Extraction of nikel (II) frome aqueous solution by using 2-[α- Naphthyl azo] -4,5-diphenyl imidazol

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Abstract:-

Extraction of nikel (II) from aqueous solution by use new ligand 2-[α-Naphthyl azo] -4,5-diphenyl imidazol (α-NADPI) which is prepared as in study [1] is proposed as a sensitive and selective analytical reagent for the extractive spectrophotometric determination and extraction of Ni^{+2}, this study shows the optimum pH for extraction Ni^{+2} was (pH_{ex}= 9) , also the two layers need(10 minutes) for shaking to reach the novel equilibrium ,as well as the optimum concentration of Ni(II) for high extraction ability was (30 µg Ni^{+2}) (1.022 x 10^{-4} M) ,stoichiometric study shows the more probable structure of ion pair complex extracted was(1:1) (metal: ligand) [Ni (α-NADPI)]$^{+2}$ $(Cl^{-})_2$, so that organic solvent studies shows there is not any linear relation between distribution ratio (D) and dielectric constant (ε) for organic solvents used,at later thermodynamic study shows the reaction between Ni^{+2} ions and ligand(α-NADPI) was endothermic reaction

1. Introduction

Among various instrumental methods of analysis , spectrophotometry is preferred as a versatile technique in exploring the use of (α-NADPI) as an effective reagent for extraction of Ni(II) , at a micro level ,in recent years have shown a growing concern in studying complexes formed by imidazole derivatives , in this regard .Mohamed et al [4] used 2-(2-beenzimidazolyl azo) -4- acetamidophenal to prepare complexes with Fe(II),Co(II),Ni(II) ,Cu(II) ,Zn (II) and Cd (II) and studied this complexes by spectroscopic , magnetic and conductance as well as determine stability constant for these complexes , Ibrahim Erden et al [6] synthesis a new imidazole ligand and studied its complexes with Co (II) , Ni (II) and Cu(II),Luciene et al [8] used4-(2-thiazolylazo)-resorcinol for spectrophoto-

metric determination of Cr (III) , Beniamin et al [3] studied the comparison extraction complexes of Zn (II) and Ni(II) with two derivatives of imidazol ligand ,Ibolya [5] copper (II) , zinc (II) complexes of several imidazole containing ligands and some methylated

derivatives of 1,3,5 – trideoxy-1,3,5,-triamino-cis-inositol ensuring rather rigid pre organized structures have been studied ,Reginalod et al [10] Iron and ruthenium complexes with benzotriazole and benzimidazole derivatives were prepared and characterized in aqueous solution by means of electrochemical and spectroelectro chemical methods . Ruijuan et al [11] synthesized a chiral complex ,salen Zn (II) and characterized . Its coordination with imidazole derivatives and amino acid ester derivatives was studied by UV-Vis spectrophotometric titrations and CD spectroscopy ,Maria Atanassova [9] studied the solvent extraction of trivalent lanthanoids (La, Nd, Eu, Ho, Lu) with mixtures of the chelating extractant and 4-(2-pyridylazo)-resorcin .Alaa [2] used 2-(α-Naphthyl azo) -4,5 diphenyl imidazole as a new ligand for extraction of Cu (II) AND Ag(I) .Zainab [12] studied extraction of Zn (II) ,Cd (II),Hg (II) by used new ligand 2-[(4-chloro-2methoxy phenyl)azo] -4,5-diphenyl imidazole Ibtehaj[7] studied the extraction of Cu(II) and Ag (I) by used new imidazole derivative as ligand 2-[(4-carboxy methyl)azo]-4,5- diphenyl imidazole and 2-[(3- methyl benzen)azo] -4,5-diphenyl imidazole .

2-Experimental:-

2.1. Apparatus :-

For all absorption measurements used schimadzu (UV-100-02 spectrophotometer single beam) and (UV-1700 double beam spectrophotometer) Japan ,and for pH measurements used (HANNA pH –meter) .

