SENSITIVE SOLVATION METHOD FOR SEPARATION SO DETERMINATION OF ZINC(II) AND CADMIUM(II) IN DIFFERENT SAMPLES

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ABSTRACT

Objective: Separation and extraction of Zn(II) and Cd(II) as a neutral compound by used methyl stearate as extractant dissolved in chloroform.

Methods: Applications of separation and extraction according to solvation method from nitrate aqueous solution by used methyl stearate which is binding coordinally with nitrate salt of metal under study Zn(II) and Cd(II).

Results: The extracted species have λ_{max}=263 nm for Zn^{2+} and λ_{max}=346 nm for Cd^{2+}. The studies about limitation optimum condition for extraction show 0.3 M salting out effect KNO_3 for Zn^{2+} and 0.7 M KNO_3 for Cd^{2+} in present 100 µg Zn^{2+}/5 ml and 50 µg Cd^{2+}/5 ml with optimum shaking time 15 minutes for both ions.

Conclusion: The separation by solvation method shows high sensitivity and selectivity in addition to high extraction efficiency for separation Zn(II) and Cd(II). As well illustrate the important rule of kind and concentration of salting out agent and different extractions efficiency with differ extractant.

Key words: Solvation method, Separation and determination, Zinc(II), Cadmium.

INTRODUCTION

Sensitive method for separation and micro amount determination of Zn^{2+} and Cd^{2+} application solvation method [1] applied solvation methodology via cloud point extraction (CPE) method for separation, extraction and determination of Mg^{2+}, in presence 0.5 M KNO_3 aqueous solution by used 2,4-dimethyl-3-pentanone the extracted species appear maximum absorbance wavelength was λ_{max}=249 nm with relative standard deviation=0.0074, DL=1.84×10^{-5} mol/L, Sandell's sensitivity=3.58×10^{-9} µg/cm^2 [1], Zn^{2+} ion extracted as complex with complexing agent 2-(4-amino-N-5-methyl isoxazol-3-yl) benzensulfonamideazo-1-naphthol-benzen, via CPE methodology at pH=9 in presence tritonx-100 as surfactant, the maximum absorbance wavelength for complex extracted was λ_{max}=380 nm [2], according to liquid ion exchange extracted Cd(II) and Hg(II) as ion pair association complex in HCl medium by use of different extractants [3]. By application CPE methodology in presence tritonx-100 extracted Zn(II) with complexing agent3-[2-pyridylazo]-1-nitioso-2-naphthol [4], the extraction of Sn, Sb, Bi, Al, Cu, Pb, and Zn from HCl medium aqueous solution with tri-n-butylphosphate as extractant [5] by application CPE methodology extracted manganese as ion pair complex with brilliant green in acidic medium and in presence tritonx-100 [6].

METHODS

Instrumentation

Double beam ultraviolet-visible (UV-Vis) spectrophotometer, (Biochrom Libra S60) (UK) and single beam (UV-Vis) spectrophotometer, Optima (SP-300) (Japan) used for spectrophotometric studies so that for absorbance measurements. HY-4 viborator with AD just about speed multiple (Italy) used for shaking the solutions.

All chemicals used after received without any purifications and all solutions prepared by dissolved in distilled water. Standard zinc solutions prepared by dissolved 0.2898 g of $Zn(NO_3)_2$ in 100 mL distilled water and for cadmium standard solutions dissolved 0.2103 g of Cd $(NO_3)_2$ in 100 mL distilled water so that all other solutions needed in the work prepared by dilution with distilled water. As well solutions of organic reagent methyl stearate (MS) as extractant prepared by

dissolved fixed quantity in a suitable volume of chloroform and for all prepared of solutions used suitable volumetric flask.

