

Extraction of Nickel (II) From Aqueous Solutions By Using 2-[(4-Bromo Phenyl) Azo]-4,5-Diphenyl Imidazole

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الخلاصة

تمت دراسة عملية استخلاص ايونات النيكل (II) من المحاليل المائية بواسطة الكاشف 2- (4- برومو فنيل) ازو - 4,5 - ثنائي فنيل أميدازول (P-BrPAI) المذاب في الكلوروفورم فقد كان هذا الكاشف جيد للاستخلاص النيكل (II) وتضمنت الدراسة النواحي الاتية تأثير الدالة الحامضية (pH) حيث كانت القيمة المثلى لاستخلاص ايونات النيكل الثنائية عند الدالة الحامضية 9 اما افضل تركيز للنيكل الثنائي الذي يعطي اعلى قيمة لنسبة التوزيع ويحقق حالة الاستخلاص الفضلى هو 80 µg (2.73 x10⁻⁴M) هو افضل تركيز ، أما الدراسة الحركية لتفاعل التعقيد بين ايونات النيكل (II) والكاشف (p-BrPAI) فقد بينت ان زمن الرج (10 دقائق) هو الأفضل للوصول المعقد الى حالة الاتزان ، كذلك تم دراسة تأثير تركيز الكاشف العضوي و وجد ان افضل قيمة لنسبة التوزيع عندما يكون التركيز 3x10⁻⁵ M كذلك تم دراسة تأثير المذيب العضوي وبينت النتائج انه لا توجد علاقة خطية بين نسبة التوزيع للاستخلاص و ثابت العزل الكهربائي للمذيبات العضوية المستخدمة ، كما أوضحت الدراسة الترموديناميكية لتفاعل التعقيد ان التفاعل باعث للحرارة في مدى درجات الحرارة من (20 C⁰ - 70 C⁰).

Abstract

The extraction of Nickel has been studied as complex with 2-[(4-Bromo phenyl) azo]-4,5-diphenyl imidazole which dissolved in chloroform .This search comprises the following aspects: the optimum pH values for extraction was (pH_{ext.} = 9), so the suitable concentration of Ni(II) ions in aqueous solution which is giving highest distribution ratio (D) was (80 µg) ,studying effect of extraction time illustrated the optimum shaking time to reach the equilibria was ten minute .It was found from experiments that the best value of D when the concentration of ligand equal to [3x10⁻⁵ M] , from other hand organic solvents shows that there is no linear relation ship between dielectric constant of organic solvents and distribution ratio (D) of extraction ,but there is an effect for the organic solvent structure. The thermodynamic study demonstrates the complexation reaction is an exothermic at temperature degrees (20 °C - 70 °C).

Key words: extraction , p-BrPAI , Nickel , azo, imidazole.

Introduction

Sensitivity and selectivity behavior of azo compounds and imidazoles as well as its derivatives for complex formation for metals , giving growing concern in synthesis it and studying extraction of metals such as the extraction of uranium and the effect of alkyl group on the extraction [1]. The extraction of Ni(II) was studied using 2-[(4-carboxy methyl phenyl) azo]-4,5-diphenyl imidazole [2]. Comparison of extraction of Zn (II) and Ni(II) by use 1-octylimidazole and 1-octyl-2-methyl imidazole [3]. 2-[(α-naphthyl) azo]-4,5-diphenyl imidazole has been used in extraction of copper and silver [4]. The extraction of imidazole chelate complex with copper [5], also Cu (II) ,Zn(II) and Ni(II) can be extracted by complexation reaction with imidazole and inositol derivatives as ligand [6] . A new type of imidazole legand has been synthesis a new imidazole ligand and studied it complexes with

Co(II), Ni (II) , and Cu(II) [7]. The cloud point extraction and determination of Zn, Co, Ni and Pb by flame atomic absorption spectrometry using 2-Guanidinobenzimidazole as the complexing agent has been studied [8]. The geometry isomerism induced by N–H -Cl, C–H-Cl, C–H-N, C–H-p and p-p supra molecular interactions in mercury(II) complexes with tri pyridyl imidazole chelating ligands has been estimated [9]. Synthesis of tri- and tetra substituted imidazoles [10]. As well as the extraction of group (IIb) metal ion by new organic reagent ", 2-[(4-Chloro-2- methoxy phenyl)azo]-4,5-diphenyl imidazole has been studied [11]. In other study used 2-[6-methyl benzothiozoly] azo]5-diethyl amino phenol to determination of Ni(II) from aqueous solutions [12].

