DETERMINATION OF NICKEL (II) BY USING ANEW SYNTHESIZED

LIGAND VIA CLOUD POINT EXTRACTION METHODOLOGY

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ABSTRACT

Sensitive cloud point extraction methodology used for extraction Nickel(II) as complex with new laboratory synthesized complexing agent 4-[antybyrenzolylazo]-1,2-dihydroxy-9,10-anthracene dione (AADAD) optimum conditions study show $pH_{ex}=9$ by use 1×10^{-4}M (AADAD)and 0.5ml of 1% TritonX-100 and heating at 80°C for 15 min. as well as this research involved stoichiometry and thermodynamic study and other parameters effect on extraction efficiency as well applications about determination Ni^{2+} spectrophotometricaly, with detection limit(D.L) $=(1.6\times10^{-5}\mu g.mL^{-1})$ and Sandell's sensitivity $(1.124\times10^{-8}\mu g.cm^{-2})$ and $\varepsilon =(5221L.mol^{-1}.cm^{-1}$)and RSD% $=(0.00628)$.

KEYWORDS: Nickel (II), Cloud Point Layer, Tritonx-100

INTRODUCTION

Nickel has a significance in industry and biological science and it is present in different quantities in plants, animals and soils. as well as the main source of nickel in nature was from iron factories combustion of coal and fuels, tobacco smoke and hydrogenation of soils, so that nickel is non toxies element and not cause any series human health hazard[1], in recent years is grown the procedures of nickel determination by using pyridoxal-3-thiosemicarbazone for spectrophotometric determination of nickel(II) in different samples the research show the wave length for complex absorption was 430nm and molar absorptivity1.6×10^{-4}l.mol^{-1}.cm^{-1}and sandell's sensitivity 3.6×10^{-3}mg/cm$^{2[2]}$.by complexation of nickel with dimethyl glyoxime performance the determination of nickel(II) in water samples via cloud point extraction methodology. By use non-ionic surfactant Tritonx-114 the experiment show detection limit of 4 ng.mol$^{-1[3]}$, Used solid phase extraction for determination of copper, nickel and cobalt in water and food samples, using multiwalled nanotubes (MW)modified by methyl (2-pyridyl) ketone oxim(MPKO, as new complexing agent). With ditection limit 0.18 µgl^{-1}for copper, 0.28 µgl^{-1}for nickel and 0.47 µgl^{-1}for cobalt[4].For determination of lead cadmium and palladium used 3-(1-(1H-indol-3-yl)-3-phenylallyl)-1H-indol at pH=8 in presence Tritonx-114 via cloud point methodology the detection limit was between of 1.6-2.6 µg.L$^{-1[5]}$.According to cloud point extraction methodology by using an anionicsurfactant sodium dodecyl sulfate (SDS) for preconcentration and spectrophotometric determination of Pb(II) and Cu(II) as well as complexing agent used was N_1,N_2diphenyl hydrazine-1,2-dicarbothioamide this procedure giving detection limit 2 ng.ml^{-1}for Pb(II) and 3ngml^{-1}for Cu(II)[6]Using two acidic extracted bis(2-diethylhexyl) phosphoric acid and 2-thenoyltri-fluoroacetone for extracted Cd(II),Co(II) and Ni(II), the experiments show pH extraction for Cd(II) and Co(II) was 5.13 but for Ni(II) was 3.82 the research involve effect of organic diluent and synergistic effect and others[7]. New synthesized thiazolylazo reagent used for determination mercury via cloud point extraction. Method by used non-ionic surfactant Tritonx-114 with detection limit 7.4 ngml$^{-1[8]}$Cloud point extraction methodology used for

preconcentration of nickel, coupled with electrothermal atomization method for determination by used non- ionic surfactant TritonX-100 and 8-hydroxy quinoline as complexing agent as well studied all effective parameters on extraction efficiency such as pH, surfactant concentration, ligand concentration and under optimum conditions D.L. was 12ng.ml^{-1} with relative standard deviation R.S.D 2.9%, the method used successfully to determination nickel(II) in different samples [9]For separation and preconcentration Ni(II) used cloud point extraction methodology complete with GFAAS for determination nickel(II),FAAS, or UV-Vis spectrophotometry, used Di-2-pyridyl ketone salcyloylhydrazone as complexing agent, and Tritonx-114 as surfactant for extraction. With D.L 1.5 µgL^{-1}[10]. Determination trace amounts of nickel by UV-Vis spectrophotometry in some environmental samples of cloud point extraction. By use TritonX-100 an SALEN as reagent the optimum condition for CPE studied such as pH, TritonX-100 concentration, temperature, time of heating, proposed method giving detection limit 0.535µgl^{-1}and RSD=0.22%[11].In order to determination trace amounts of cobalt by FAAS, used cloud point extraction methodology for separation and preconcentration cobalt(II) by using complexing agent 2-[(2-mercaptophenylimino)methyl]phenol, and Tritonx-114 as surfactant, studied all optimum conditions for extraction efficiency, proposed method giving detection limit 0.21µgL^{-1}, RSD=1.2% [12].