2.2. Reagents and preparation of solutions:-

All reagents and solvents were obtained form commercial sources and used as resaved and for preparation of solutions used distilled water ,the ligand (α-NADPI) was synthesized as in the study [1] ,stock solution of Zn (II) in concentration of (1mg/ml) was prepared by dissolved (1mg) of Zn metal in 20 ml (1:1) HCl and after that diluted this solution to 1 liter in volumetric flask ,needful prepared 4% potassium persulphate solution instantaneously for determination Ni^{+2} ions in aqueous solution , so dimethyl glyoxime solution in concentration of 1% dissolved in ethanol , for extraction method prepare ligand solution (α- NADPI) dissolved in chloroform at($1x10^{-2}$ M) solution and other working solution prepared by dilution by organic solvent.

2.3. General procedure :-

For extraction experiments we take (5ml) of aqueous solution contain exact quantity of Ni^{+2} ions at optimum pH_{ex} afterward adding(5ml) of ligand (α- NADPI) dissolved in chloroform at ($1x10^{-4}$ M) concentration ,aftershaking these two layers for optimum shaking time separate aqueous phase from organic phase and determine the remainder quantity of Ni^{+2} ions in aqueous phase by followed the spectrophotometric determination

method (DMG) [13] wich is include added (1ml) of 1% dimethyl glyoxime and (2ml) of 4% potassium persulphate solution and (5ml) of concentration ammonia afterward dilute the solution to (50 ml) with distilled water in volumetric flask after 10 minutes determine the absorbance at wave length λ_{max} =445 nm. By used distilled water as blank . And from absorbance value and calibration curve Fig (2) can be determine the remainder quantity of Ni^{+2} ions in aqueous phase , from other hand to determine transferred quantity of Ni^{+2} ions to organic phase in order to form ion pair complex must be followed striping method by shaking organic phase with three portion of nearly concentrated HCl and then determine Ni^{+2} ions in aqueous acidic solution by followed (DMG) method [13] ,at last calculate distribution ratio (D)

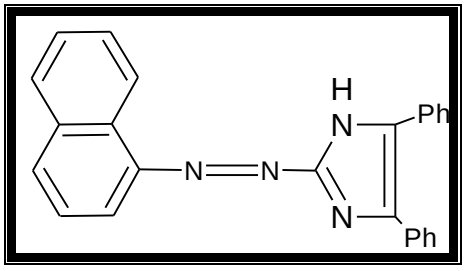


Figure (1) : Ligand structure

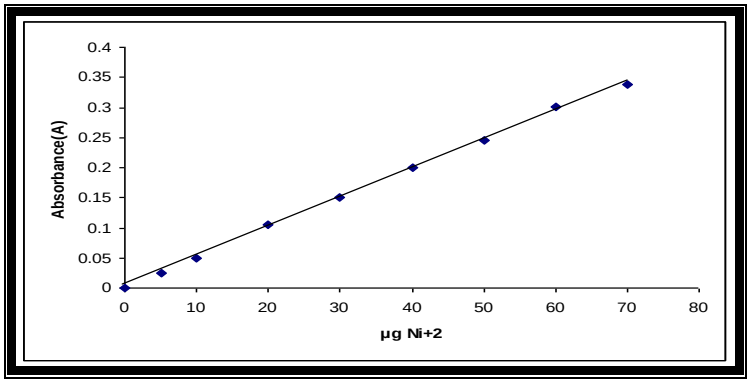


Figure (2) Calibration curve for Ni^{+2} ions

3. Results and Discussion :-

3.1-Effect of pH:-

Extracted 30 µg ($1.02x10^{-4}$ M) of Ni^{+2} ions in 5 ml aqueous phase at different pH (5-10) by (5ml) of ($1x10^{-4}$ M) ligand solution (α-NADPI) dissolved in chloroform , after shaking for (10 minutes) separate organic phase from aqueous phase and determined remainder quantity in aqueous phase and transferred quantity to organic phase from Ni^{+2} ions by followed DMG method [13] detailed in general procedure ,after ward calculate

distribution ratio (D) and percentage of extraction (E) ,to get the results as illustrated in Table (1) and Figure (3) .