Procedures

About 5 mL aqueous solution contains 100 µg of Zn^{2+} or 50 µg of Cd^{2+} with an optimum concentration of salting out agent KNO_3, added to each solution 5 mL of fixed concentration of MS as extractant afterward shaking these solutions for 15 minutes and separated at the end of shaking the organic phase from the aqueous phase and measure the absorbance of organic phase at λ_{max}=263 nm for extracted species of Zn^{2+} and λ_{max}=346 nm for extracted species of Cd^{2+}. So that the aqueous phase of extracted species treated according to spectrophotometric studies for determination the remainder quantity of Zn^{2+} and Cd^{2+} after returned to calibration curve Figs. 1 and 2 and calculate distribution ratio (D).

$$D=\frac{[M^{n+}]o}{[M^{n+}]_{aq}} M^{n+}=Zn^{2+},Cd^{2+}$$

RESULTS

Spectrophotometric studies

About 5 mL aqueous solution 100 µg of Zn^{2+} or 50 µg Cd^{2+} and 0.3 M KNO_3 for Zn^{2+} extraction so that 0.7 M KNO_3 for Cd^{2+} extraction and for each solution added 5 mL solution of MS dissolved in chloroform at 1×10^{-4} M and shaking these two layers for 15 minutes after that separated organic phase from the aqueous phase and take the spectrum for organic phase contain extracted species for each ion via solution of MS. The spectrum obtained was as in Figs. 3 and 4 [7].

The spectrum at Fig. 3 shows maximum absorbance wavelength was λ_{max}=263 nm as well the spectrum Fig. 4 appears maximum absorbance wavelength for extracted species for Cd^{2+} was λ_{max}=364 nm.

Salting out effect

About 5 mL aqueous solution contains 50 µg Zn^{2+} or Cd^{2+} with different concentration of KNO_3 as salting out shaking with 5 mL of MS solution at 1×10^{-4} M concentration dissolved in chloroform at time 15 minutes at the end separated the two layers and measure the absorbance of

organic layer at λ_{max}=263 nm for Zn^{2+} and λ_{max}=364 nm for Cd^{2+} against MS solution as blank. In addition to treat the aqueous layer dithizone spectrophotometric study [7] such as the procedure detailed in general procedure to calculate D. The results were as in Figs. 5 and 6.

DISCUSSION

The results show optimum KNO_3 concentration for extraction Zn^{2+} or Cd^{2+} was 0.3 M and 0.7 M, respectively, at this concentration reached to thermodynamic equilibrium of formation and high stability of extracted species for each ion MS; $Zn(NO_3)_2$ and MS; Cd $(NO_3)_2$ any concentration less than optimum not allow to reach thermodynamic equilibrium and effect to decrease formation and stability of extracted species so

absorbance and D values so that any concentration more than optimum value show decreases in absorbance and D values also because increase KNO_3 concentration appears electrophoretic effect in the solution to hinder the formation and stability of extracted species.

Effect metal ion concentration
About 5 mL aqueous solution contains different concentration of Zn^{2+} or Cd^{2+} with 0.3 M KNO_3 for Zn^{2+} and 0.7 M KNO_3 for Cd^{2+} extracted according to general method. The results were as in Figs. 7 and 8.

The results show optimum concentration of metal ion giving higher absorbance and D values was 100 µg Zn^{2+} and 50 µg Cd^{2+} at this concentration obtained the best rate for the forward direction of formation
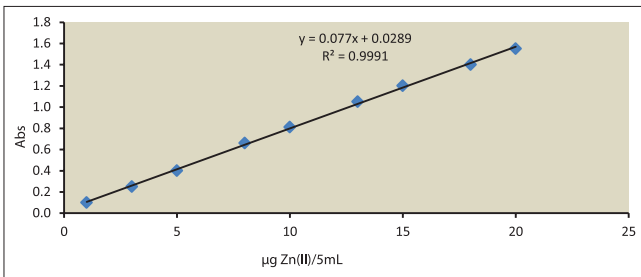

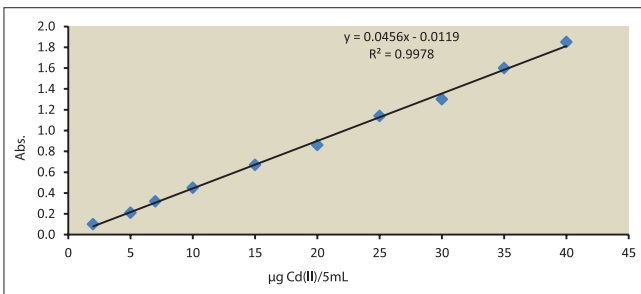**Fig. 1: Calibration curve for determination Zn^{2+} in aqueous solution**

