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Solvation Method for Separation and Determination Zinc(II) and Acetophenone

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Abstract

By following Solvation technique with Acetophenone as organic agent for separation and determination zinc(II) so that Acetophenone through formation solvation species in the presence of salting out $NaNO_3$, as well as extraction solvation species into chloroform organic solvent
The experimental studies shows 0.1 M $NaNo_3$ was the optimum concentration of salting out in presence 90 µg of Zn^{2+} in 5mL aqueous solution and 10 minutes shaking time so that the extraction need $1x10^{-4}$ M acetophenone, the extraction procedure shows the presence of methanol in aqueous solution effect to enhancement the extraction efficiency. The experimental study demonstrate 30% methanol was the optimum concentration giving highest extraction efficiency.
Thermodynamic study show thermodynamic data was
$\Delta Hex = 0.0571$ KJ mol^{-1} ; $\Delta Gex = -57.34$ $kJmol^{-1}$; and $\Delta Sex = 183.38$ $Jmol^{-1}$ k^{-1}

Keyword: Zinc (II), Acetophenone, Solvent extraction

INTRODUCTION

Solvent extraction with different application use on a wide range For separation preconcentration and determination a lot of metal cations, as it is sensitive methods. By combined solvation as un application for solvent extraction with cloud point extraction in order of separation and determination of magnesium (II) as solvation species by using of 2,4-dimethyl pentan – 3- one and TritonX – 100 and application this method for determination of Mg^{2+} with DL=1.84 x 10^{-5} µg/mL and RSD=0.0074% and sandel sensitivity equal to 3.58 x 10^{-9} µgcm^{-2} [1]. Cloud point extraction CPE used for separation and determination platinum(II) as anion chloro complex $PtCl_4^{=}$ after formation ion pair association complex with Junnas green in presence, TritonX–100 the extraction shows DL=6.8028 $x10^{-6}$ µg/ml sandal sensitivity equal to 0.003 µg cm^{2-} RSD=0.00885% [2]. Extraction and Determination cadmium (II) in different samples by onium technique as un application for solvent extraction by using 2,4- Dimethyl -3- pentanone [3]. By application liquid ion exchange extracted Zn^{2+} and Cd^{2+} by 4-[N-(5-methylisoxazol-3-yl) benzene sulfonamide azo]–1–Naphthol benzene (AIBSNB), as complexing agent in order to formation ion pair association complex [4]. By using 2-[N-5-methyl isoxazol-3-yl] benzene sulfonamide azo-1-Naphthol-Benzene as complexing agent for extraction Zn(II) via cloud point extraction method in presence non ionic surfactant, TritonX–100 at PH=9 [5]. Joined CPE with solvation for separation and determination of lanthanum (III) by using 2,4- Dimethyl pentan – 3-one as well as used 8-Hydroquinoline and safranin dissolved in chloroform as spectrophotometer method for determination lanthanum in aqueous solutions [6]. By CPE method and by using 7(1,5-dimethyl-3.oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylazol-8Hydroxyquinoline-5-sulphonic acid (DPPAHS) as an innovation complexing agent at pH 4.5, separated and determined iron in water sample in the presence Non ionic surfactant TritonX–114 [7]. Used CPE methodology for separation and Determination Hg^{2+} in different sample in presence TritonX-100 and TritonX- 114 and organic reagents DDTP, 4-(2-pyridyazo) resorcinol, ThioMichlers ketone [8-11] Extraction and determination Cd (II) from nitrate medium by using quaternary ammonium ion to study many parameter effect ion extraction efficiency [12].

EXPERIMENTAL

A double beam spectrophotometer Biochrom model (80-200-11) Libra 560 cambridge CB40FJ was used for spectrophotometric studies, Electrostatic water bath (WNB7-45) (England) has been used for heating as well as all Experiments needed balance (A& D company, Limited, Dook, CE, HR200, Japan)
All solution prepared with distilled water, standard solution of 1000 µg Zn(II) prepared by dissolved 0.1 g of Zn(II) metal in 5 ml (1:1 Hcl) and diluted the solution by distilled water into 100 ml by using volumetric flask.