EXPERIMENTAL

Instrument

For spectrophotometric studies used double-beam spectrophotometer: Biochrome(80-7000-11) Libra s60 cambridge CB4 0FJ (England).

But for absorption measurements used single beam: optima, model: sp-300, serial No: 322951, Japan. And for the pH measurement used pH meter (HANNA Germany) as well as used shaker: Triup international copper. LOT: 03320203, Ret: 03-7326T-09(Italy). And electrostatic water bath (WNB7-45) (England).FTIR-spectrophotometer was FTIR 8400S, Shimadzu corporation, serial No. A21274501282LP, (Japan).

Materials and Solutions

All chemical used as received without of more purification stock solution of Ni^{2+}prepared from Ni(NO$_3$)$_2$ (in coming BDH 98%) by dissolved 0.311 gm in 100ml distilled water contain 0.5 concentrated HNO$_3$ in volumetric flask, but other working solutions prepared by dilution with distilled water Dimethyl glyoxime (Flukain coming 99%) solution of 1% prepared by dissolved 1gm in 100ml ethanol as well as potassium per sulphate (Merck 98%) Its solution4% prepared by dissolved 4gm in 100 ml distilled water in volumetric flask.

Synthesis New Organic Reagent

According to general procedure synthesized new azo derivative as complexing agent to the Ni^{2+} 4-(antybyrenzolylazo)-1, 2-dihydroxy-9, 10-anthracene dione (AADAD) according to the mechanism below:
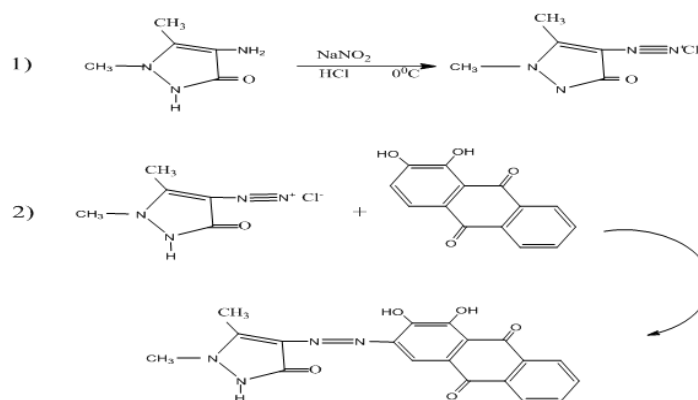
Figure 1: Synthesis of Ligand

General Method

10ml aqueous solution contain fixed quantity of Ni^{2+} at optimum pH and 1×10^{-4} M of(AADAD) in presence 0.5ml of 1% TritonX-100 heated this solutions in electric water bath for limited temperature to produce cloud point layer with high density and small volume after heating to suitable time, then separate cloud point layer (CPL) from aqueous solution and dissolved (CPL) in 5 ml ethanol and measure its absorbance at λ_{max} of complex extracted to (CPL) against blank prepared at the same manner without Ni^{2+} ion, but the aqueous solution treated according to dimethyl glyoxime spectrophotometric method[13]and return to calibration curve Figure 1 to determine remainder quantity of Ni^{2+}in aqueous solution and subtraction the remainder quantity of $Ni^{2+}$from the origin quantity to determine transferred quantity as complex into (CPL) then divided transferred quantity on remainder quantity to calculate distribution ratio (D).

RESULTS AND DISCUSSIONS

Spectrophotometric Studies

UV-VIS spectrum and IR spectrum for new synthesized organic reagent was as in figures 2, 3 below:
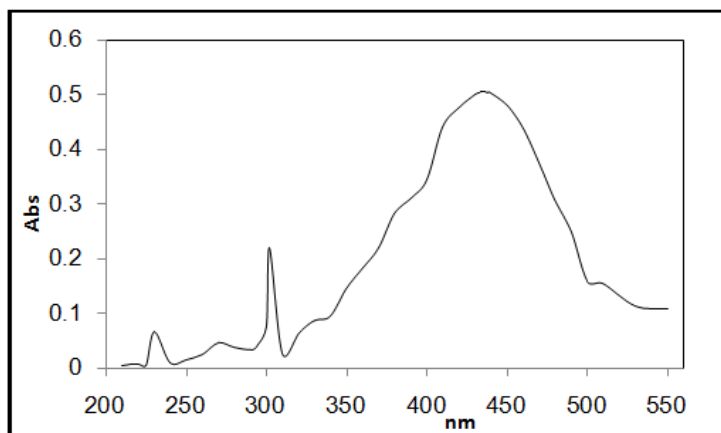

