

Extraction of Nickel (II) from aqueous solution by use 2-[(4-Chloro-2-methoxy phenyl)azo]-4,5-di phenyl imidazole

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Abstract

Dependence on sensitivity and selectivity for imidazole compounds to transition metal elements as cations, extracted Ni^{+2} ions from aqueous solutions by solvent extraction method to produce ion pair association complex by use ligand 2-[(4-Chloro-2-methoxy phenyl)azo]-4,5-di phenyl imidazole (4-CIMePADPI). The study demonstrated the optimum conditions for extraction was ($\text{pH}_{\text{Hex}}=9$), shaking time was (15-minute) and Ni^{+2} ions concentration was ($70\mu\text{g}$) ($2.38 \times 10^{-4}\text{M}$), the organic solvents effect on the extraction shows there is not any linear relation between distribution ratio (D) and dielectric constant (ϵ) for organic solvents used, but shows there is an effect for the structure of organic solvent on the extraction ability and stability of ion pair complex extracted, from other hand the stoichiometric study shows the more probable structure for ion pair complex extracted was (1:1) (metal:ligand) $[\text{Ni}(4\text{-CIMePADPI})]^{+2}\text{SO}_4^{-2}$. Thermodynamic study illustrated the complexation reaction between Ni^{+2} ion and ligand (4-CIMePADPI) was exothermic.

الخلاصة

اعتماداً على الحساسية والانتقائية العاليتين لمركبات الأيميدازول للأيونات الموجبة للعناصر الانتقالية، تم استخلاص أيونات النيكل Ni^{+2} من المحاليل المائية بواسطة طريقة الاستخلاص بالمذيب لتكوين معقد ترابط أيوني باستعمال الليكاند 2-[(4-كلورو - 2-ميثوكسي فينيل)أزو]-4,5-ثنائي فينيل اميدازول (4-CIMePADPI). الدراسة أوضحت ان عملية الاستخلاص تحتاج إلى ظروف مثلى وهي الدالة الحامضية يجب ان تكون ($\text{pH}_{\text{Hex}}=9$) وزمن رج الطورين يكون (15min) أما تركيز ايونات النيكل في الطور المائي يجب ان تكون في (5ml) من المحلول المائي بمقدار ($70\mu\text{g}$) ($2.39 \times 10^{-4}\text{M}$) أما تأثير المذيب العضوي على عملية الاستخلاص فقد أوضحت الدراسة انه لا توجد علاقة خطية بين نسبة التوزيع (D) وثابت العزل الكهربائي (ϵ) للمذيبات العضوية المستخدمة في عمليات الاستخلاص، ولكن أظهرت الدراسة ان هناك علاقة وتأثير لتركيبة المذيب العضوي على عملية الاستخلاص، من جانب آخر دراسة تركيب المعقد المستخلص أوضحت ان للمعقد تركيب (1:1) (فلز:ليكاند) $[\text{Ni}(4\text{-CIMePADPI})]^{+2}\text{SO}_4^{-2}$. الدراسة الترموديناميكية بينت ان تفاعل التعقيد بين ايونات النيكل Ni^{+2} وجزيئات الليكاند (4-CIMePADPI) كان تفاعل باعث للحرارة وقد تم حساب الثوابت الترموديناميكية لهذا التفاعل .

1.Introduction

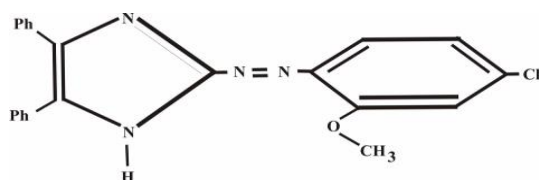
The extra ordinary applications of azo compounds as areagents for complexation with different metal cation open the door about widespread applications for extraction and spectrophotometric determination of metal cations, there is astudy about synthesis of anew azo compound used for spectrophotometric determination of Ni^{+2} ions [Xnezhouy *et al.*, 1998]. Study about complexation of Zn (II) and Cd (II) with 2-[2-Benzimidazolylazo]4-acetamidophenol [Mohamed *et al.*, 2001]. Another study about comparison of the extraction process of Zn(II) and Ni(II) complexes by 1-octylimidazole and 1-octyl-2-methylimidazole [Biniamin Lnarcik *et al.*, 2003], effect of alkyl chain length on the stability and extraction properties of Ni^{+2} ions was studied by using 1-alkylimidazole [Lenercik *et al.*, 2002]. Achiral complex, salen Zn(II) was synthesized and characterized its coordination with imidazole derivatives and amino acid ester derivatives was studied by UV-vis spectrophotometric titration [Ruijuan Yuan *et al.*, 2006], the reaction of 5,6-diamino-1,10-phenanthroline with 4'-formylbenzo-15-crown-5. Produce anew ligand and study characterization of this ligand and its complexes with Co^{+2} & Ni^{+2} and Cu^{+2} was studied [Ibrahim Evden *et al.*]