Comprehensive method

5 ml aqueous solution contain 50 µg of Zn^{2+} ion with 0.1M $NaNO_3$ salting out then added 5ml of 1x 10^{-4} M acetophenone dissolved in chloroform, shaking the solution for 10 min. afterward separation organic phase from aqueous phase, then measure the absorbance of organic phase at λ_{max}=291 nm against blank prepared at the same manner without Zn^{2+} ion, so that aqueous phase treated according to dithizon spectrophotometric method [1] and to return to calibration curve Fig (2) to determined remainder quantity of Zn^{2+} ion in aqueous solution after complete extraction , the remain quantity of Zn^{2+} ion subtraction from the initial quantity 50 µg Zn^{2+} ion to determine the transfer quantity Zn^{2+} ion into organic phase after formation solvation species and calculate distribution ratio D

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

RESULTS AND DISCUSSION

Spectrophotometric studies

5 mL aqueous solution contain 50 µg Zn^{2+} ion with 0.1 M $NaNO_3$ as salting out. Add 5ml of 1 x 10^{-4} M acetophenone and shaking the solution for 10 minutes then separated the organic phase from the aqueous phase and performed the

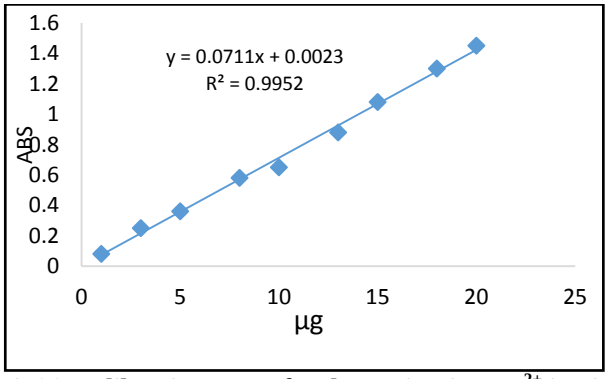
absorption spectrum of organic phase via blank prepared at the same manner in absence Zn^{2+} ion, the results was as in Fig (1)

Fig(1) = UV-Vis absorption spectrum of solvation species The spectrum show λ_{max}=291 nm was the wave length of maximum absorption for solvent species of Zn^{2+} ion

Effect of salting out

A series of aqueous solutions 5 ml in volume each one contain 50 µg Zn^{2+} ion with rising concentration of salting out $NaNO_3$, add to each solution 5 ml of $1x10^{-4}$ M acetophenone dissolved in chloroform and shaking for 10 min. and then separate organic phase form aqueous phase and complete the experiment as in comprehensive method, the results were as in Fig (3,4)

The results demonstrate 0.1 M $NaNO_3$ was the suitable conc. Salting out in order to give best equilibrium for formation and extraction solvation species, any concentration less than optimum value not allow to giving best suitable equilibrium and decrease formation and extraction solvation species, so that any concentration of salting out more than optimum value effect to decrease formation and extraction solvation according to mass action low as well as effect to prevent Zn^{2+} to prepare solvation species.



Fig(2): calibration curve for determination Zn^{2+} ion in aqueous solutions by dithiazone method.

Effect of Zn^{2+} Concentration.

A series of aqueous solutions 5 ml in volume contain rising quantity of Zn^{2+} ion and 0.1 M salting out $NaNO_3$ add to each solution 5 ml of 1 $x10^{-4}$ M acetophenone then shaking the solution for 10 min. afterward separate organic phase from the aqueous phase and complete the work as in comprehensive method the results were as in Fig (5,6).

