - R T ln K_{ex}	ΔG_{ex} = -53.95 kJmol^{-1}
$\Delta G_{ex} = \Delta H_{ex} - T\Delta S_{ex}$	ΔS_{ex}= 172.58 J.mol^{-1}.K^{-1}

The results show extraction efficiency of $Zn^{2+}$was endothermic behavior and giving highest extraction at 40°C then appear maximum absorbance and D-value, the small values of ΔH_{ex} reflect the good approach of ion pair association complex extracted, as well as high value of ΔS_{ex} mean the major effect of entropy on extraction step to form stable extracted oxonium species and reflect the extraction procedure was entropic in region.

ORGANIC SOLVENT EFFECT

Extracted 50µg Zn^{2+} in 5mL aqueous solutions according to principle procedure at optimum conditions by used different organic solvents to dissolve organic reagent Methyl stearate ester. The results were as in Table (3):

Table (4): Effect of Organic Solvents on Extraction Efficiency

Organic Solvent	*Dielectric Constant (ε)*	*Abs. at λ_{max}=275nm*	*D*
Nitrobenzene	35.74	0.898	6.873
Amyl alcohol	15.8	0.222	3.910
50%NB+50%T	15.6	0.347	5.233
1,2-Dichloromethane	10.65	0.269	4.681
30%NB+70%T	10.65	0.108	2.880
Dichloromethane	9.08	0.636	5.832
Bromobenzene	5.4	0.598	5.571
Chloroform	4.806	0.242	4.263
5%NB+95%T	3.4	0.339	4.952
Benzene	2.804	0.226	4.012
Toluene	2.438	0.859	6.224

The results show there is not any linear relation between dielectric constant of organic solvents and D-values of extraction but appear there is in effect for organic solvent structure and this result reflect the participation of organic solvent in the formation and stability of oxonium species extracted.

SPECTROPHOTOMETRIC DETERMINATION OF ZN^{2+} ION

For determination metal Zinc (II) in different environmental and vital samples by UV-Vis. spectrophotometric study after separation according to application onium system as detailed in principal procedure prepared calibration curve as in Figure (16):

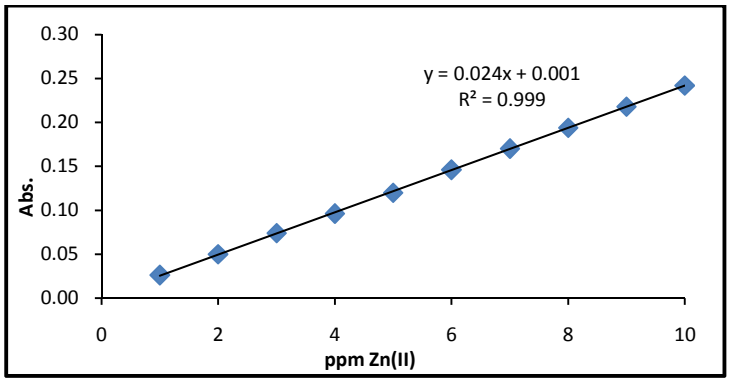

Figure 16: Calibration Curve for Spectrophotometric Determination of Zn^{2+}

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