(2006)],thesis about complexes between imidazole and cations of copper(II), zinc(II), and nickel (II)[Ipolya Apro_Torok *et al.*, 2002].synthesis derivatives imidazoles and study the reactivity and molecular structure by this derivatives [Anita Kornicka *et al.*, 2009]. the crystal and molecular structures of $[\text{Ni}(\text{Im})_6](\text{dtp})_2$ [Shusheng zhang *et al.*, 2003]. spectral and electrochemical characterization of the product for imidazole ligand [Sanjib pal *et al.*, 2001].The synthesis of extended dicationic bis-benzimidazoles [Zhijan kang *et al.*, 2004]. .

2.Experimental

All reagents and solvents were obtained from commercial sources and used as received ,absorption and spectrophotometric measurements were made using a single beam UV-Visible spectrophotometer (Shimadzu-UV-1000-02)and double beam (UV-1700)UV-Visible spectrophotometer shimadzu ,pH measurements was carried out using (Ascott Gersale) pH-meter model 820.

Stock solution (1mg/ml) of Ni^{+2} ions is prepared by dissolving 0.673gm of $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ salt in 100 ml of distilled water contain 2ml conc. H_2SO_4 in volumetric flask ,other working solution was prepared by dilution with distilled water for determination of Ni^{+2} ions in aqueous phase needing to prepare 4%solution of potassium persulphate by dissolving 4gm from this salt in distilled water and completing the volume with water in volumetric flask and this solution must be prepared instantaneously ,1%di methyl glyoxime is prepared by dissolving 1gm in 100ml ethanol by used volumetric flask ,ligand solution in concentration $1 \times 10^{-2}\text{M}$ prepared by dissolved 0.3885gm of ligand (4-ClMePADPI) in 100ml chloroform by used volumetric flask ,other working solutions prepared by dilution with organic solvent , $1 \times 10^{-2}\text{M}$ dithizone solution prepared by dissolved 0.5232gm in 100ml CCl_4 in volumetric flask ,other working solutions prepared by dilution with CCl_4 organic solvent.



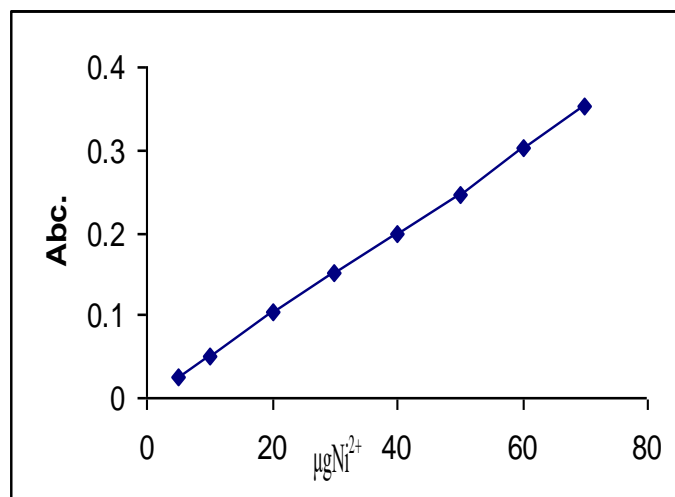
2-[(4-Chloro-2-methoxy phenyl)azo]-4,5-diphenyl imidazole

Fig(1) :Structure of ligand used in extraction method.