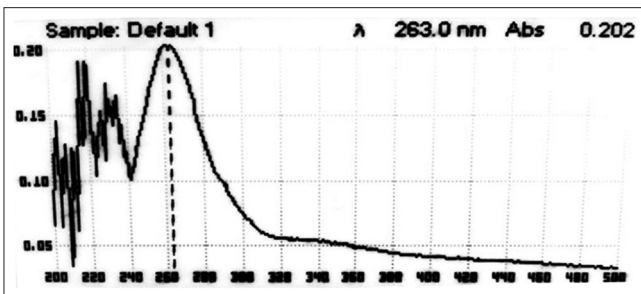**Fig. 2: Calibration curve for determination Cd^{2+} in aqueous solution**

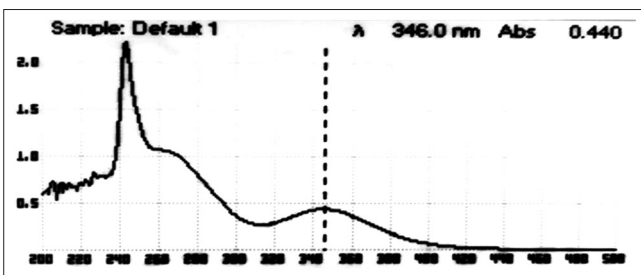**Fig. 3: Ultraviolet-visible spectrum for extracted species of Zn^{2+}**

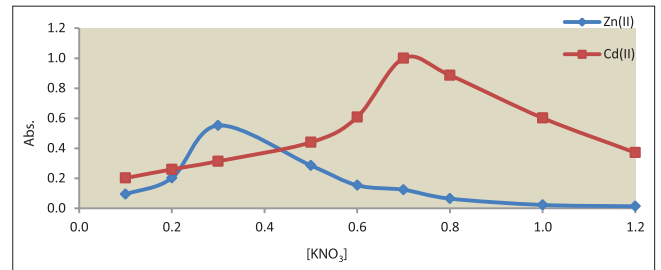**Fig. 4: Ultraviolet-visible spectrum for extracted species of Cd^{2+}**

Fig. 5: KNO_3 concentration effect on formation and stability of extracted species for Zn^{2+} or Cd^{2+}
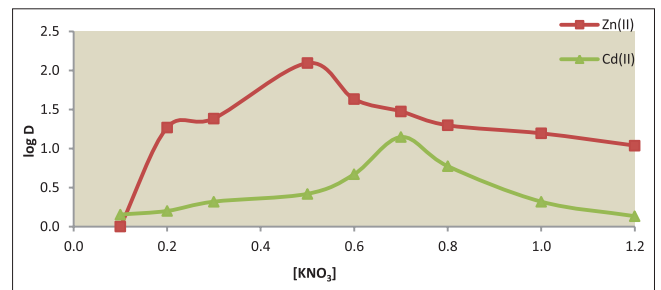

Fig. 6: Salting out concentration effect on extraction efficiency for Zn^{2+} or Cd^{2+}
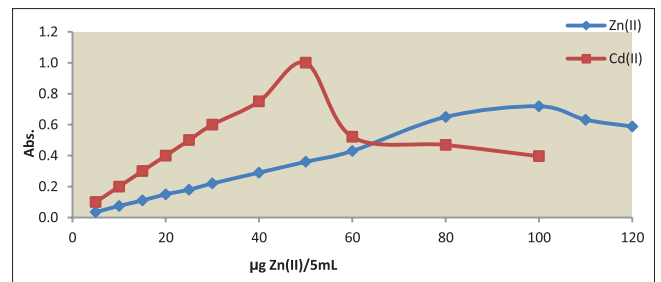

Fig. 7: Metal ion concentration effect on formation and stability of extracted species
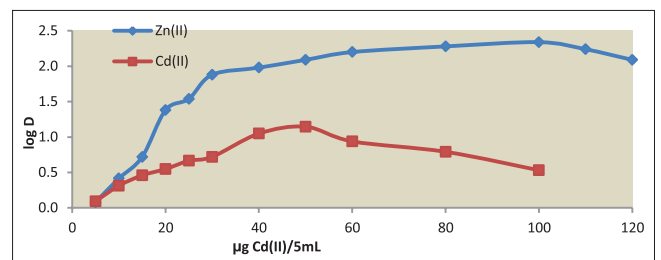