Apparatus

Used TRUV754(UV – Visible Spectrophotometer) for absorption measurements also pH measurements done by using 3320 Jenway pH Meter .

Materials

NiCl₂.6H₂O , Dimethyl glyoxime (DMG) , HCl , NH₄OH , K₂S₂O₈ ,Chloroform, Dichloromethane, 1,2-Dichloroethane, Carbon tetra chloride , Benzene , and Toluene from BDH. and Merck companies ,The ligand 2-[(4-Bromo phenyl) azo]-4,5-diphenyl imidazole synthesized [13] .

Procedures

Preparation of standard stock solutions

A solution of Nickel (II) 663 ppm was prepared by dissolving 2.685 gm NiCl₂.6H₂O (0.011 mol) in 1 liter of distillation water containing 1 ml of conc. HCl . A standard solution of 4.7×10^{-5} M of (p-BrPAI) prepared by dissolve 0.0022 gm in 100 ml of CHCl₃. A solution of 1% Dimethyl glyoxime (DMG) prepared by dissolve 1gm in 100 ml of ethanol. A solution of 4% potassium persulphate (K₂S₂O₈) instantaneously prepared by dissolve 4 gm in 100 ml of distillation water.

Calibration Curve

To serious of 50 ml volumetric flask add 5 ml of solution containing a different concentration (1– 70) µg of Ni(II) ,1ml of 1% Dimethyl glyoxime solution , 2ml of 4% potassium persulphate solution. a 5ml of conc. NH₃ solution are added then dilution to the mark with D.W.,and mix well . After 10 minutes , measure the absorbance at 445 nm against D. W.(DMG method) [14],the calibration curve illustrated in **Figure 1**.

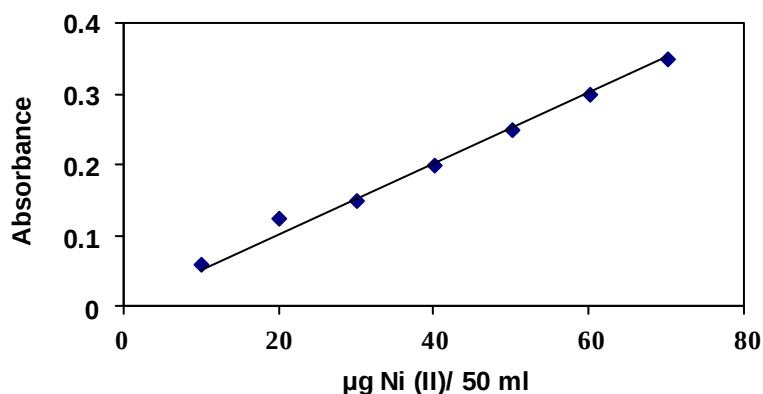


Fig. 1: Calibration Curve of Ni (II)

Extraction of Nickel (II)

A 5ml of aqueous solution of Ni(II) has a specific concentration placed in (25 ml) separating funnel with equivalent volume of organic solution of ligand. Then shake the separation funnel within 10 sec . A two layer was separate.

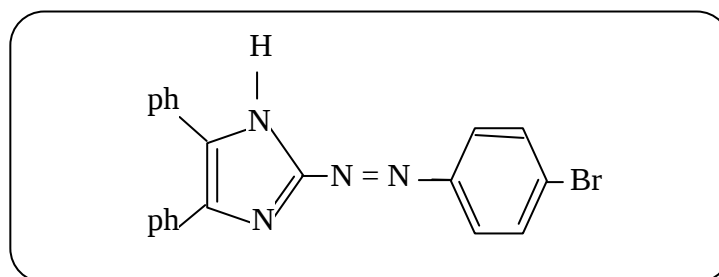


Fig. 2 : Structure Of Ligand Used In Extraction Method

Determination of distribution ratio

A residue of Ni(II) was determinate using spectrophotometric method ,then a value of D was calculated using the relationship below :

$$\text{Distribution ratio (D)} = \frac{\text{Conc. of Ni (II) in organic phase}}{\text{Conc. of Ni (II) in aqua. phase}} \quad [15,16].$$