2-1 General procedure

For extraction experiments have to take (5ml) of aqueouse solution contain quantity of Ni^{+2} ions at fixed pH ,adding(5ml) of organic solution for ligand (4-ClMePADPI)at concentration of ($1 \times 10^{-4}\text{M}$) ,shaking these two layers for suiTable time afterward separate organic from aqueous phase ,after that determine remainder quantity of Ni^{+2} ions in aqueous phase by followed spectrophotometric method (di methyl glyoxime) [Marczenko *et al.*, 1974],for (5ml) aqueous phase add (1ml)of 1% di methyl glyoxime) solution and (2ml) of 4% potassium persulphate solution and (5ml) of concentration ammonia solution NH_3 ,after that diluted with water to (50ml) by using volumetric flask, after(10minutes) determine the absorption of the solution

at($\lambda=445\text{nm}$) by use water as blank ,from absorbance and calibration curve Fig(2) can be determine the quantity of Ni^{+2} ions in organic phase as complex with the ligand (4-CIMePADPI) by stripping method which include shaking organic phase with three portions nearly concentrated hydrochloric acid HCl for dissociation the complex and transfer the Ni^{+2} ions to aqueous phase then determine Ni^{+2} ions transferred by dithizone method, as well as can be determine the quantity of Ni^{+2} ions in organic phase by subtraction remainder quantity of Ni^{+2} ions in aqueous phase from the initial quantity before extraction method, at later divided the quantity of Ni^{+2} ions in organic phase on the quantity of Ni^{+2} ions in aqueous phase to determine distribution ratio(D).



Fig(2) :Calibration curve of Ni^{+2} ions .

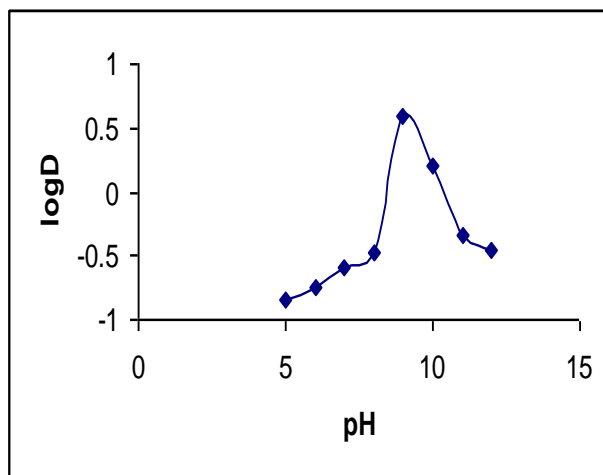
3- Results and Discussion

3-1 Effect of pH

Extracted of (30 μg) ($1.022 \times 10^{-4}\text{M}$) Ni^{+2} ions in 5ml aqueous solution of different pH (5-12) ,adding 5ml organic solution of ligand (4-CIMePADPI) dissolved in chloroform at ($1 \times 10^{-4}\text{M}$) concentration ,afterward shaking these two layers for(10minutes),at later separate the organic phase from aqueous phase ,afterward determine the remainder quantity in aqueous phase and transferred quantity to the organic phase and calculate the distribution ratio(D) and percentage of extraction (E) by followed the spectrophotometric method [Marczenko *et al.*, 1974] detailed in general procedure ,the results in Table(1) and Fig(3) shows the optimum pH was (pH_{ex}=9), pH values less than optimum value effect to decline distribution ratio(D) and percentage of extraction (E) by effect of protonated the ligand molecule and occupy the lone pair of electron and minimizing complexation reaction ,as well as at pH value more than optimum may be produced stable species for Ni^{+2} ions not extracted and may be participate (OH^-) ions to produce ion pair complex with high solubility in aqueous phase and effected to decrease distribution ratio (D) and percentage of extraction (E).

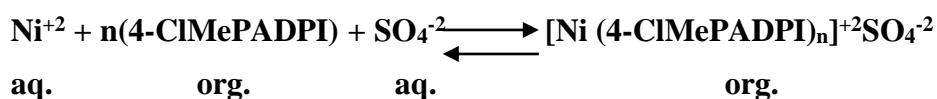
Table (1):Effect of pH on the extraction of Ni²⁺ions.