Fig. 8: Effect of metal ion concentration on extraction efficiency and D values

extracted species for thermodynamic equilibrium, any concentration less than optimum not permit to reached the suitable rate of formation giving decrease in concentration of extracted species so that absorbance and D values, as well as any metal ion concentration more than optimum value effect to decline extraction efficiency and decrease absorbance and D values also by effect of mass action law and increase backward direction of thermodynamic equilibrium by increase rate of dissociation.
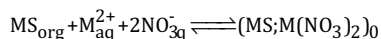
Shaking time effect
Extracted metal elements under study according to the procedure detailed in general method at the optimum condition with different shaking time. The results were as in Figs. 9 and 10.

The results show optimum shaking time was 15 minutes for both extraction Zn^{2+} and Cd^{2+} in view of the fact that solvation is un application of solvent extraction, and indirect method depend on thermodynamic and kinetic laws whereas shaking time mean kinetic energy and 15 minutes as the optimum value of shaking time supply suitable kinetic energy for formation extracted species MS; $Zn(NO_3)_2$ and MS; $Cd(NO_3)_2$, any shaking time <15 minutes not provide the necessary kinetic energy for formation extracted species. So that shaking time more than 15 minutes provide excess kinetic energy effect to increase the rate of backward direction of equilibrium and increase dissociation and decrease in extraction species.
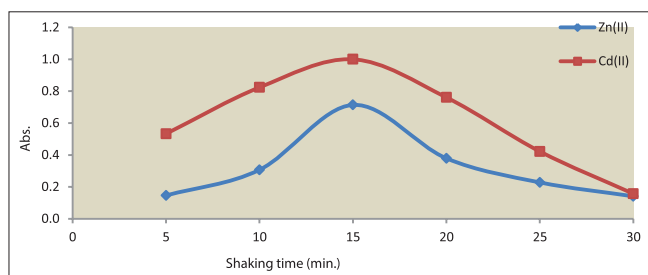
Variation MS concentration
According to the procedure detailed in general method at optimum conditions extracted Zn^{2+} and Cd^{2+} by the use of different concentration MS dissolved in chloroform, the results were as in Figs. 11 and 12.
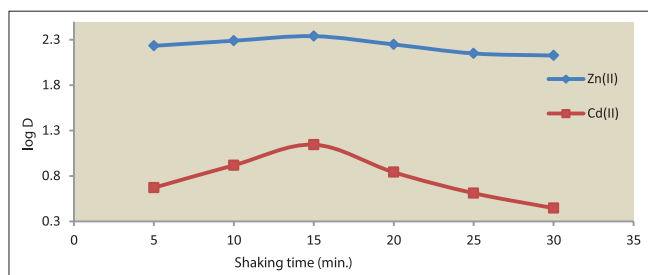
The results show there is as straight line relation between absorbance and MS concentration as well as log D and MS concentration this relation prove the thermodynamic equilibrium for formation extracted species and according to thermodynamic concept the formation of extracted species increase with extractant increase such as the equilibrium below:

$$MS_{org} + M^{2+}_{aq} + 2NO^-_{3q} \rightleftharpoons (MS;M(NO_3)_2)_0$$

After formation $M(NO_3)_2$ in aqueous phase started the transfer to organic phase after binding MS coordinately with metal cation of $M(NO_3)_2$ and from the relation increasing MS concentration meaning increasing the chance of binding and transfer to the organic phase.

Effect of kind salting out
According to general method extracted Zn^{2+} and Cd^{2+} at optimum conditions in presence different salting out at a range of concentration, the results were as in Figs. 13 and 14.