Results and Discussion

Table 1 and **Figure 3** show that the optimum value of pH extraction was ($\text{pH}_{\text{ex}}=9$) . At pH less than optimum value caused an protonation of the imidazole molecule ligand which caused to occupy the pair of electron and then cannot coordinate strongly with Ni (II) ions and give less stable ion pair complex and minimize the distribution ratio (D),also at pH value more than optimum value and a decrease in the distribution ratio (D) by reason increase concentration of $[\text{Ni}(\text{p-BrPAI})]^{+2}(\text{HO}^-)_2$ complex this complex more soluble in aqueous phase

and less extracted to organic phase and sovereignty the dissociation equilibria [2]. The optimum concentration of Ni (II) ions in aqueous phase, which is (80µg) (2.73×10^{-4} M) was illustrated by **Table 2 and Figure 4**. Due to that conc. which was giving highest distribution ratio .The conc. of Ni(II) ions less than optimum conc. not allowed to reach the equilibria therefore, the value of D minimizes, according to Lechatlier principle [17] . These results demonstrate the effect of metal ion conc. on the equilibria of complexation reaction



Table 3 and Figure 5 show that the best time for shaking was 10 minutes , and at this time show that the complex reach the equilibrium state, and it was adopted in a residue of experiments. The study of effect of P-BrPAI concentration on the extraction process illustrated in **Table 4 and Figure 6** that probability forming specie enable for extraction $[\text{Ni}(\text{p-BrPAI})]^{+2}\text{Cl}_2$, from the slop of straight line of these specie , that the more probable structure of ion pair complex extracted was (1 : 1) (metal : ligand).The results in **Table 5** show that there is no linear relationship between dielectric constant of organic solvents and distribution ratio (D) of extraction ,but there is an effect for the structure of organic solvent. **Tables 6 and 7** demonstrate values of free energy of transition of ions from aqueous phase to organic phase and the ΔH_{ex} values shows that the extraction of Ni(II) decrease with increasing temperature (i.e process is exothermic) from study different heat degree (20 C⁰ - 70 C⁰) depending on (Vant- Hoff) relationship [18] , while

$$\log K_{\text{ex.}} = \frac{-\Delta H}{2.303RT} + \text{Constant} \dots\dots(1)$$

The log K_{ex.} verses (1/T k⁰) show the slope equal to $\frac{-\Delta H}{2.303R}$ from this relationship calculate

the Value $\Delta H_{\text{ex.}} = -28.417 \text{ kJ. mole}^{-1}$

$$\Delta G_{\text{ex.}} = -RT \ln K_{\text{ex.}} \dots\dots(2)$$

and

$$\Delta G_{\text{ex.}} = \Delta H_{\text{ex.}} - T\Delta S_{\text{ex.}} \dots\dots(3)$$

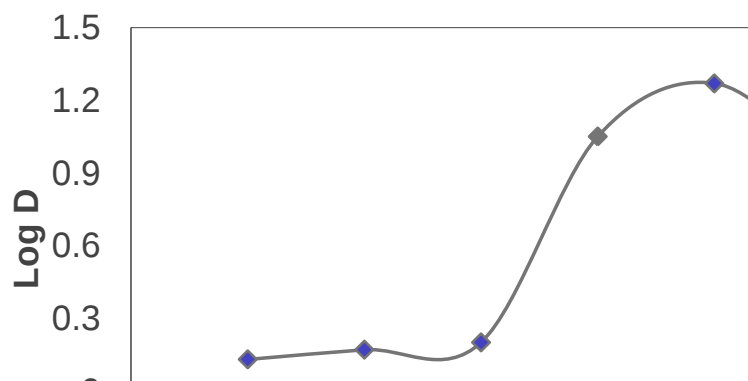
We used log D instead of log K_{ex.} after application of these relations , the values of Gibbs free energy and entropy values show in Table (7) ,this result suggested that the extraction of Ni(II) is easy and the negative value of $\Delta H_{\text{ex.}}$ and this mean decrease in value of $\Delta H_{\text{solv.}}$ and increase of $\Delta H_{\text{hyd.}}$

$$\Delta H_{\text{ex.}} = \Delta H_{\text{solv.}} - \Delta H_{\text{hyd.}} \dots\dots(4) \text{ [15,16].}$$