PH	5	6	7	8	9	10	11	12
D	0.141	0.178	0.250	0.333	3.99	1.588	0.457	0.355
E	12.4	15.1%	20%	24.98%	79.9%	61.4%	31.4%	26.2%

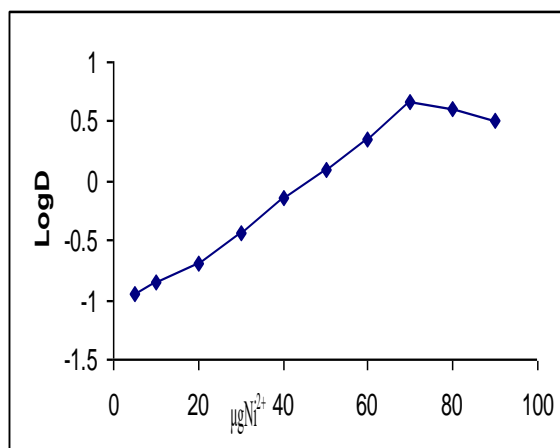
Fig (3): pH effect on the extraction of Ni²⁺ions .

3-2 Effect of metal ion concentration

Thermodynamically metal ion concentration effect on the formation constant of ion pair complex and the rate of complexation reaction, from this truth extracted Ni²⁺ions from (5ml) aqueous solution contain different quantity of Ni²⁺ions at (pH=9) by 1×10^{-4} M ligand solution (4-ClMePADPI) dissolved in chloroform ,after shaking these two layers for (10 minutes) separate organic phase from aqueous phase and determine the remainder Ni²⁺ions in aqueous phase and transferred Ni²⁺ions to organic phase by followed spectrophotometric method detailed in general procedure, afterward calculate distribution ratio (D) and percentage of extraction(E).The results in Table (2) and Fig (4) shows the optimum quantity of Ni²⁺ions in (5ml) aqueous solution giving highest (D) value and (E) value was (70µg) (2.39×10^{-4} M) according to aquilibria relation below

Table (2) : Effect of Ni²⁺ions concentration on the extraction method.

µg Ni ²⁺	5	10	20	30	40	50	60	70	80	90
[Ni ²⁺] ×10 ⁻⁴ M	0.17	0.34	0.68	1.02	1.36	1.7	2.04	2.39	2.73	3.1
D	0.112	0.141	0.204	0.363	0.708	1.259	2.291	4.571	3.999	3.199
E	10.1%	12.36%	16.9%	26.6%	41.5%	55.7%	69.6%	82.05%	80%	76.2%



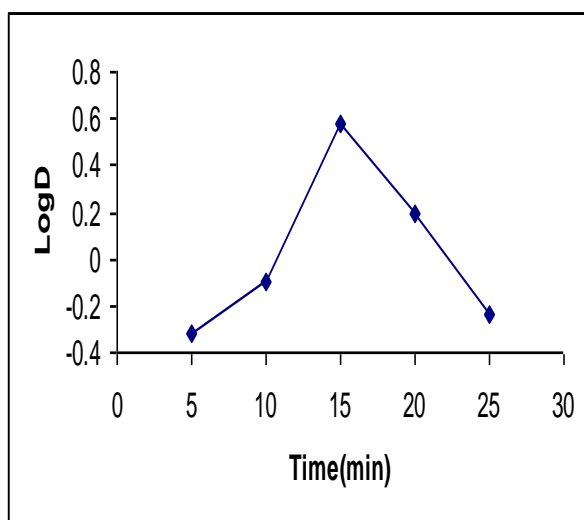
Fig(4):Effect of Ni^{+2} ions concentration on the extraction method.

3-3 Effect of shaking time:

From the side of kinetic effect on the complexation reaction between Ni^{+2} ions and ligand (4-CIMePADPI), extracted ($70\mu\text{g}$) ($2.39 \times 10^{-4}\text{M}$) of Ni^{+2} ions in (5ml) aqueous solution at (pH=9) by (5ml) organic solution of ligand (4-CIMePADPI) dissolved in chloroform, after that shaking the two layers at different shaking time (5-4-CIMePADPI) the remainder quantity Ni^{+2} ions in aqueous phase and transferred quantity Ni^{+2} ions to organic phase to produce ion pair complex with the ligand (4-CIMePADPI), and calculate the distribution ratio (D) and percentage of extraction (E) by followed the method detailed in general procedure. The results in Table (3) and Fig(5) shows the optimum shaking time (15minutes) which is effect to reached the equilibrium kinetically to the high equilibria and increase the stability of ion pair complex produced.

Table (3):Effect of shaking time on extraction of Ni^{+2} ions.

Time(min)	5	10	15	20	25
D	0.469	0.792	3.88	1.588	0.573
E	31.9%	44.2%	79.5%	61.4%	36.4%



Fig(5):Effect of shaking time on extraction Ni^{+2} ions.