The results show there are different effects on extraction efficiency and the rate of extracted species formation according to behavior of salting out in aqueous solution in addition to kind metal cation presence to attainment suitable thermodynamic environment to giving the adequate rate of the forward direction of thermodynamic equilibrium for formation extracted species.
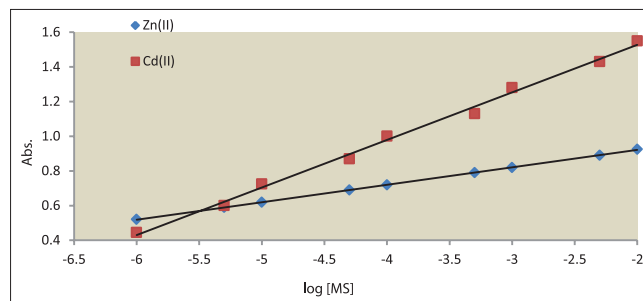
Variation extractants
Extracted metal cations understudies according to general method at optimum conditions by used of different organic reagent as extractant, the results were as in Table 1.
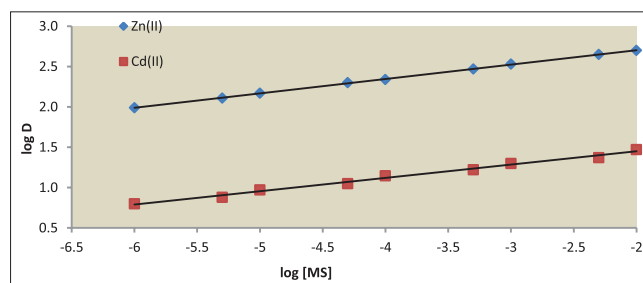
The results show there is different extractions efficiency with differ extractant, according to behavior of extractant binding with the metal cation in the extracted species in addition to each one of the extractant need special optimum conditions.

Electrolyte effect
Extracted Zn^{2+} and Cd^{2+} according to solvation method at optimum conditions in presence different electrolyte salts, the results were as in Table 2.

Fig. 11: Absorbance = F [methyl stearate]

Fig. 12: D = F [methyl stearate]

Fig. 9: Effect of shaking time on extracted species formation and stability

Fig. 10: Effect of shaking time on extraction efficiency and D values

Table 1: Variation extractant effect

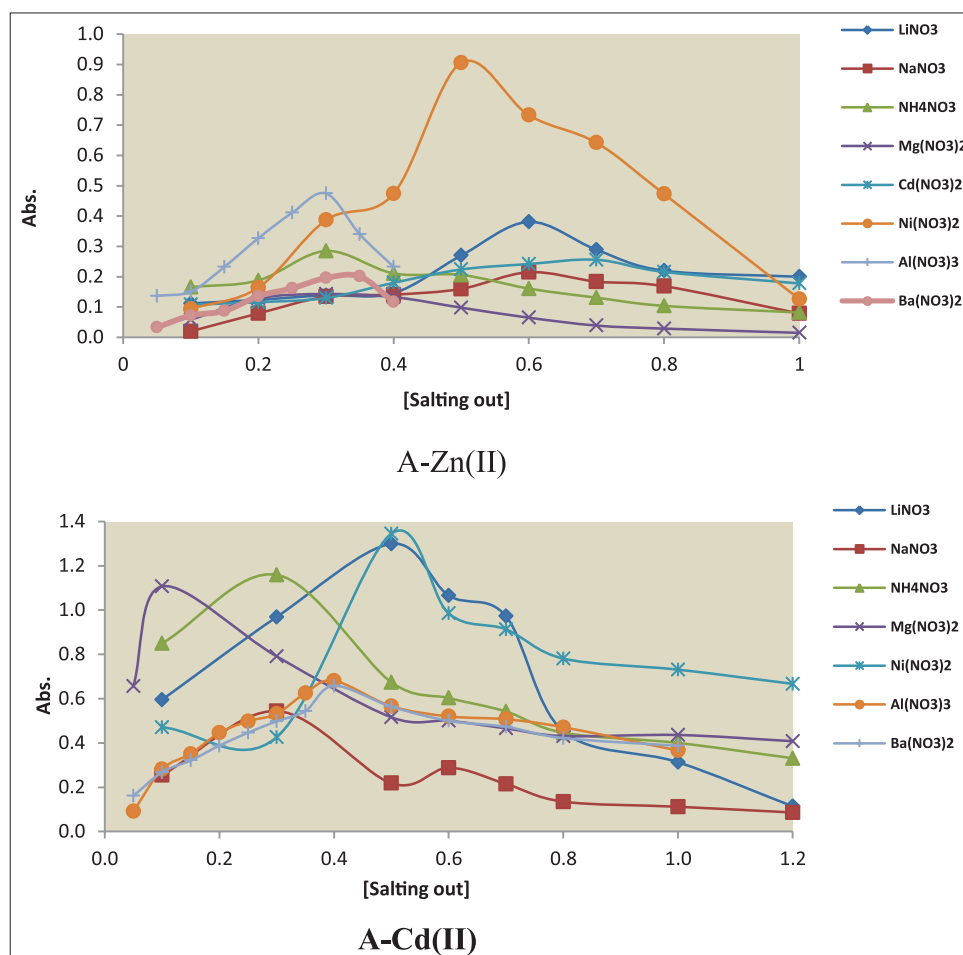| Extractant	Zn^{2+}			Cd^{2+}		
	λ_{max}	Absorbance	D	λ_{max}	Absorbance	D
2.4-DMP	349	0.629	5.94	243	0.141	63.75
Butanom	370	0.979	9.00	346	0.311	122.75
MIBK	339	0.849	7.33	280	0.204	85.42
Acetophenone	316	0.655	6.35	245	0.132	51.34
Methyl stearate	346	1.000	14.00	263	0.719	216.39