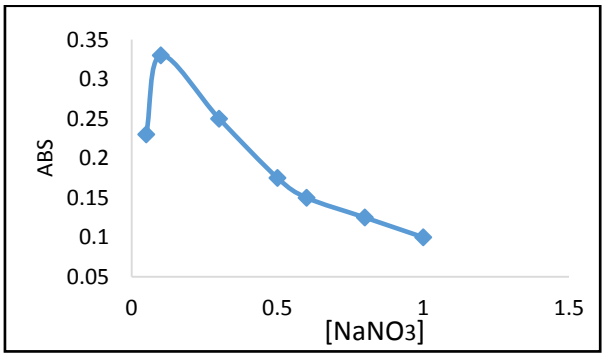


Fig (3): Effect of salting out conc. On formation and stability of solvation species

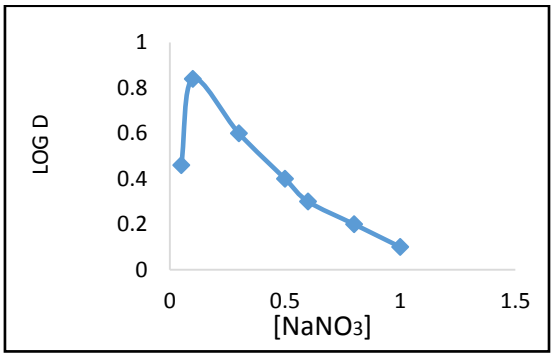
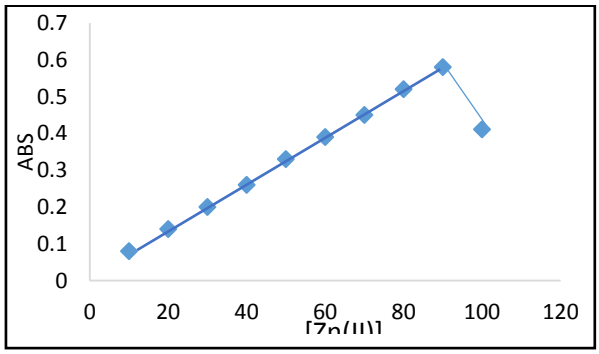


Fig (4): Effect of salting out con. On extraction efficiency and D value



(5): Effect of Zn^{2+} ion concentration on formation and stability of solvation species

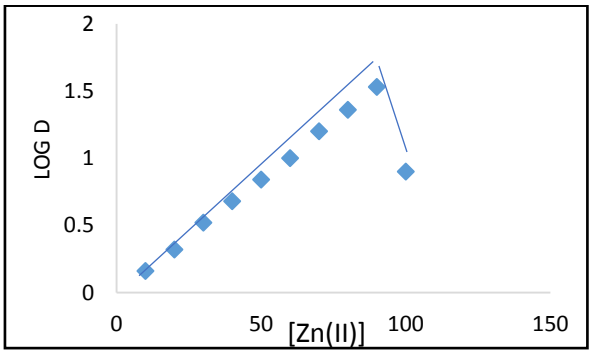
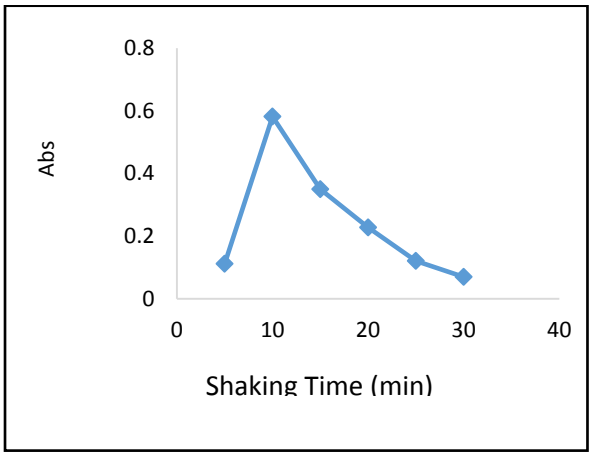