Figure 2: UV-VIS Spectrum for Organic Reagent

The UV-VIS spectra for the synthesized organic reagent AADAD show three significant absorption peaks, the first appear at λ=230nm due to π-π* in benzene ring [13],and the second peak at λ=302nm due to π-π* transition in aromatic

rings [14], as well as there is high absorption peak appear at $\lambda=430$nm belong to intra molecular charge transfer n-π^* for the –N=N- bridge azo[15].
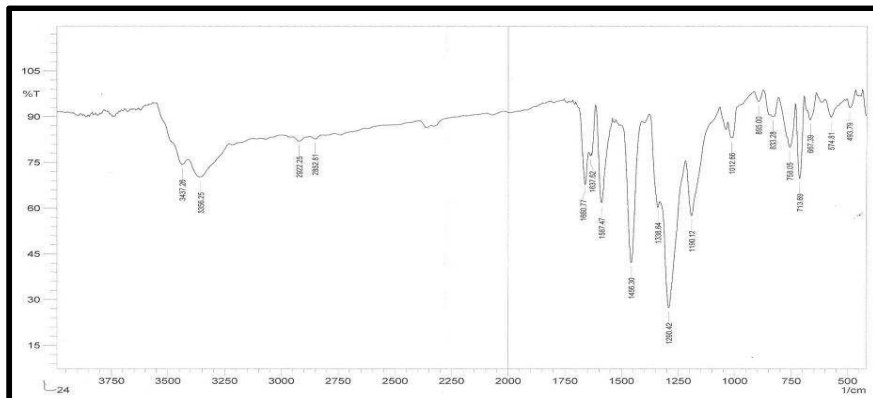
IR Spectrum Show

Figure 3: FTIR Spectrum for Organic Reagent

FTIR spectra appear absorption band in 3437 cm^{-1}due to O-H and at 3356cm^{-1}for stretching vibration of N-H, absorption band at 1660cm^{-1} due to stretching vibration for C=O, The absorption band at 1587cm^{-1} due to C-N stretching vibration, and –N=N- appear stretching vibration absorption band at 1456cm^{-1}, at 1290cm^{-1} appear absorption band for isolated stretching vibration for O-H.

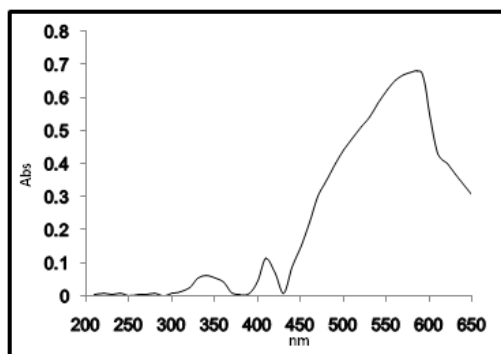But UV-Vis of complex (AADAD) with $Ni^{2+}$was as in Figure 4:

Figure 4: UV-VIS Absorption Spectrum for Ion-Pair Complex Extracted

The absorption UV-VIS spectrum show maximum absorbance at wave length 585nm.

Effect of pH

Several aqueous solution 10 ml in volume each one contain 50 µg Ni^{2+}at different pH values and contained 1×10^{-4}M (AADAD) and 0.5 ml of 1% TritonX-100 heated these solutions in electrostatic water bath for suitable temperature and time untilproduce cloud point layer with higher density and smaller volume then separated CPL from aqueous solutions and dissolved CPL in 5 ml ethanol and measure its absorbance atλ_{max}=585nm against blank prepared at the same manner without Ni^{2+} ion, so aqueous solution treated according to DMG spectrophotometric method and calculate distribution ratio at each pH as detailed in general method. the result was as in Figures (5,6):
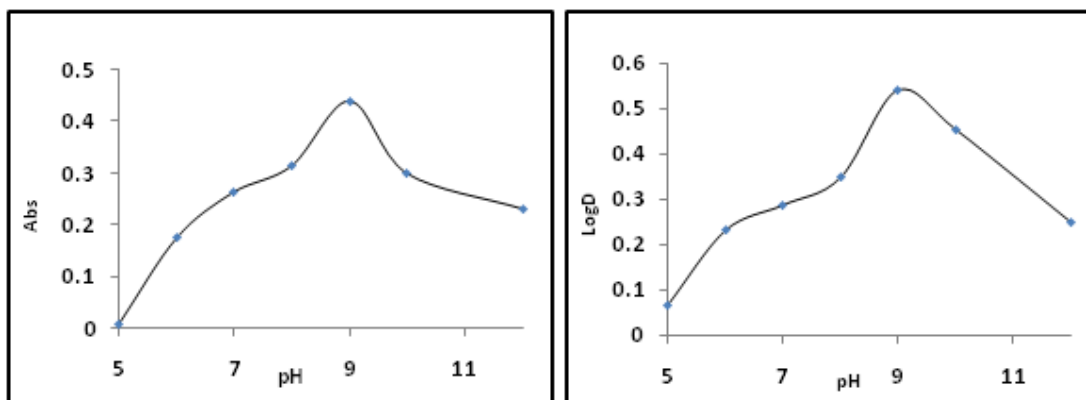
Figure 5: Effect of pH on Complex Formation and Extraction   Figure 6: D = F(pH)

The results show enhancement in extraction efficiency with rising in pH to optimum value of pH=9 giving higher absorbance and D-value any pH value less optimum effect to decline extraction efficiency by protonated coordination position on organic complexing agent (AADAD) and minimizing the complexation chance in solutions as well as any pH value more than optimum value effect to decrease extraction efficiency also by formation stable compound of nickel(II) as well as participation of hydroxyl ion in formation ion pair association complex which is partitioning to the aqueous phase and dissociation.