Fig. 13: Effect of different salting out on extracted species formation and stability for Zn(II) and Cd(II)

The results show the presence electrolyte in aqueous solution overshadowed enhancement in extraction efficiency, this effect connect with the ionic radius of metal cation in electrolyte salts which is effect to making dehydration for the metal cation under study to increase the rate of formation and stability for extracted species as well as strongly attainment of extractant with metal cation.

Interferences effect

About 5 mL aqueous solution contains optimum quantity of Zn^{2+} or Cd^{2+} at optimum conditions in presence 0.1 M interferences, afterward replenishment extraction according to general method, the results were as in Table 3.

The results appear that there are clearly interferences for Co^{2+}, Ni^{2+}, Fe^{3+}, Hg^{2+} which are effected to decline extraction efficiency for Zn^{2+} and Cd^{2+} and minimization absorbance and D values, and these results reflect these ions able to formatted extracted species with extractant MS but in different ability returned to behavior of these interferences ions in aqueous solution at optimum conditions of extraction Zn^{2+} and Cd^{2+}.

Effect of methanol

Extracted Zn^{2+} and Cd^{2+} according to general method from 5 mL aqueous solution in presence different percentages of methanol. The results were as in Figs. 15 and 16.

The results show 40% and 50% was the optimum percentage of CH_3OH giving highest absorbance and D values for Zn^{2+} and Cd^{2+}, respectively, as

Table 2: Electrolyte effect

Electrolytes	Zn^{2+}		Cd^{2+}	
	Absorbance 263 nm	D	Absorbance 346 nm	D
LiCl	1.099	554.56	1.342	32.33
NaCl	0.965	499	1.285	21.22
KCl	0.872	356.14	1.205	17.87
NH_4Cl	0.833	276.78	1.144	13.49
$MgCl_2$	0.667	249.00	1.291	22.81
$CaCl_2$	0.581	226.27	1.178	16.54
$BaCl_2$	0.677	293.11	1.331	19.00
$AlCl_3$	0.577	255.41	1.144	13.93

Table 3: Interferences effect

Interferences	Zn^{2+}		Cd^{2+}	
	Absorbance 263 nm	D	Absorbance 346 nm	D
$CoCl_2$	0.230	75.96	0.533	9.89
$NiCl_2$	0.277	98.61	0.487	8.52
$FeCl_3$	0.102	43.11	0.642	10.93
$HgCl_2$	0.442	151.44	0.423	7.11