Fig (6): Effect of Zn^{2+} ion conc. On extraction efficiency and D-Values



Fig(7): Effect of shaking time on formation and stability of solvation species

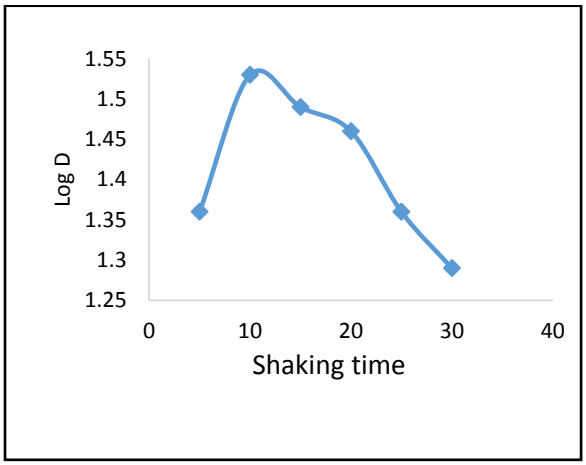
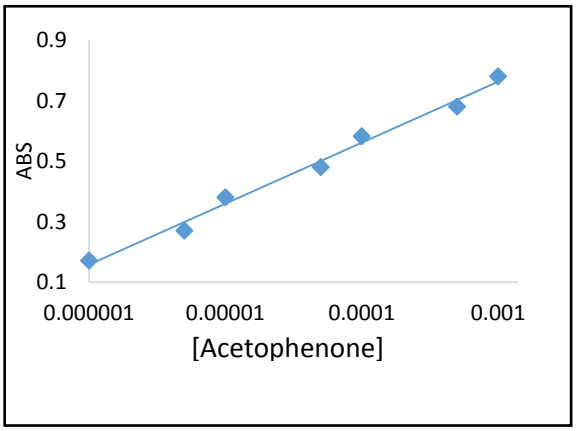
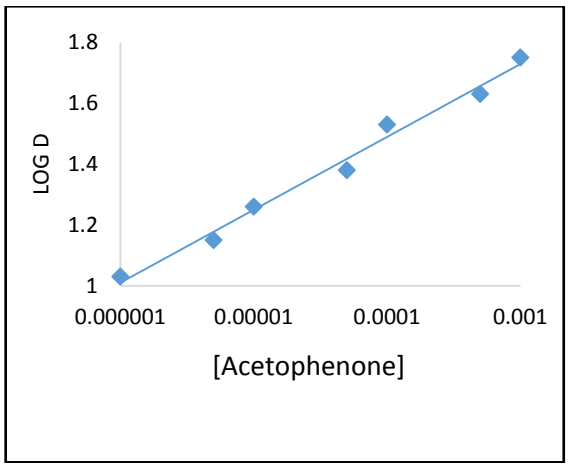


Fig (8): Effect of shaking time on Extraction efficiency and D-value



Fig(9): Effect of acetophenone concentration on formation and stability of solvation species