Effect of Ni^{2+} Concentration

Extracted $Ni^{2+}$from 10ml aqueous solutions contain different quantity of Ni^{2+}ion at optimum pH according to procedure detailed in general method.The results was as in Figures 7, 8.
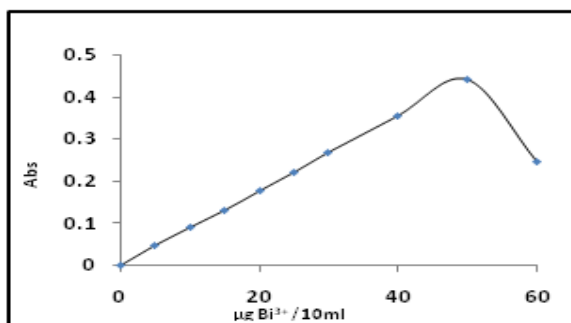

Figure 7: Complex Formation and Extraction as Function of Metal Ion Concentration
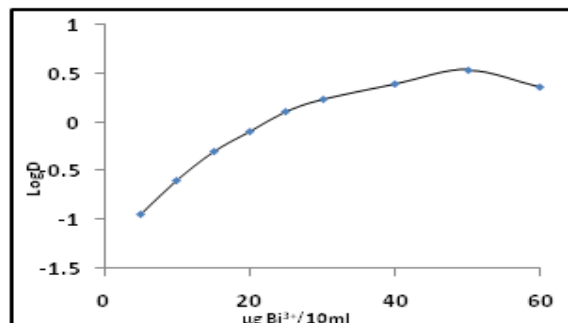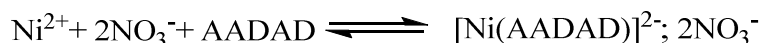
Figure 8: Extraction Efficiency and D-Value Change as Function of Metal Ion Concentration

The result demonstrate metal ion concentration play as thermodynamic parameter for complex formation as in equilibrium below:

$$Ni^{2+} + 2NO_3^- + AADAD \rightleftharpoons [Ni(AADAD)]^{2-}; 2NO_3^-$$

With optimum value 50µg/10ml giving favourable thermodynamic equilibrium to produced higher concentration of complex extracted. Any concentration less optimum not enough to reach equilibrium as well as concentration more than optimum effect to increase rate backward reaction and dissociation according to Lech atelier principle and mass action law.

Effect of AADAD Concentration

Extracted 50µg $Ni^{2+}$from 10ml aqueous solution of pH=9 and in presence different concentrations of AADAD and 0.5ml of 1% TritonX-100, after heated these solutions at fixed temperature and time until formation CPL and separated CPL from aqueous solutions so determined absorbance of ethanolic CPL solution at 585nm and calculated distribution ratio (D).The results were as in Figures 9, 10.
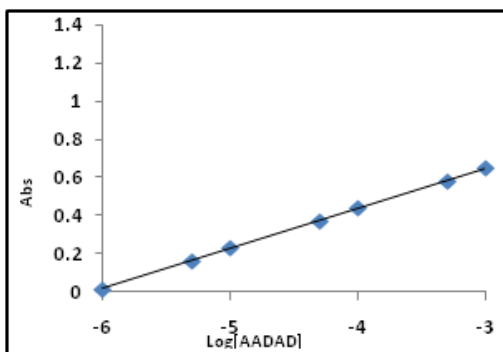

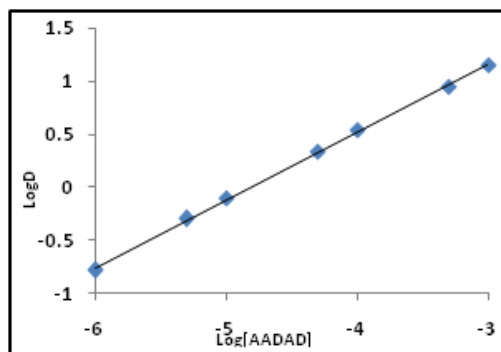**Figure 9: Effect of Complexing Agent Concentration on Complex Formation**   **Figure 10: Effect of Complexing Agent Concentration on Extraction Efficiency**

The results demonstrated there is alinear relation between complex formation and extraction efficiency and appear there is an extraction for Ni^{2+}very sensitive and effective.