well as the presence of methanol in aqueous solution effect to decrease polarity of water and effect to destroyed hydration shell of metal cation and increase formation of extracted species and absorbance and D values.
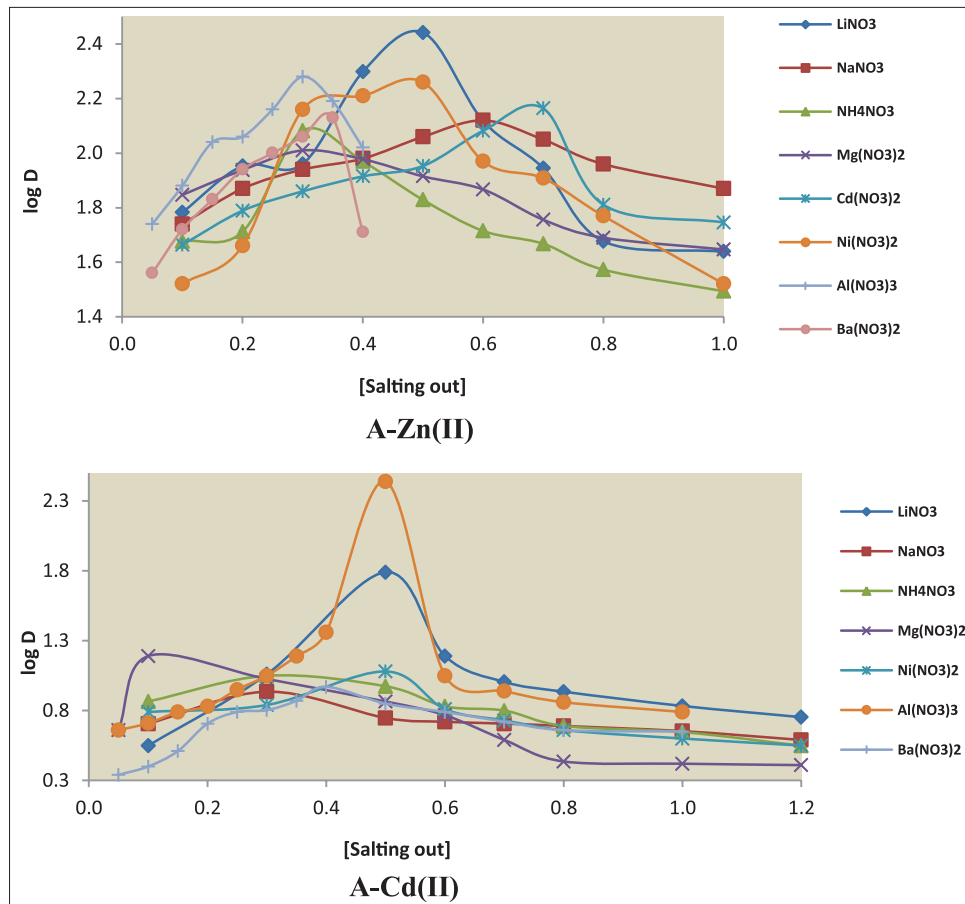
Fig. 14: Effect of salting out on extraction efficiency and D values for Zn(II) and Cd(II)
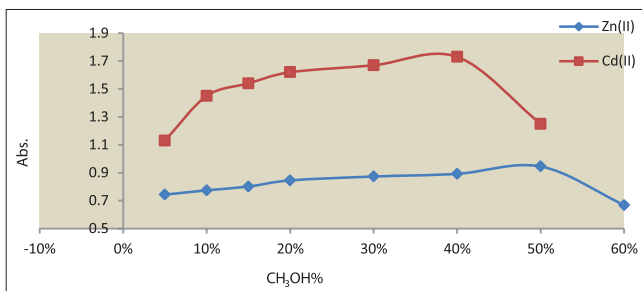

Fig. 15: Percentage of methanol effect on the rate of formation extracted species
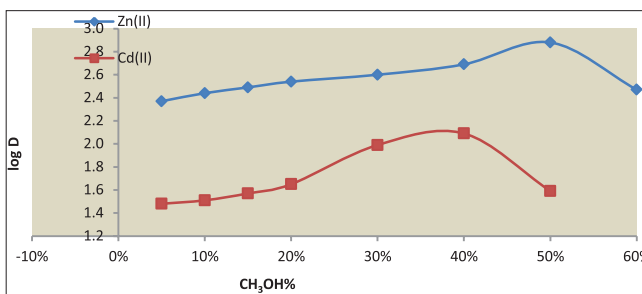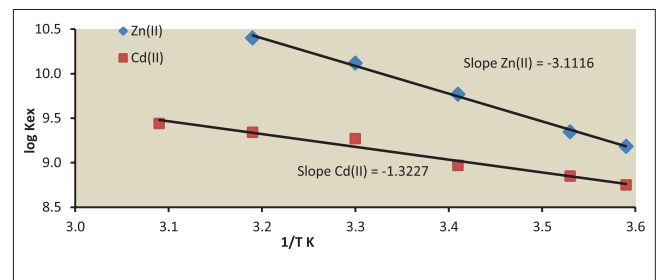