Fig(10): effect of acetophenone conc. On Extraction efficiency and D-Values

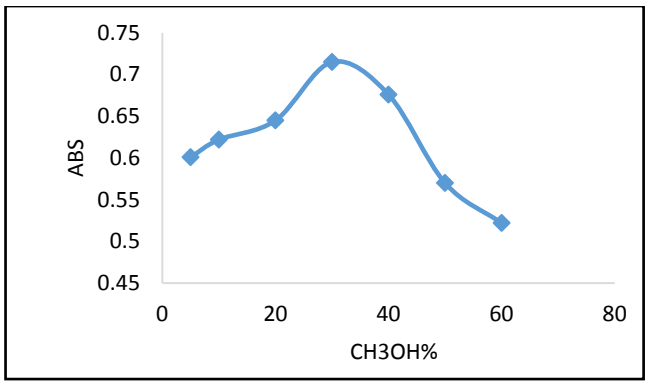


Fig (11): Effect of methanol percentage on formation solvent species

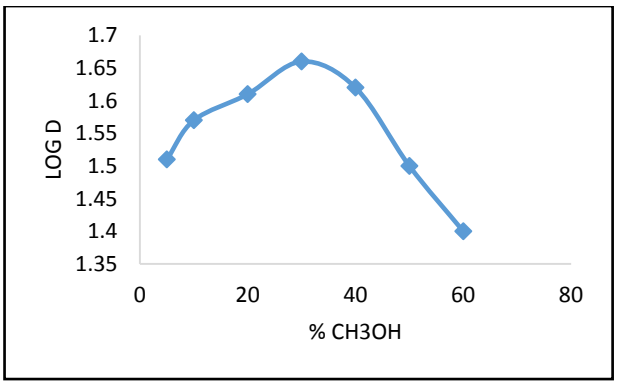


Fig (12): Effect of methanol percentage extraction sufficiency and D-Values

The results show, 90 µg Zn^{2+}/ 5ml was the optimum conc. Necessary to reach best thermodynamic equilibrium to formation with high stability of solvation species any conc. Less or more than optimum value effect to extraction efficiency as well as, the results demonstrate there a straight line relation between extraction efficiency and metal ion concentration to optimum value.

Effect of shaking time

A series aqueous solutions 5 ml in volume contain 90 µg Zn^{2+} ion and 0.1 M $NaNO_3$ on salting out add to each

solution 5 ml of 1x 10^{-4} M acetophenone dissolved in chloroform, shaking these solutions in electrostatic shaker for different time, after ward separate the organic phase and from the aqueous phase complete the experiment as in comprehensive method, the results were as in Fig (7,8)

The results demonstrate 10 minutes was the optimum shaking time to give higher extraction efficiency whereas shaking time represent kinetic energy of formation and extraction of solvation species, any shaking time less than optimum value not allow to reach thermodynamic equilibrium so shaking time more than optimum effect to increase diffusion and decrease extraction efficiency.

Effect of Acetophenone Concentration.

Aqueous solutions 5 ml in volume contain 90 µg Zn^{2+} and 0.1 M $NaNO_3$, add to each solution 5 ml of acetophenone dissolved in chloroform at rising concentrations. Shake these solutions 10 minutes in electrostatic. Shaker and complete the experiment as in comprehensive method. The results were as in Fig (9,10).

The results shows that a straight line relation between solvation species formation and extraction efficiency with acetophenone concentration represent as thermodynamic parameter.

Methanol Presence Effect

A series of aqueous solution 5 ml in volume contain 90 µg Zn^{2+} ion and 0.1 M $NaNO_3$ in presence rising percentage of methanol. Add to each solution 5 ml of 1x10^{-4} M acetophenone dissolved in chloroform, then shaking these solutions for 10 min in electrostatic shaker and complete the work as in comprehensive method, the results were as in Fig (11, 12).

The results shows presence methanol in aqueous solution effect to increase quantity of solvation species formed and extraction efficiency, so 30% CH_3OH was the optimum percentage give highest extraction efficiency because methanol effect to decrease polarity and dielectric constant of aqueous solution and destroy the hydration shell on metal cation and increase in formation and stability of solvation species.

Thermodynamic Study

According to comprehensive method and at optimum condition in presence 30% CH_3OH extracted solvation species of Zn^{2+} at different Temperature the results were as in Fig(13,14).

After calculate extraction efficiency by relation below

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

The results demonstrate in Fig (15).