Table (1) : Effect of pH on the extraction of Ni^{+2} ions .

pH	5	6	7	8	9	10
D	0.132	0.398	0.875	1.38	4	1.5
E	11.7	28.47	46.77	57.98	80	60

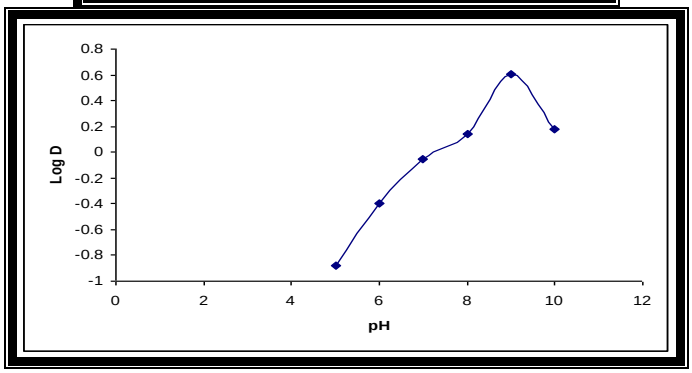


Figure (3) :Effect 0f pH on the extraction of Ni^{+2} ions

The results in Table (1) and Fig (3) shows the optimum pH_{ex} was ($pH_{ex} = 9$)Which is giving higher distribution ratio (D) and percentage of extraction (E) ,all pH values less than optimum in view of fact that not good condition for extraction ,may be by effect of predominate dissociation equilibria and in acidic media effect to protonated molecule and decrease extraction ability , and may be formed stable species can not be extracted . at pH value more than optimum may be formed ion pair complex as Ni^{+2} $(\alpha\text{-NADPI})_n$ $(OH)_z$ which more soluble in aqueous phase and predominate dissociation equilibria .

3.2 . Effect of metal ion concentration :-

Extracted different Ni^{+2} ions concentration (5-30 µg) ($1.7x10^{-5}$ -$1.02x10^{-4}$ M)in 5ml aqueous phase at ($pH_{ex} = 9$) by (5ml) ligand solution (α- NADPI)dissolved in chloroform at concentration of ($1x10^{-4}$ M) after shacking for (10minutes) separate these two layer and determine distribution ratio (D) and percentage of extraction (E) by followed DMG method [13]

Table (2) effect of metal ion concentration

µgNi^{+2}	5	10	20	30	40	50	60	70
$[Ni^{+2}]\times10^{-4}$	0.17	0.34	0.68	1.02	1.36	1.7	2.04	2.39
D	0.25	0.428	1.66	4	0.77	0.47	0.33	0.25
E	20	29.97	62.4	80	43.5	31.97	24.6	20

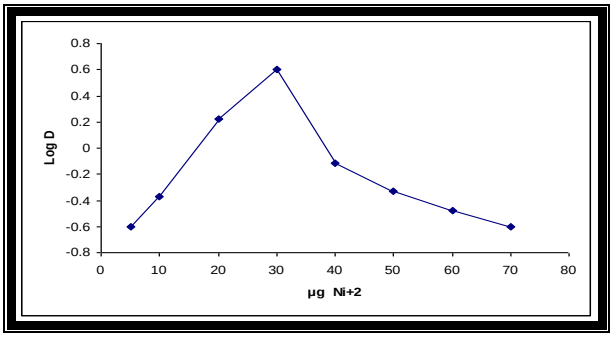


Fig (4) :Effect of metal ion concentration

The results at Table (2) and Figure (4) shows the optimum quantity of Ni^{+2} ions giving higher distribution ratio (D) and percentage of extraction (E) was (30µg) ($1.02x10^{-4}$ M) ,this quantity good equilibria for formation of ion pair complex and increase the stability of complex in organic phase according to the equilibrium below

$$Ni^{2+}_{aq.} + n(\alpha\text{-NADPI})_{org.} + 2Cl^{-}_{aq.} \longleftrightarrow [Ni\ (\alpha\text{-NADPI})n]^{+2}\ (2Cl^{-}\ )_{2org.}$$

The quantity of Ni^{+2} ions in aqueous solutions less than (30 µg) not allow to reached the equilibrium and predominate the dissociation equilibria by reason of decrease the stability of ion pair complex formation ,as well as quantity more the(30 µg) effect to decline distribtion ratio according to thermodynamic equilibrium the concentration more than optimum value effected to increase the rate of dissociation equilibrium by effect of mass action low and the Shatelier principle .