Effect of TritonX-100Concentration

50µg of Ni^{2+}in 10ml aqueous solution at pH=9 extracted by CPE method in presence 1×10^{-4} M AADAD and different volume of 1% TritonX-100 heated these solutions to suitable temperature and time to formation cloud point layer with higher density and smaller volume afterward dissolved CPL in 5ml ethanol and determined its absorbance at λ_{max}=585nm against blank prepared at the same manner as well as aqueous solution treated according to DMG spectrophotometric method as detailed in general method and calculated D-values. the results were as in Figures (11,12).
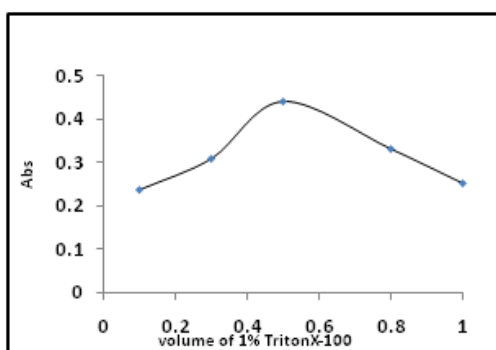

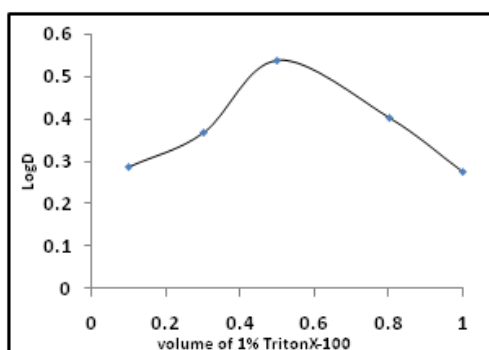**Figure 11: Effect of Tritonx-100 Concentration on Complex Extraction**   **Figure 12: Effect of Tritonx-100 Concentration on Partition Complex to CPL**

The results show increasing in extraction efficiency by increase TritonX-100 concentration and this relation reached to optimum value at to 0.5ml of 1% TritonX-100 this result reflect very important side in cloud point extraction methodology, this side is the new layer of TritonX-100 formed at suitable heating and time which is enough to good

extraction and partition the complex from aqueous phase to micelles layer phase. And this study 0.5ml from 1% TritonX-100 giving higher absorbance and higher D-value that is main this volume is very suitable for good extraction to the extraction of complex of Ni^{2+}.

Temperature Effect

Extracted 50µg of Ni^{2+} in 10 ml aqueous solution at pH=9 in presence 1×10^{-4}M AADAD and 0.5ml from 1% TritonX-100 heated these solutions of different temperature for 15 min then determine the absorbance of ethanolic CPL solution after separation at 585nm against blank prepared at the same manner as well treated aqueous phase according to DMG spectrophotometric method as detailed in general method and calculated D-value at each temperature the results were as in Figures (13, 14).
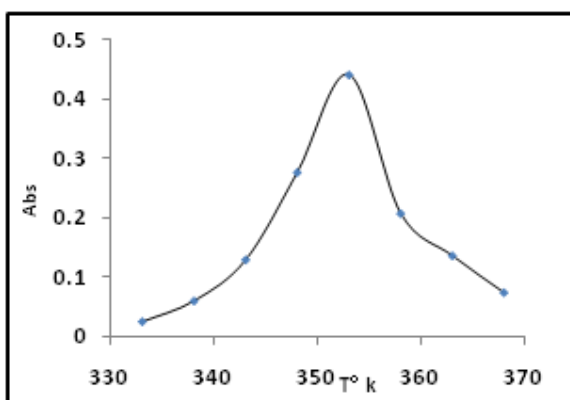

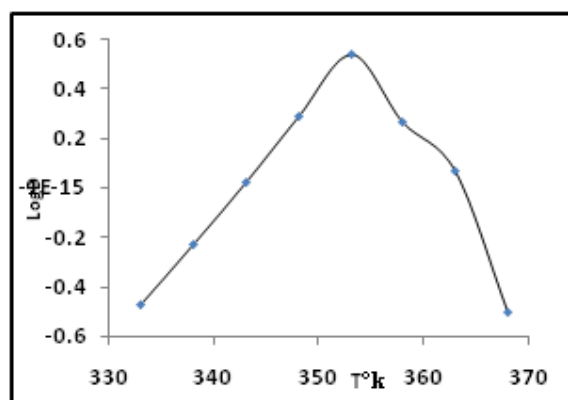**Figure 13: Temperature effect on formation CPL and extraction**

Figure 14: Effect of Temperature on Extraction Efficiency and D-Value

Afterward calculated extraction constant (k_{ex}) by application the relation below:

$$K_{ex}=\frac{D}{[Ni^{2+}]aq[AADAD]org}$$

After determine (K_{ex}) at each temperature plotted Log K_{ex} against 1/Tk. the results as in Figure 15:
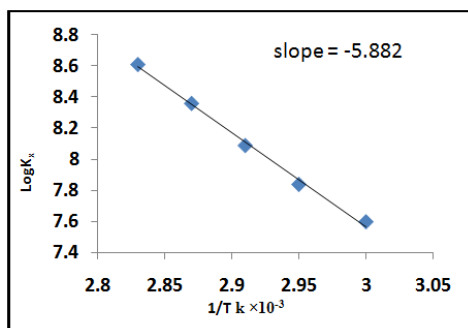

Figure 15: The Relation between k_{ex} and Temperature in Kelvin

From the slope of straight line in Figure 15 determined in enthalpy of extraction by application the relation below:

$$Slope = \frac{-\Delta H}{2.303R}$$

And free energy of extraction by relation below:

$$\Delta Gex = -RT \, LnKex$$

As well as entropy of extraction calculated by relation:

$$\Delta Gex = \Delta Hex - T\Delta Sex$$

The results of thermodynamic data after application the relation above was:

Table 1

$\Delta H_{ex} = 0.1126 \ KJ.mol^{-1}$
$\Delta G_{ex} = -58.19 \ KJ.mol^{-1}$
$\Delta S_{ex} = 165.16 \ J.mol^{-1}.k^{-1}$

The small value of enthalpy of extraction reflect the near each ion together in ion association complex, as well as appear the extraction method was endothermic relation. As well as the large value of entropy demonstrate the extraction method was entropic in region.