Fig. 16: D= F[CH₃OH]

Fig. 17: K_{ex}=F(T K)

temperature. After that calculated extraction constant Kex according to the relation below:

$$K_{ex} = \frac{D}{[MS][M^{n+}]} M^{n+} = Zn^{2+}, Cd^{2+}$$

Afterward plot Kex against 1/T K, the results were as in Fig. 17.

From the slope of linear relation above and thermodynamic equation calculated thermodynamic data and demonstrated as below:

Metal cation	ΔH_{ex} (kJ/mol)	ΔG_{ex} (kJ/mol)	ΔS_{ex} (J/mol¹/K)
Zn^{2+}	0.0595	−62.32	198.92
Cd^{2+}	0.0253	−58.69	180.66

Temperature effect

Extracted the metal cations under study according to general method at different temperature and calculated D-value of extraction at each

The results show the extraction of both ions was endothermic behavior and giving increasing in extraction efficiency with temperature

<div style="text-align:center">**Table 4: Organic solvent effect**</div>

| Organic solvents	ϵ_r	D	
		Zn²⁺	Cd²⁺
Nitrobenzene	35.74	165.67	3.90
Amyl alcohol	15.8	311.50	3.31
50% nitrobenzene+5%toluene	15.6	70.428	3.63
1,2-dichloro ethane	10.65	62.69	6.81
30% nitrobenzene+70% toluene	10.65	118.05	4.32
Dichloromethans	9.08	37.02	3.39
Bromo benzene	5.40	199.00	5.25
Chloroform	4.806	216.39	14.00
5% nitrobenzene+95% toluene	3.40	38.37	6.14
Benzene	2.804	26.03	6.25
Toluene	2.438	34.71	4.88
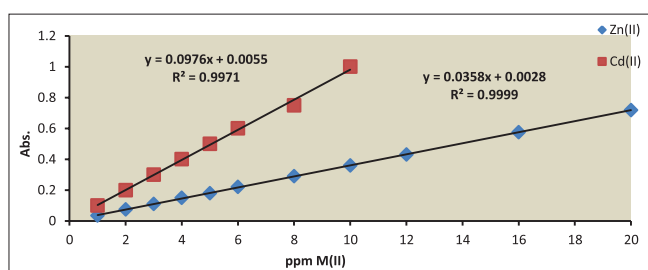
Fig. 18: Calibration curve for spectrophotometric determination of Zn(II) and Cd(II)

increasing to 50°C as well as the lower value of ΔH_{ex} reflect the high nearly ions of ion pair complex each one to other to form more stable contact ion pair or loose ion pair so that high positive value of ΔS_{ex} reflect the mechanism of thermodynamic extraction depend on intropy that is mean this method is intropic in region.

Organic solvent effect
According to the general method at optimum condition extracted metal cations understudies by use of different organic solvent differ in dielectric constant as a solvent for dissolved organic reagent MS. The results were as in Table 4.

The results in Table 4 demonstrated that there is not any linear relation between dielectric constant of organic solvents used and D values

that is mean there is not any effect for polarity of organic solvents on the extraction according to solvation method, but the results appear there is an effect for the structure of the organic solvent on extraction efficiency giving higher distribution ratio (D) with amyl alcohol which is have dielectric constant equal to (15.8) and the second organic solvent was chloroform which is have dielectric constant equal to (4.806) at extraction Zn²⁺. But with extraction Cd²⁺ illustrated chloroform giving higher distribution ratio then 1,2-dichloroethane and benzene.

Spectrophotometric determination
For determination of metal under study in different samples according to this solvation method prepared calibration curve such as in Fig. 18.

CONCLUSION

Separation method carried out on different metal ions as nitrate salt and by using different extracts such as ketones or esters or separation metal ions as chloride salt if the metal not form chloroanion complexes. Finally could be used different theories of extraction and separation such as solvent extraction, liquid ion exchange, onium which giving high efficiency and high sensitivity too.

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