3.3. Effect of shaking time:-

Extraction (30µg) ($1.02x10^{-4}$ M) of Ni^{+2} ions from (5ml) aqueous solution at(pH_{ex} =9) by (5ml) organic solution of ligand (α-NADPI)dissolved in chloroform at ($1x10^{-4}$ M) at different shaking time (5-30 minutes) to determine the kinetic sid of complexation reaction , after shaking separate organic phase form aqueous phase and determine the remainder quantity of Ni^{+2} ions in aqueous phase and transferred quantity to the organic phase by followed (DMG) method [13] as detailed in general procedure ,after calculated distribution ratio (D) and percentage of extraction (E) obtaine the results as in Table (3) and Figure (5).

Table (3): Effect of shaking time on extraction method

Min	5	10	15	20	25	30
D	2.52	4	2.307	2.14	2.04	1.95
E%	7106%	80%	96.76%	68.15%	67.1%	66.1%

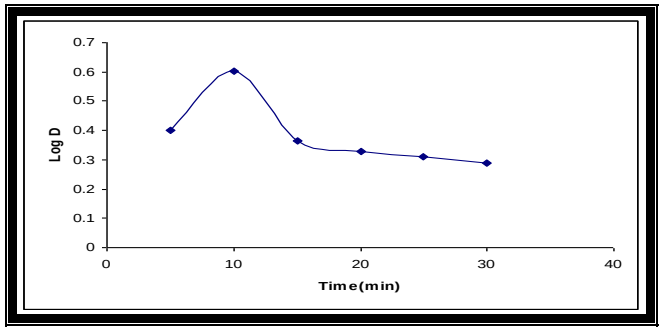


Figure (5): Effect of shaking time on extraction method

The results at Table (3) and Figure (5) shows the optimum shaking time was (10 min) less than that is not allow to reach the equilibrium to giving stable ion pair complex , shaking more than (10min) effect to predominate dissociation equilibria and decrease distribution ratio (D) and percentage of extraction (E)

3.4.stoichiometry :

3.4.1. Slope Analysis Method :

To prove the more probable structure of ion pair complex extracted for Ni^{+2} ions extracted (30 µg) (1.02 $x10^{-4}$ M)Ni^{+2} ions in (5ml) aqueous phase at (pH=9) by (5ml) organic solution of ligand (α-NADPI) dissolved in chloroform at different concentration ($5x10^{-6}$ -$1x10^{-3}$ M)after shaking for (10 minutes) and separate the two layers ,determine remainder quantity of Ni^{+2} ions in aqueous phase by followed (DMG) method [13] detailed in general procedure ,after calculate distribution ratio (D) get the results at Table (4) and Figure (6)

Table (4):Effect of (α-NADPI) concentration on extraction of Ni^{+2}ions

[αNADPI]	$5x10^{-6}$	$1x10^{-5}$	$5x10^{-5}$	$1x10^{-4}$	$2x10^{-4}$	$3x10^{-4}$	$8x10^{-4}$	$1x10^{-3}$
D	0.063	0.126	0.5	1	4	6.31	12.589	14
Slope	1.09							

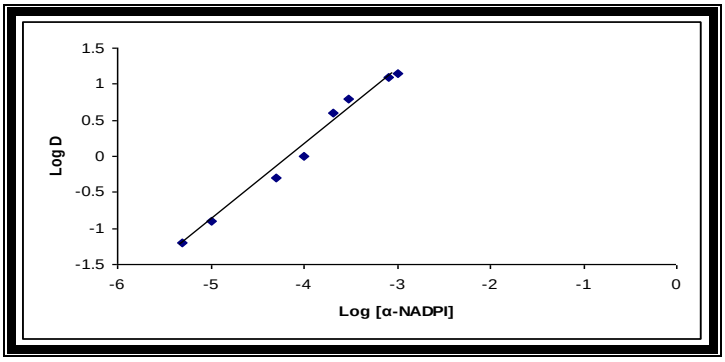


Figure (6) Effect of [α-NADPI] concentration on extraction of Ni^{+2} ions

The results at Table (4) and Figure (6) shows the more probable structure of ion pair complex extracted was (1:1) (metal :ligand) $[Ni^{+2}(\alpha\text{-NADPI})]^{+2}(Cl^{-})_2$