Extraction data illustrated below

$Slope = \frac{-\Delta H_{es}}{2.3>2\vartheta}$ $\quad \Delta H_{ex} = 0.0571\ KJ\ mol^{-1}$

$\Delta G_{ex} = -Rt\ in\ k_{ex}$ $\quad \Delta G_{ex} = -57.34\ KJ\ mol^{-1}$

$\Delta G_{ex} = \Delta H_{ex} - T\Delta S_{ex}$ $\quad \Delta S_{ex} = 183.38\ J\ mol^{-1}\ k^{-1}$

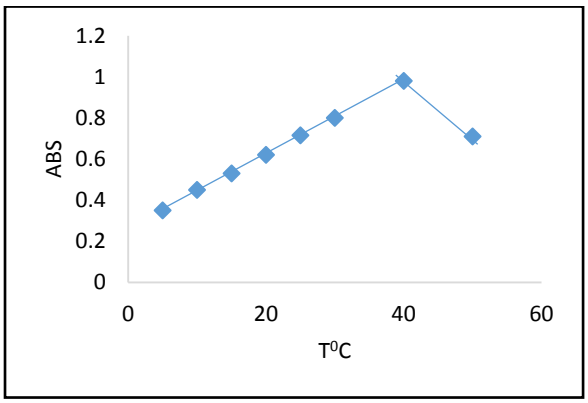


Fig (13): Effect of temperature on solvation species formation and stability

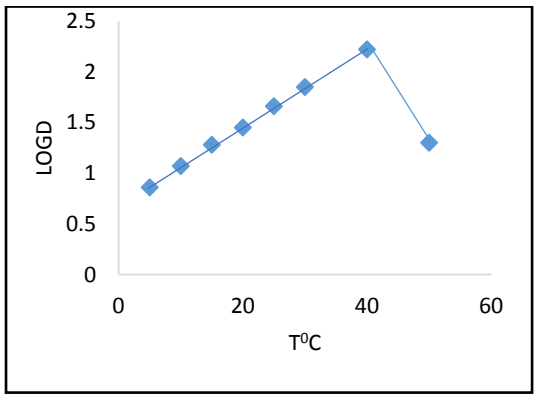


Fig (14): Effect of Temperature on Extraction efficiency and D-Values

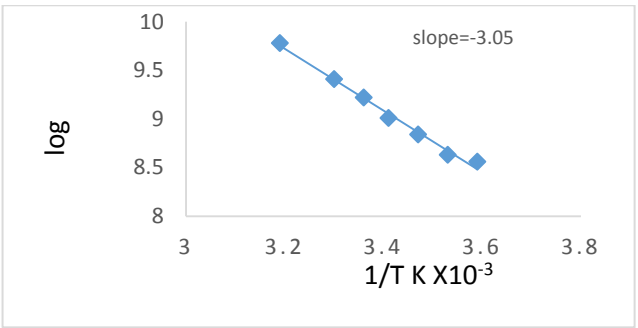


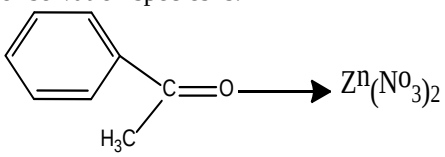
Fig (15): Effect of Temperature on extraction constant values.

Stoichiometry

In order to pinpoint the structure of solvation species extracted to organic phase with the spectrophotometric methods which in slope analysis and slope ratio The Result demonstrated in Fig (16-18).

$$Slope\ ratio = \frac{840.84}{830.83} = 1.012$$

The results and the slope values demonstrate the structure of solvation species is.