The results show shaking for time less than optimum time not allow to reach equilibria and decline distribution ratio and percentage of extraction ,but shaking for time longer than optimum time effect to predominate the dissociation equilibria and decrease complexation ability and distribution ratio(D) and percentage of extraction(E).

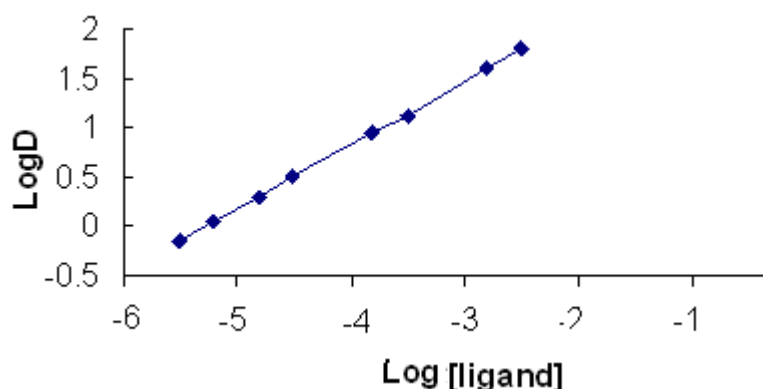
3-4 Stoichiometry

3-4-1 Slope analysis method :

To reach to the more probable structure of Ni^{+2} ion pair pair complex produced ,extracted (70 μg)($2.39 \times 10^{-4}\text{M}$) of Ni^{+2} ions in (5ml)aqueous solution at(pH=9) by (5ml) organic solution of ligand (4-ClMePADPI) dissolved in chloroform with different concentration ($5 \times 10^{-3}\text{M}$ - $5 \times 10^{-6}\text{M}$) after shaking the two layers for(15min) ,separate these layers and determine the remainder quantity of Ni^{+2} ions in aqueous phase and transferred quantity Ni^{+2} ions to the organic phase and calculate distribution ratio (D) ,according to method detailed in the general method the result in Table(4) and Figure(6)shows the more probable structure of ion pair complex was (1:1) (metal:ligand) $[\text{Ni}(\text{4-ClMePADPI})]^{+2}\text{SO}_4^{-2}$.

Table(4) :Slope analysis method for extraction of Ni^{+2} ions.

[ligand]	5×10^{-3}	2.5×10^{-3}	1×10^{-3}	5×10^{-4}	1×10^{-4}	5×10^{-5}	1×10^{-5}	5×10^{-6}
D	39.8	25.7	14.13	8.9	3.16	2.09	0.708	0.447
slope				0.65				



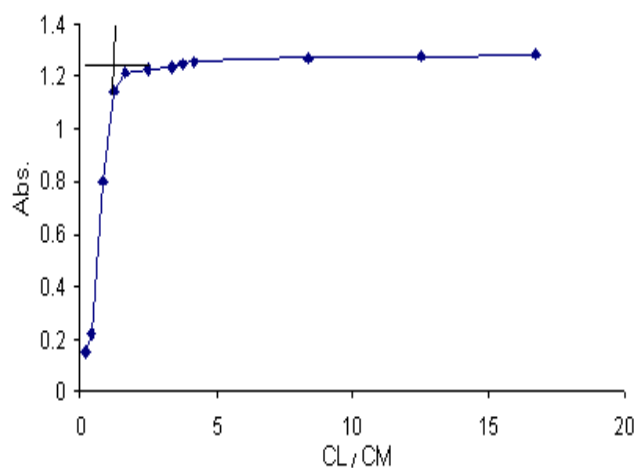
Fig(6): Slope analysis method for extraction of Ni^{+2} ions.

4-3-2 Mole Ratio Method :

Extraction $70\mu\text{g}$ ($2.39 \times 10^{-4}\text{M}$) of Ni^{+2} ions in (5ml) aqueous solution at (pH=9) by (5ml) organic solution contain different concentrations ($1 \times 10^{-5}\text{M}$ - $4 \times 10^{-3}\text{M}$), after shaking these two layers for (15 minutes) separate the organic phase from the aqueous phase, afterward measurement the absorbance (Abs.) of organic phase at $\lambda=522\text{nm}$ by use the ligand solution as blank and then plot the absorbance values (Abs.) against mole ratio (C_L / C_M). The results in Table(5) and Figure(7) shows the more probable structure of ion pair complex for Ni^{+2} ions was (1:1) (metal:ligand) $[\text{Ni}(4\text{-ClMePADPI})]^{+2}\text{SO}_4^{-2}$.