3.4.2. Mole Ratio Method :-

Extracted (30 µg) $1.02x10^{-4}$ M) of Ni^{+2} ions in 5ml aqueous phase at (pH_{ex} =9) by 5ml organic solution of ligand (α-NADPI) dissolved in chloroform at different concentration ($5x10^{-6}$ -$1x10^{-3}$ M)after shaking for (10 minutes) and separate the two layers ,determine remainder quantity of Ni^{+2} ions in aqueous phase by followed (DMG) method [13] detailed in general procedure ,after calculate distribution(D) and mole ratio for ligand to metal ion obtained the results at Table (5) and figure (7) .

Table (5) :mole ratio method

[α-NADPI]	1×10^{-6}	5×10^{-6}	1×10^{-5}	5×10^{-5}	1×10^{-4}	2×10^{-4}	3×10^{-4}	5×10^{-4}	8×10^{-4}	1×10^{-3}
A	0.066	0.099	0.118	0.768	1.387	2.246	2.246	2.34	2.57	2.59

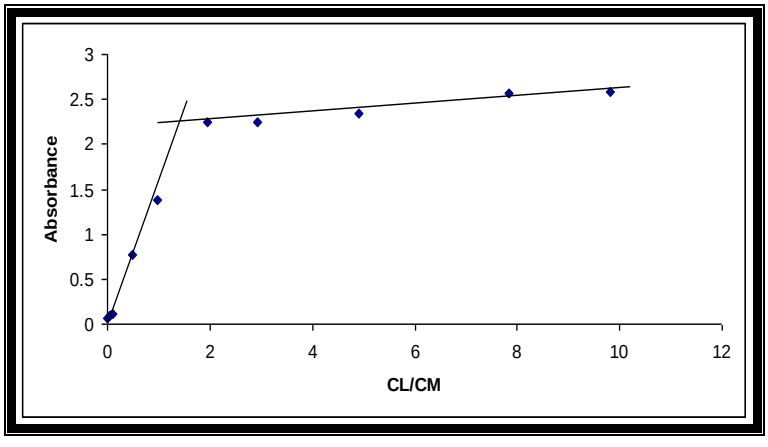


Figure (7) :Mole ratio method

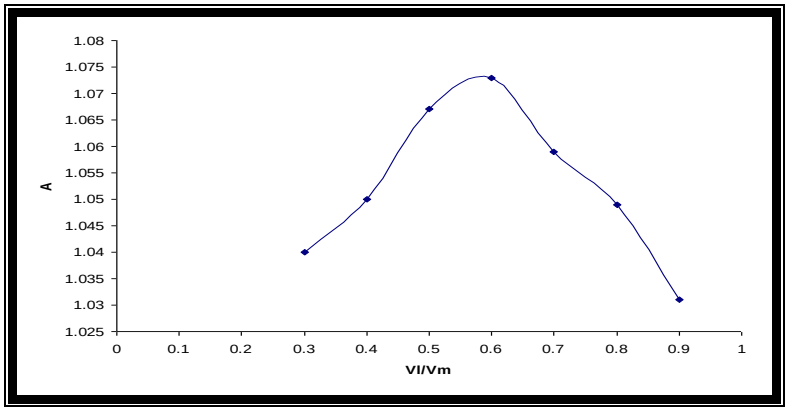
The results at Table (5) and Figure (7) illustrated the more probable structure of ion pair complex extracted was (1:1) (metal : ligand)as in slope analysis method [Ni (α-NADPI)]$^{+2}$ $(Cl^-)_2$

3.4.3. Continuous variation method :

For verification the reality of ion pair complex structure prepared aqueous solution for Ni^{+2} ions and organic solution for ligand (α-NADPI) dissolved in chloroform at same concentration ($1x10^{-4}$ M) ,and then mix different volume of the two solution to maximum volume (5ml) ,at (pH_{ex} = 9)after shaking each solution for (10 minutes) ,separate the two layer and Appling (DMG) method [13] in order that calculate distribution ratio to obtain the results at Table (6) and Figure (8) .