Effect of Heating Time

Extraction 50µg of Ni^{2+} from 10ml aqueous solution at pH=9 and in presence 1×10^{-4}M of AADAD and 0.5 ml 1% TritonX-100. Afterward heating the solutions for optimum temperature at different time. At later separated CPL from aqueous solution and dissolved CPL at 5ml ethanol and determined the absorbance at 585nm against blank prepared at the same manner without Ni^{2+} so that aqueous solution treated as DMG method and calculated D-value according to the procedure detail in general method, the results were as in Figures 16,17:
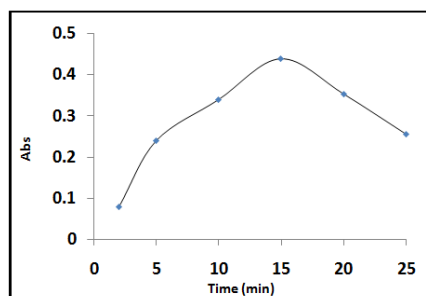

Figure 16: Effect of Heating Time on Complex Formation and Extraction
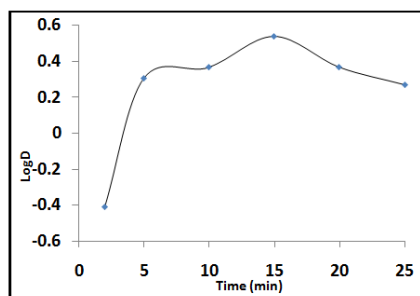
Figure 17: Distribution Ratio (D) Change as a Function of Heating Time

Heating time appear from the results a parameter effective for extraction according to CPE methodology from the results appear optimum heating time was 15 min. giving higher absorbance and D-value. This heating time help to reach favorable thermodynamic equilibria for extraction by formation CPL with smaller volume and higher density as well as help to increase the dehydration from the micelles layer but time less than optimum value not allow to reach thermodynamic equilibria and not reached to the optimum dehydration also time of heating more than optimum effect to increase the quantity of heating in solution. This effect to increase diffusion of micelles in aqueous solution and increase hydration and decrease the density of CPL formed as well as its volume. All this effected cause decrease in extraction efficiency.

Stoichiometry

In order to known the more probable structure of complex extracted to cloud point layer follow four spectrophotometric method which is slope analysis, slope ratio, mole ratio, job method. The results of these methods were as in Figures 18 to 21.
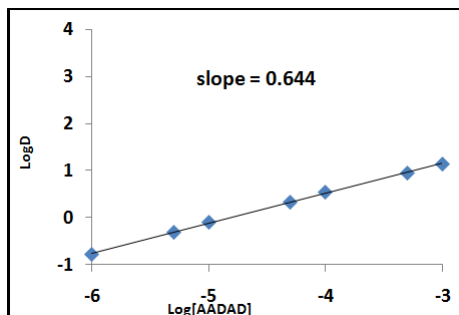

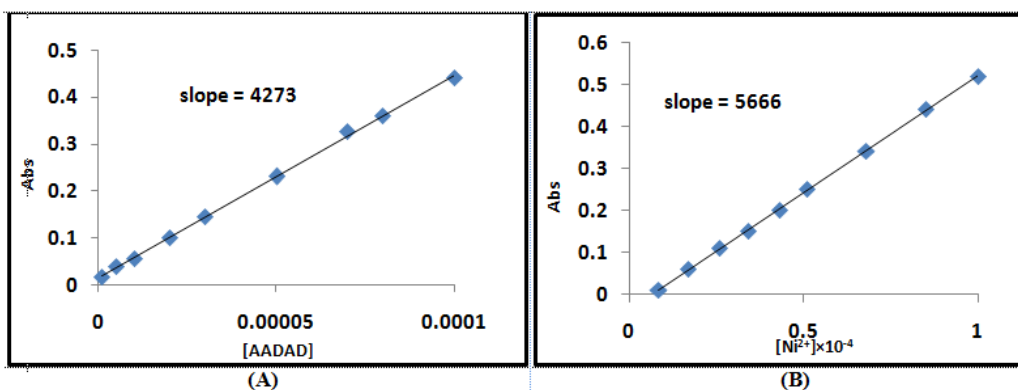**Figure 18: Slope Analysis Spectrophotometric Method**

(A)

(B)

**Figure 19: Slope Ratio Method (A) Extraction at Different Concentration of [AADAD]
(B)Extraction at Different Concentration of Metal Ion**