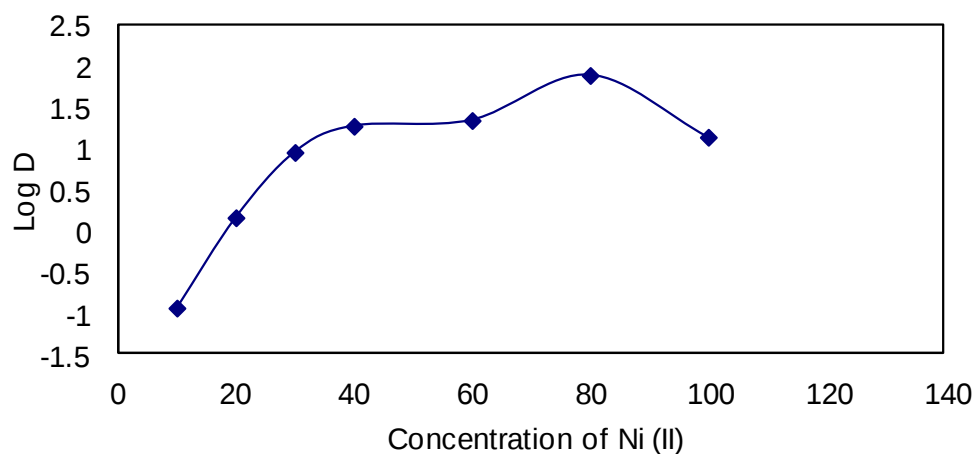
While at low heat degree (0 C⁰ , 10 C⁰) decreasing the distribution ratio.

Table 1: Effect of pH on Extraction of Ni(II) Ions

pH	5	6	7	8	9	10	11	12
D	1.35	1.5	1.6	11.3	25.6	8.4	----	----
Log D	0.13	0.17	0.20	1.05	1.40	0.92	----	----

**Fig. 3:** pH Effect on The Extraction of Ni(II) Ions**Table 2 :** Effect of Ni(II) Ions Concentration on The Extraction Method

$\mu\text{g Ni (II)}$	10	20	30	40	60	80	100	120	200
ppm	2	4	6	8	12	16	20	24	40
D	0.1	1.42	9	19	22	79	13.7	----	-----
Log D	-0.95	0.153	0.95	1.27	1.34	1.89	1.136	----	-----

**Fig. 4 :**The Effect of Ni(II) Ions Concentration on The Extraction Method**Table 3 :** Effect of Shaking Time on Extraction of Ni(II) Ions

Time(Min.)	5	10	15	20	25	30
D	8.69	79	68.5	63	7.8	13.5
Log D	0.93	1.89	1.83	1.79	0.89	1.13

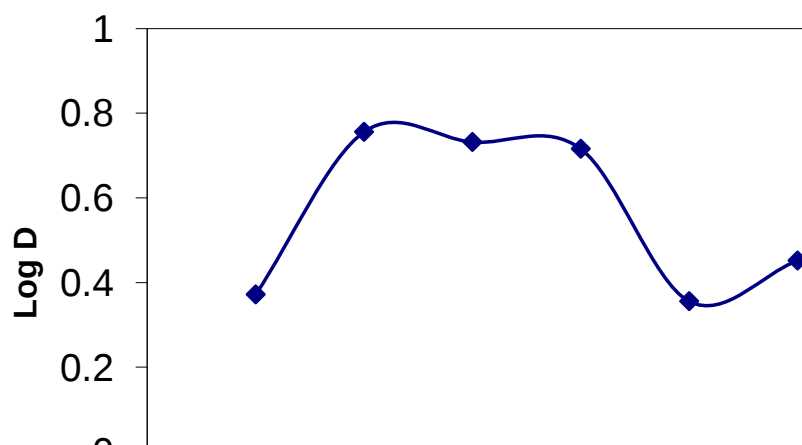


Fig. 5: The Effect of Shaking Time on The Extraction Method

Table 4 : Effect of Ligand Concentration on The Extraction Method

[Ligand] x 10 ⁻⁵ M	1	2	3	6	8	10
D	6.61	17.8	79	39	52	78.5
Log D	0.82	1.25	1.89	1.59	1.71	1.89