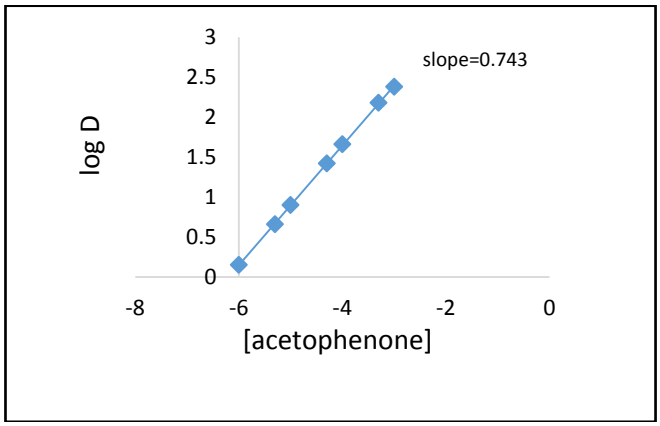


Fig (16): slope analysis. Effect acetophenone, on formation solution species

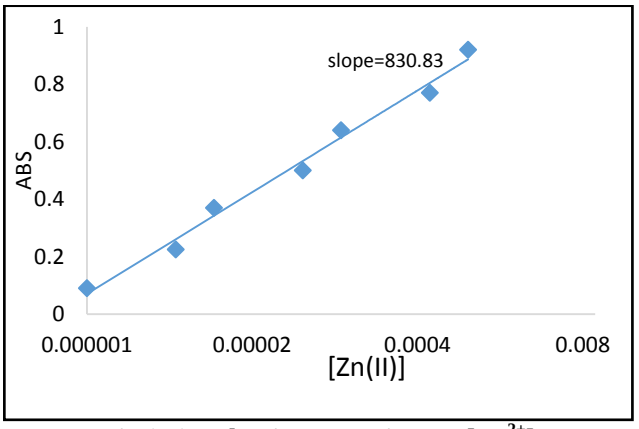


Fig (17): solvation = species = F [Zn^{2+}]

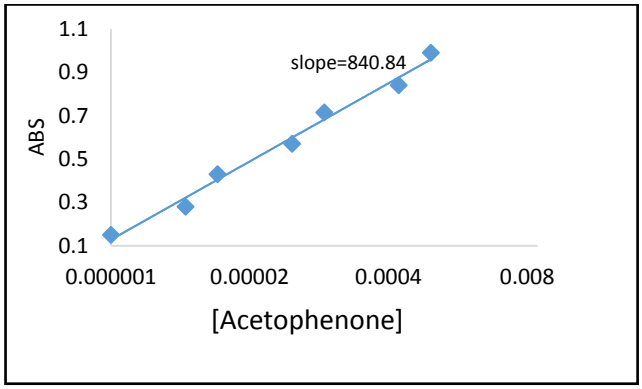


Fig (18): Solvation species = F [acetophenone]

Table (1): Effect of organic solvents on Extraction Efficiency

Organic solvents	Dielectric constant	Abs.λmax= 291 m	D
Nitrobenzene	35.74	0.510	24.000
Amyl alcohol	15.8	0.205	14.000
50% Nitrobenzene +50% Toluene	15.6	0.460	22.680
30% Nitrobenzene +70% Toluene	10.65	0.421	19.930
1.3-Dichloroethane	10.65	0.586	31.140
Chloroform	4.806	0.715	45.710
Benzene	2.804	0.321	15.360
Toluene	2.438	0.331	17.000

Solvation species

Effect of organic solvent

Extracted Zn^{2+} ion as solvation species according to comprehensive method at optimum condition by acetophenone dissolved in different organic solvents, the results demonstrated in Table (1)

The results appear there is not any linear relation between Extraction efficiency and Dielectric constant of the organic solvent that is mean there is not any effect for the polarity of the solvent on extraction but there in an effect for organic solvent structure on extraction efficiency because the organic. Solvents participate in the formation of solvation species in the coordination bonding of acetophenone to $Zn(NO_3)_2$ molecules

Effect of interference

The presence of foreign metal cation in the aqueous phase side by side with Zn^{2+} effect to decrease extraction efficiency of Zn^{2+} ion as solvation because the foreign ions participate in the formation solvation species by effect of consumption part of acetophenone and this effect differ from foreign cation to other depend on its behavior in aqueous solution. The results demonstrate in Table (2).