Table (5) : Mole ratio method for extraction of Ni^{+2} ions.

[ligand]	1×10^{-5}	5×10^{-5}	1×10^{-4}	2×10^{-4}	3×10^{-4}	4×10^{-4}	6×10^{-4}	8×10^{-4}	9×10^{-4}	1×10^{-3}	2×10^{-3}	3×10^{-3}	4×10^{-3}
Abs.	0.12	0.15	0.22	0.8	1.15	1.22	1.23	1.24	1.25	1.26	1.27	1.28	1.29



Fig(7): Mole ratio method for extraction of Ni^{+2} ions .

3-4-3 Continuous variation method :

Third method for stoichiometric study needed prepare aqueous solution for Ni^{+2} ions and organic solution for ligand (4-CIMePADPI) dissolved in chloroform at the same concentration ($3 \times 10^{-4} \text{M}$) and then mixed different volume of the two solution to maximum volume (5ml) at (pH=9), after shaking the two layers for (15min.) separate organic phase from aqueous phase and determine the absorbance of organic phase at $\lambda=522\text{nm}$ against ligand solution as blank, afterward plot absorbance values against the proportion of metal solution volume V_m over total volume (5ml). The results in Table (6) and Figure (8) demonstrate the structure of ion pair complex extracted was (1:1) (metal:ligand) $[\text{Ni}(\text{4-CIMePADPI})]^{+2}\text{SO}_4^{-2}$.

Table (6) : Continuous variation method for extraction of Ni^{+2} ions .

V_L ml	0.0	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5.0
V_M ml	5.0	4.5	4	3.5	3	2.5	2	1.5	1	0.5	0.0

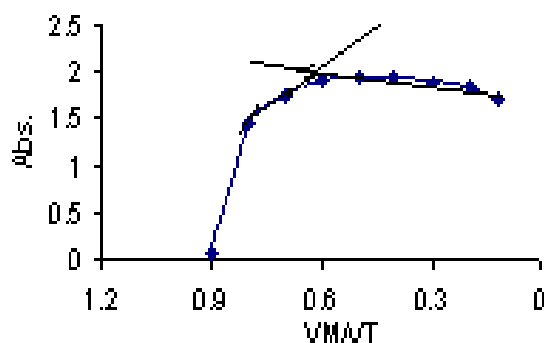
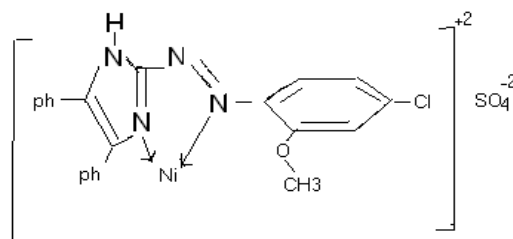


Fig (8) : Continuous variation method for extraction of Ni^{+2} ions .

According stoichiometric results the suggested structure of ion pair complex extracted was:



Fig(9): The suggested structure of ion pair complex for Ni^{+2} ions.

3-5 Organic solvent effect

Solvent extraction method take care of organic solvent used in extraction method ,according to this concept extracted $70\mu\text{g}$ ($2.39 \times 10^{-4}\text{M}$) of Ni^{+2} ions in (5ml)aqueous solution at (pH=9) by (5ml) organic solution contain ligand (4-CIMePADPI) dissolved in different organic solvents at concentration of ($1 \times 10^{-4}\text{M}$) ,after shaking for (15min) separate the two layers and determine the remainder Ni^{+2} ions in aqueous phase and Ni^{+2} ion stransfered to organic phase as complex ,afterward calculate the distribution ratio(D) and percentage of extraction (E) according to spectrophotometric method detailed in general procedure .The results in Table(7) shows there is not any linear relation between distribution ratio(D) and dielectric constant(ϵ) for organic solvents used in extraction method of Ni^{+2} ions,from the other hand the results illustrate there is an effect for the organic solvent structure on the extraction method and ion pair complex extracted may be form (tight ion pair) or solvent separated ion pair (loose ion pair) .

Table(8):Organic solvents effect on the extraction of Ni^{+2} ions.