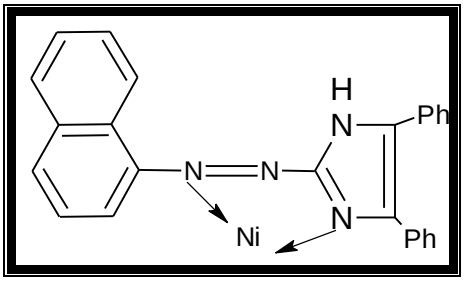
Table (6): continuous variation method .

$V_L$ml	1.5	2	2.5	3	3.5	4	4.5
$V_M$ml	3.5	3	2.5	2	1.5	1	0.5
A	1.04	1.05	1.067	1.073	1.059	1.049	1.031



Figure(8): Continuous variation method

The results at Table (6) and Figure (8) shows the more probable structure of ion pair complex extracted was (1:1) (metal: ligand) which is identify with the results in slope method and mole ratio method [Ni(α-NADPI)]$^{+2}$ $(Cl^-)_2$



Fig(9): Complex Structure

3.5.Organic solvent effect :-

To determination the effect of organic solvents on the extraction in solvent extraction method , extracted (30µg)($1.02x10^{-4}$ M)Ni^{+2} ions in (5ml) aqueous solution at (pH =9) by (5ml) organic solution of ligand (α-NADPI) dissolved different organic solvents differ in dielectric constant (ε) at ($1x10^{-4}$ M) concentration , after shaking for (10 minutes)separate the two layers and determine distribution ratio (D) and percentage of extraction (E) according to the (DMG) method [13] in general procedure to get the results illustrated in Table (7) .

Table (7): Organic solvents effect on extraction of Ni^{+2} ions .

Organic solvent	ε	D	E%
Amyl alcohol	15.8	11	91.7%
Dichloromethane	9.08	0.62	38.3%
Chloroform	5.708	4	80%
Benzene	2.804	11	91.7%
Toluene	2.438	9	90%
Carbon tetrachloride	2.238	1.4	58.3%

The results shows there is not any linear relation between dielectric constant (ε) of organic solvents and distribution ratio (D) and here is not any effect for polarity of organic solvents but there is an effect for organic solvent structure on the such as contact ion pair (tight ion pair) or solvent separated ion pair (loose ion pair)
according to solvent extraction method , the organic solvent participate in the structure of complex formation by formation more stable complex and this property not related with polarity or dielectric constant but return to structure of solvent .

3.6 .temperature effect .

From thermodynamic side extracted (30µg) ($1.02x10^{-4}$ M) Ni^{+2} ions from (5ml) aqueous solution at (pH_{ex} =9)by(5ml) organic solution of ligand (α-NADPI) dissolved in chloroform at ($1x10^{-4}$M) concentration in different temperature (5-30 min.) ,after shaking for (10 minutes) and separate the two layers determine distribution ratio (D) at each temperature by followed (DMG) method detailed in general procedure obtained the results illustrated at Table (8) .

Table (8): Temperature effect on extraction on Ni^{+2} ions

Tc^0	T k	1/Tk x10^{-3}	D	K_{ex}
5	278	3.59	6.15	6.03x10^8
10	283	3.53	8.099	7.94x10^8
15	288	3.47	11.44	11.22x10^8
20	293	3.41	17.03	16.7x10^8
25	298	3.36	21.3	20.89x10^8
30	303	3.3	28.74	28.18x10^8