Table (2): Effect of interference

interferences	Abs.λmax=291 nm	D
Cd^{2+}	0.229	2.240
Hg^{2+}	0.559	10.240
Co^{2+}	0.622	15.630
Fe^{3+}	0.419	8.560
Ni^{2+}	0.388	5.130

Effect of salting out kind

Extraction Zn^{2+} ion from 5 mL aqueous solutions by 1 $x10^{-4}$ M acetophenone dissolved in chloroform in presence different salting out according to comprehensive method the results were demonstrated in Table (3)

The results appear there is a different extraction efficiency with different salting out because there is a different behavior in aqueous solution as in Fig (19,20).

Table (3): Effect of salting out kind on extraction efficiency of Zn^{2+} ion

Salting out	Abs.max=291 nm	D
$LiNO_3$	0.742	59.000
KNO_3	0.688	44.000
$NaNO_3$	0.715	45.710
NH_4NO_3	0.618	39.910
$Mg(NO_3)_2$	0.720	50.430
$Ca(NO_3)_2$	0.690	44.450

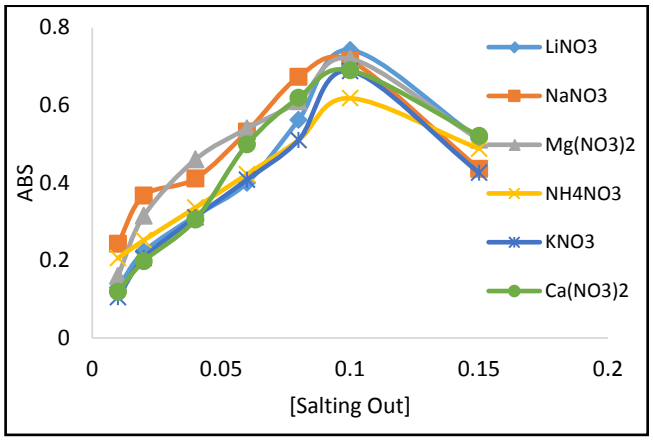


Fig (19): Effect of salting out on formation and stability of solvent species.

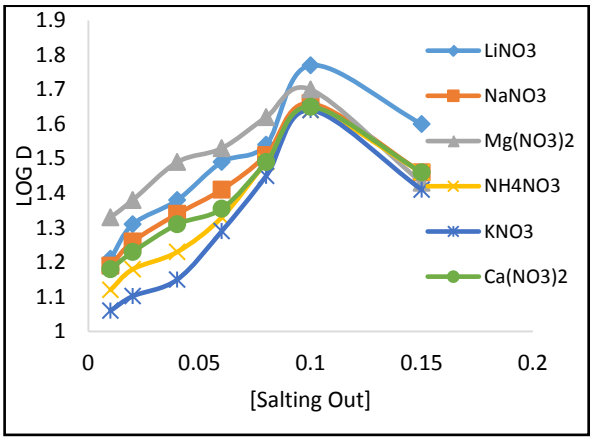


Fig (20): effect of salting out on extraction efficiency and D-values

Table (3): quantities Zn(II) metal and acetophenone in different samples

Samples	ppm Zn(II)	Acetophenone (µg/g)
Beef	38	1.0
sheep meat	43.2	1.08
chicken meat	41.2	0.8
fish	36.0	--
celery	46	1.4
Metal	40	--
bean	58	--
apple	36.2	--
orange	35.2	0.2
Banana	--	0.52
peach	42.6	0.92
apricot	44.2	0.44
Cauliflower	--	0.94

Spectrophotometric Determination

By application solvation method at optimum conditions according to the procedure detailed in comprehensive method determined Zn(II) as well as acetophenone in different samples as demonstrate at Table 3.

CONCLUSION:

Our concluded shows stoichiometry there is one molecule of acetophenone coordinately binding with $Zn(NO_3)_2$ to formation solvation species which is extracted to the chloroform by application slope analysis and stope ratio method , the research involved many other experimental studies and application to determination Zn(11) and acetophenone in different samples.

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