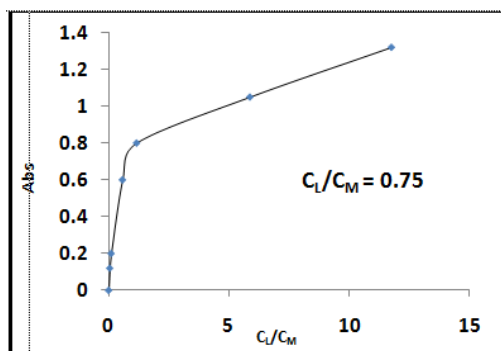Slope ratio $=\dfrac{4273}{5666} = 0.754$

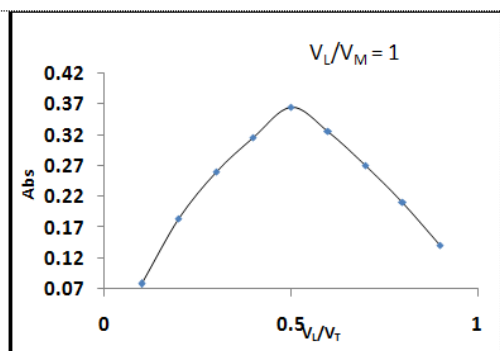**Figure 20: Mole Ratio Method**

Figure 21: Job Method

The results in these spectrophotometric method demonstrate the more probable structure of ion pair complex extracted was (1:1) [metal: ligand] as in figure 22:
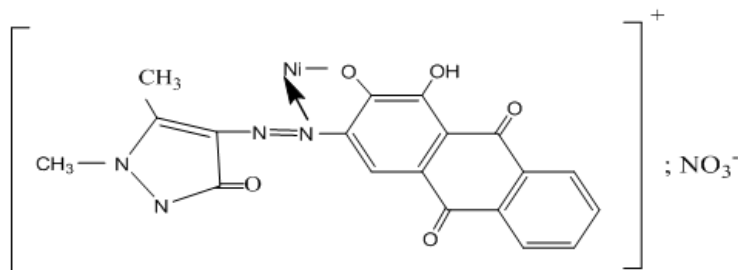
Figure 22: The More Probable Structure of Ion Pair Complex Extracted

Synergism Effect

Extracted 50μg Ni^{2+} in 10ml aqueous solution at pH=9 according to CPE method in presence 1×10^{-4}M (AADAD) and 0.5 ml of 1% TritonX-100 and different concentrations of TBP and MIBK, heating these solutions at 80°C for 15 minutes at the end of heating separated CPL from aqueous solution, and dissolved CPL in 5ml ethanol and determined the absorbance at 585nm against blank prepared at the same manner without Ni^{2+} ion, and aqueous solutions treated according to DMG spectrophotometric method and calculate D-value according to procedure detailed in general method. the result were as in Figures 23, 24:

(A)   (B)