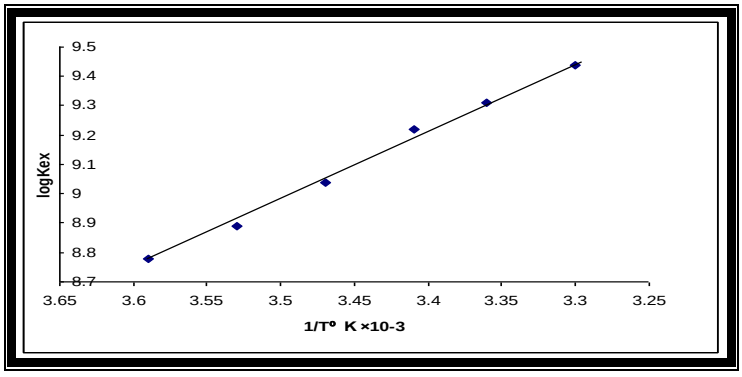


Fig (10): Temperature effect on extraction method

The results illustrated the enthalpy of extraction was (ΔH_{ex} =0.043 KJ $mole^{-1}$) ,free energy of extraction was (ΔG_{ex} = -53.6 $KJmole^{-1}$) and entropy of extraction was (ΔS_{ex} =177.04 $Jmole^{-1}$ K^{-1}).All this results shows the complexation reaction between ligand (α-NADPI) and Ni^{+2} ions was endothermic reaction as well as value of enthalpy of extraction shows the ion pair complex extracted was (1:1) as in stoichiometric study ,the high value of entropy emphasis the complexation reaction is entropic in region that is mean there is high number of free water molecules produce from the hydration shell of Ni^{+2} ions at coordination binding with ligand molecules to form stable complex ,in addition of increase temperature help to destroy the hydration shell of Ni^{+2} ions in present of suitable organic solvent to produce free ion and free water molecules .

4.Conclusion

The results in this study determined optimum condition for complexation between Ni^{+2} and ligand (α-NADPI) from the side of pH and metal ion concentration and shaking time in addition the suitable organic solvent for extraction which is showed there is an

effect for organic solvent structure on complex formation and stability to givening contact ion pairs or loose ion pairs as well as this study shows the more probable structure for ion pairs complex .

Extraction (1:1) and the thermodynamic behavior for complexation reaction between metal cations and ligand molecule which was endothermic reaction , determination these results open the door about used some azo compound , derivatives as ligand to many research can be doing for extraction different transition metal cations by use different derivatives for azo compound and may be used this compound as ligands for extraction some anions for transition matelsas oxy anions or anther anion complex like chloro anion complexes according to solvent extraction method as well for different metal cations could be find separation factors and finding the good optimum conditions for separation these cations from different samples as well as may be spectrophotometric for transition metal cation .

استخلاص النيكل (II) من المحاليل المائية بواسطة الليكاند الجديد

2 – [α - نفثايل ازو]-5,4- ثنائي فنيل اميدازول

غصون فيضي حميد كليه التربية/ جامعه القادسية

الخلاصة

الليكانـد الجديـد 2-[α-نفثايـل ازو]-5,4- ثنـائي فنيـل اميـدازول (α-NADPI) والمحضـر حسـب الطريقـة الموضـحة في الدراسة [1] استخدم ككاشف تحليلي للتقدير الطيفي واستخلاص ايونات النيكل Ni^{+2}وقد أوضحت الدراسة ان الدالة الحامضية المثلى لأستخلاص ايونات النيكل كانت (pH_{ex}= 9) وان زمن الرج الأمثل لإعطاء أنسب استخلاص كان (10 دقيقة) ، اما التركيز الأمثل لايونات النيكل التي تعطي افضل استخلاص وأعلى قيمة نسبة توزيع (D) كانت (30 µg Ni^{+2}) (1.022×10^{-4} M) . كما ان الدراسة أوضحت ان التركيب المحتمل لمعقد الترابط الأيوني المستخلص هو (1:1) (metal: ligand) $(Cl^-)_2$ [Ni (α-NADPI)]$^{+2}$ كما ان دراسة تأثير المذيب العضوي اثبتت انه لاتوجد أية علاقة خطية بين ثابت العزل الكهربائي للمذيب العضوي (ε) ونسب التوزيع ولكن هناك تأثير لتركيب المذيب العضوي على عملية الأستخلاص . اما الدراسة الثرموديناميكية أثبتت ان تفاعل التعقيد بين الليكاند (α-NADPI) وايونات النيكل Ni^{+2} كان تفاعل ماص للحرارة Endothermic

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