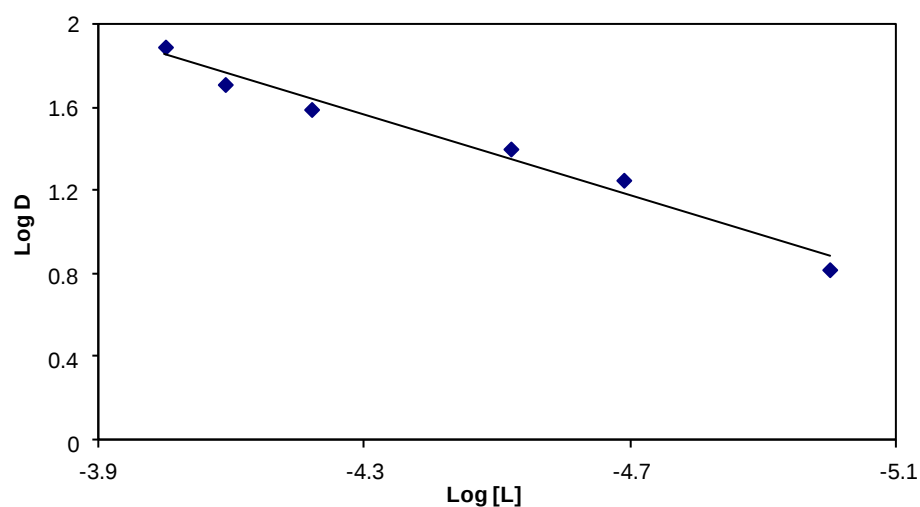


Fig. 6: The Effect of Ligand Concentration on The Extraction Method

Table 5: Effect of Organic Solvent on The Extraction of Ni(II) Ions

Organic solvent	ϵ	D
1,2-Dichloro ethane	10.65	7
Chloroform	5.807	79
Toluene	2.438	9.6
Carbon tetra chloride	2.38	4.3
Benzene	2.804	8
Dichloro methane	9.08	5.4

Table(6) : Effect of Temperature on The Extraction of Ni(II) Ion

T °C	T °K	1/T °K x10 ⁻³	D
0	273	3.6	2.4
10	283	3.5	4
20	293	3.4	79
30	303	3.3	4.92
40	313	3.2	3.44
50	323	3.1	2.33
60	333	3	1.75
70	343	2.9	1.53

Table 7 : Gibbs Free Energy and Entropy Values of Extractions in Different Temperature

T k ⁰	ΔH_{ex} KJ mole ⁻¹	ΔG_{ex} KJ mole ⁻¹	ΔS_{ex} J mole ⁻¹
293	-28.417	-10.624	60.726
303		-4.006	80.564
313		-3.208	80.539
323		-2.265	80.965
333		-1.545	80.696
343		-1.209	79.323

References

- 1) Giridhar P, Venkatesan K A, Srinivasan T G, and Vasa Dera Rae PR. *J . Nuclear and Radichemical Science*.(2004), 5, 2: 21-26.
- 2) Ali I R. M.Sc. Thesis , Chemistry Department , Collage of Education for Girls , University of Kufa (2005).
- 3)Lenarcik B. The Comparison Of The Extraction Process of Zn (II) and Ni (II) Complexes With 1-Octylimidazole And1-Octyl-2-Methylimidazole. XVIIIth ARS Separatoria-Zloty Potok , Poland.(2003).
- 4) Hassan A K. M.Sc. Thesis , Chemistry Department , Collage of Education for Girls , University of Kufa. (2006).
- 5) Payer C A, and Ahamirano E B. *J. Inorganic Chemistry Communication*. (2006), 9, 901-906
- 6) Apro-Torok I. Ph.D. Thesis , Inorganic and Analytical Chemistry Department, university of Szeged . (2002).
- 7) Erden I and Demirhan N. *J. Uni Avecata Separation Science and Technology*. (2006), 36,559-562.
- 8) Dallali N, Zahedi1 M M, and Yamini Y. *J.Scientia Iranica*. (2007),14, 4, 291-296.
- 9) Jose´ J, Campos G , Herbert H, and Miguel P H. *J. Inorganic Chimica Acta*. (2008),361, 248-254.
- 10)Daniel V, Paone A, Anthony W, and Shaw A. *J. Tetrahedron Letters*. (2008), 49, 6155–6159.
- 11) Abdul Muttalib Z. M.Sc. Thesis , Chemistry Department , Collage of Education for Girls , University of Kufa (2006).
- 12) Kumar S K, Rao P S, Krishnaiah L, Jayarj B, and Chiranjeevi P. *J. Analytical Science*. (2004), 20,95,4323-4333.
- 13) Ali A R, and Karim A K. *J. Kufa for Chem. Science* . (2010), 1,1,431- 443.

- 14)** Marczenko Z . Separation and Spectrophotometric Determination of Elements . John Wiley and Sons Company. Inc. 4th Eddition. England **(1976)**.
- 15)** Maki N F. M.Sc. Thesis , Chemistry Department , Collage of Science , University of Babylon. **(2000)**.
- 16)** Al. Muraib S. : Analytical Chemistry . 5th Edition . Higher Education and Scientific Research , Iraq. **(1988)**.
- 17)** Al. Muraib S.: General Principal Of Gravimetric Analysis . 5th Edition , Higher Education and Scientific Research , Iraq. **(1988)**.
- 18)** Atkine P.W. : Physical Chemistry. 5th Edition, Oxford University, United Kingdom. **(1994)**.