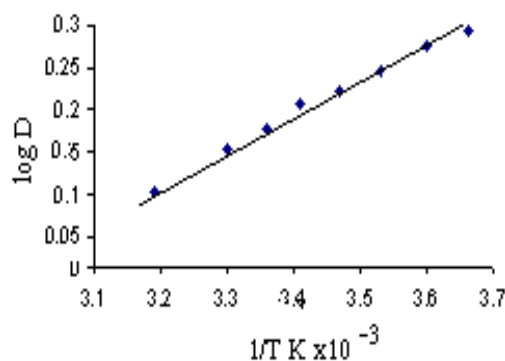
Organic solvents	ϵ	D	E
Dichloromethane	9.08	1.854	64.96%
Chloroform	5.708	3.999	80%
Bromo Benzene	5.40	2.495	71.39%
Benzene	2.804	2.818	73.8%
Toluene	2.438	2.477	71.24%
Carbon tetra chloride	2.38	1.057	51.39%

3-6 Effect of temperature

Extraction of $70\mu\text{g}$ ($2.39 \times 10^{-4}\text{M}$) of Ni^{+2} ions in (5ml)aqueous solution at (pH=9) by (5ml) organic solution of ligand (4-CIMePADPI) dissolved in chloroform at ($1 \times 10^{-4}\text{M}$) and different temperature ($0 \rightarrow 40\text{C}^\circ$) after shaking for (15min) of fixed temperature separate organic phase from aqueous phase , afterward determine the remainder Ni^{+2} ions in aqueous phase and transferred Ni^{+2} ions to organic phase by dimethyl gluoxime method which is detailed in general procedure .The results in Table(9) and Figure (10) shows the complexation reaction between ligand(4-CIMePADPI) and Ni^{+2} ions was exothermic reaction

Table (9) :Temperature effect on the extraction of Ni^{+2} ions.

T $^\circ\text{C}$	T $^\circ\text{K}$	1/T $^\circ\text{K} \times 10^{-3}$	D
0	273	3.66	1.905
5	278	3.6	1.819
10	283	3.53	1.70
15	288	3.47	1.66
20	293	3.41	1.55
25	298	3.36	1.45
30	303	3.3	1.38
40	313	3.19	1.36

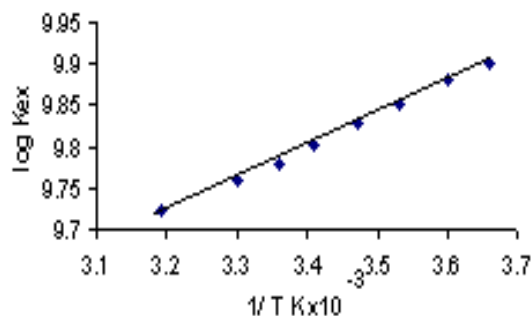


Fig(10) : Temperature effect on the extraction of Ni²⁺ions.

After that extraction constant K_{ex} is calculated by application the relation:

$$K_{ex} = \frac{D}{[Ni^{+2}]_{aq} \cdot [Ligand]_{org.}}$$

log K_{ex} was plotted against 1/T°K as in Fig(11)



Fig(11) :Effect of temperature on extraction of Ni²⁺ions.

from the slope of straight line above and application of the relations below , the thermodynamic data of complexation reaction between Ni²⁺ions and ligand (4-CIMePADPI) were obtained:

$$\text{Slope} = -\Delta H_{ex} / 2.303R$$

$$\Delta G_{ex} = -RT \ln K_{ex}$$

$$\Delta G = \Delta H_{ex} - T\Delta S_{ex}$$

After application these relations, shows the value of enthalpy for extraction of Ni²⁺ions was ($\Delta H_{ex} = 0.00597 \text{Kj mole}^{-1}$) and Gibbs free energy was ($\Delta G_{ex} = -40.37 \text{Kj mole}^{-1}$) as well as the entropy was ($\Delta S_{ex} = 147 \text{Jmole}^{-1}$), these results shows the reaction between Ni²⁺ions and ligand (4-CIMePADPI) to produce ion pair complex was entropic reaction ,from other hand the value of ΔH_{ex} illustrate the ion pair complex extracted have structure of 1:1 $[Ni(4-CIMePADPI)]^{+2}SO_4^{-2}$ [Arifien, 2003] .

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