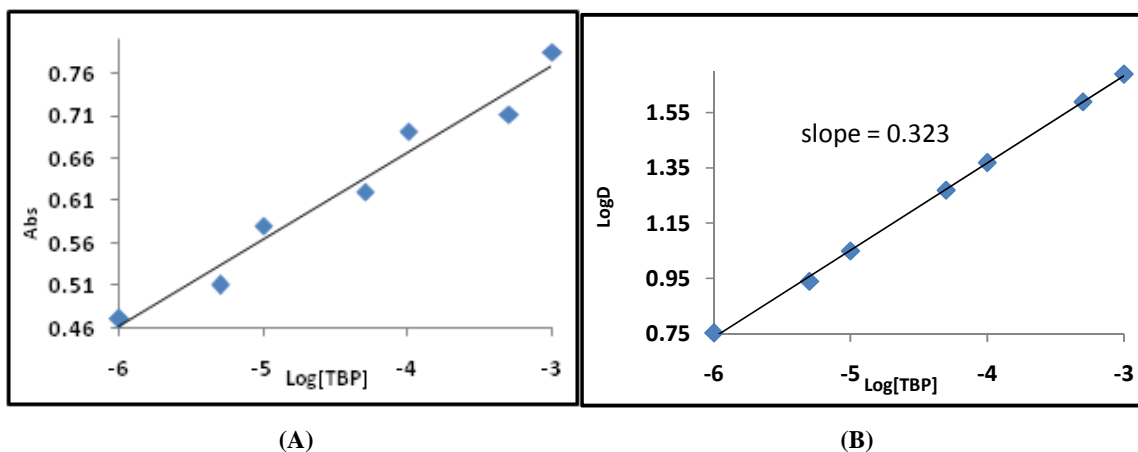**Figure 23: Synergism Effect by TBP**

(A)   (B)
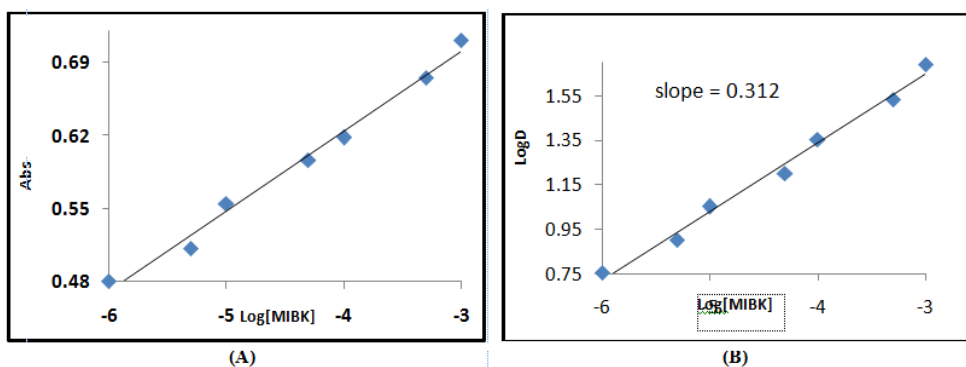
Figure 24: Synergism Effect by MIBK

The results show extraction of Ni^{2+} increasing presence TBP or MIBK in all concentration and emphasize the

organic reagent AADAD by combination with Ni^{2+}ion not saturated all coordination positions in this case water molecules occupied this position and effect to increase partitioning the complex to aqueous solution and decline extraction efficiency but TBP or MIBK able to substitution Water molecules in the coordination shell and increase hydrophobility and easy to transfer the complex to the CPL and increase extraction efficiency as well as the slope of straight line relation demonstrate one molecule of TBP or MIBK participate in the ion pair structure extracted such as $[Ni(AADAD)(TBP)]^+;NO_3^-$ and $[Ni(AADAD)(MIBK)]^+; NO_3^-$

Interferences Effect

Extracted 50µg Ni^{2+}in 10ml aqueous solution at pH=9 at optimum conditions and in presence 0.1M from different metal cations, according to general procedure and determine absorbance and D-values,The result were as in Table 3.

Table 3: Interferences Effect

Cations	CPL Absorbance	D
Hg^{2+}	0.071	1.5
Ag^+	0.058	1.08
Cd^{2+}	0.059	1
Pb^{2+}	0.103	1.173

The results show large interferences of these ion in the extraction of Ni^{2+}, that is mean these metal cations participate Ni^{2+}in complex formation with AADAD, this behavior effect to decrease concentration of complex Ni^{2+}formed and extracted appear as decrease in absorbance and D-values.

Electrolyte Effect

Extracted 50µg Ni^{2+}ion in 10mL aqueous solution at pH=9 according to CPE methodology at optimum condition and as procedure detailed in general method in presence 0.1M of different electrolyte salts, after determine absorbance and D value the results were as in Table 4:

Table 4: Electrolyte Effect

Electrolytes	CPL Absorbance	D
$LiNO_3$	1.083	7.33
$Na NO_3$	0.743	4.55
$K NO_3$	0.689	4.26
$NH_4 NO_3$	0.504	4.00
$Mg(NO_3)_2$	1.059	6.43
$Ca(NO_3)_2$	0.690	4.26
$Al(NO_3)_2$	0.581	4.00

The results show in presence electrolyte in aqueous solution effect to enhancement extraction efficiency because the electrolytes cause to increase dehydration to the micelles aggregation to increase CPL with higher density and smaller volume as well as these electrolyte effect to destroyed the hydration shell of metal cation Ni^{2+} and remove the water molecules nearly to functional group of organic reagent AADAD this behavior effect to increase the chances of interaction between ligand and metal cation and increase it's stability. and the results appear Li^+ giving higher absorbance and D-value because having smallest ion radii and with drawing more of water molecule, it's hydration shell and the effect as the series:

$Li^+>Na^+>K^+>NH_4^+$

$Mg^{2+} > Ca^{2+} > Al^{3+}$
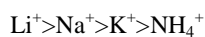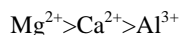
Spectrophotometric Determination

For determination Ni^{2+} spectrophotometricaly in different samples prepared calibration curve by application CPE method at optimum conditions to extraction Ni^{2+} ion from 10ml aqueous solution contain different quantity (ppm) of Ni^{2+} ion, the results were as in Figure 25.
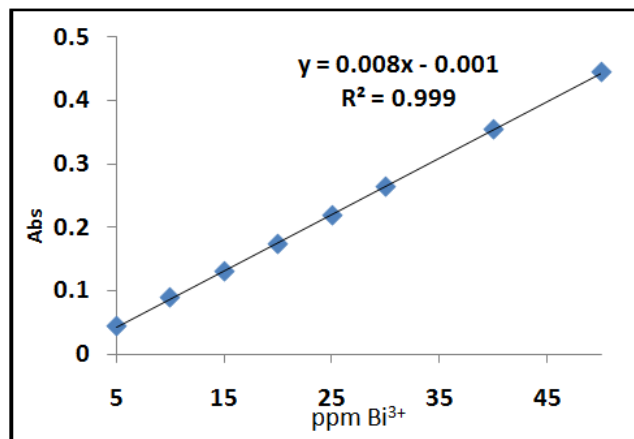

Figure 25: Calibration Curve for Spectrophotometric Determination of Ni^{2+}

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