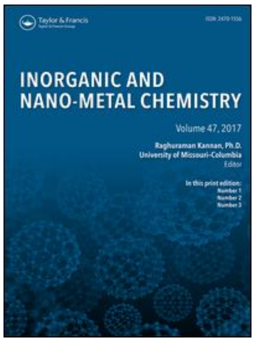


Inorganic and Nano-Metal Chemistry

ISSN: 2470-1556 (Print) 2470-1564 (Online) Journal homepage: http://www.tandfonline.com/loi/lsrt21

Synergistic Extraction of Nickel(II) from Sulfate Medium by a Mixture of N -(2-hydroxybenzylidene)aniline and Methyl-Isobutyl Ketone

S. Almi, F. Adjel & D. Barkat

To cite this article: S. Almi, F. Adjel & D. Barkat (2017): Synergistic Extraction of Nickel(II) from Sulfate Medium by a Mixture of N -(2-hydroxybenzylidene)aniline and Methyl-Isobutyl Ketone, Inorganic and Nano-Metal Chemistry, DOI: 10.1080/24701556.2017.1357612

To link to this article: http://dx.doi.org/10.1080/24701556.2017.1357612

Synergistic Extraction of Nickel(II) from Sulfate Medium by a Mixture of N -(2-hydroxybenzylidene)aniline and Methyl-Isobutyl Ketone

S. ALMI*, F. Adjel and D. BARKAT

Laboratoire de chimie moléculaire et environnement, université de Biskra, Biskra, BP 145, Algérie

*sbenakcha@yahoo.fr

The synergistic solvent extraction of Nickel(II) from sulfate medium with N-(2-hydroxybenzylidene)aniline in the absence and presence of Methyl-Isobutyl Ketone (MIBK) in chloroform at 25°C, has been studied. Synergistic effect is observed for the metal at low and high (MIBK) concentration ratios, respectively. The synergistic extraction of nickel (II) with the mixtures has been investigated with the analysis methods of slope. The extractable species has been identified as NiL_2 and $NiL_2(MIBK)_2$. The extraction constants are reported.

Keywords

Solvent extraction; nickel(II), N-(2-hydroxybenzylidene)aniline; Methyl-Isobutyl Ketone; Synergism.

1. Introduction

The key to an efficient separation process is the development of an extractant with a strong preference for relevant chemical species. Examples of such extractants include macrocyclic Schiff bases. Solvent extraction studies from our laboratory have shown that bidentate Schiff bases such as N-salicylideneaniline were found to be powerful extractants for metal ions, including transition metal [1-4]. These compounds are well known as ligands that are easy to be synthesized and have structural rigidity [5-7]. They show interesting properties, e.g., their catalytic activity in hydrogenation of olefins [8] and transfer of an amino group [9], photochromic properties [10], and complexing ability towards toxic metals [11].

In the present work, we study the solvent extraction of Nickel (II) ions, which is a highly toxic metal ion that is readily encountered in the environment [12–14]. The extraction of Ni(II) is vulnerable to third phase formation **[15]**, but the addition of Méthyl-Isobutyl Ketone (MIBK) to the organic phase leads to a synergistic enhancement and improvement of the extraction of this ion. The synergic extraction of metal chelates has been mostly explained by an increase in the hydrophobicity of extracted chelates. By a replacement reaction of water molecules bound to the central metal ion by basic neutral organic molecules: pyridine, Methyl-Isobutyl Ketone (MIBK), trioctylphosphine oxide (TOPO), tri-n-butyl phosphate (TBP), etc. [16] or by hydrogen-bonding between metal chelates and phenol derivatives in the organic phase [17].

2. Experimental

2.1.Chemicals and apparatus

All of the chemicals and solvents used for the synthesis of the ligand were of commercially available reagent grade and they were used without purification. Chloroform was pre-equilibrated with aqueous solution. NiSO4, 6H2O was purchased from Fluka. Infrared spectra were recorded as KBr discs on a SHIMADZU, FTIR-8400S spectrophotometer in the 4000–400 cm^{-1}. UV–Vis spectra were recorded on a PYEUNICAM SP6-350 (PHILIPS) spectrophotometer in the range 400–1100 nm. The powder X-ray diffraction pattern of the complex was scanned in the range 3–40°(h) with a D8 Advance-Brucker using a CuK$_\alpha$ line at 0.1540 nm in steps of 0.03 at scan speed 2°/min.

The calculation was carried out with GAUSSIAN 09W software package (19). The optimization of the geometry was performed employing density functional theory (DFT) with Becke three-parameter hybrid functional combined with Lee-Yang-Parr correlation functional (B3LYP) (20) with the standard 6-311G(d,p)/basis sets.

2.2. Synthesis of Schiff base ligands

The N-(2-hydroxybenzylidene)aniline (HSA) was synthesized by literature procedure (21). Refluxing equimolar quantities of salicylicaldehyde and aniline dissolved in minimum pure ethanol (figure 1) is done inside a balloon tricol provided with a magnetic stirrer, a cooling agent, and a graduated thermometer. The unit is maintained with backward flow and under agitation for approximately 2 h. The mixture is cooled at room temperature and then concentrated by the elimination of solvent using a rotary evaporator. The solid product (Yellow crystals) obtained is filtered and then recrystallized in minimum pure ethanol with Yield = 80 (%).

2.3. Extraction and analytical procedure

An aqueous nickel solution (40 ml, $[Ni^{2+}] = 6.81\times10^{-3}$mol dm^{-3} with $[Na_2SO_4] = 0.33$M) was placed in thermostated vessels at 25°C with an equal volume of chloroform solutions, which pre-equilibrated with aqueous solution contain Na_2SO_4 only, containing 0.4, 0.8 and 1.6 mol dm^{-3} of HSA alone or a mixture of 0.4 mol dm^{-3} of HSA with different concentration of MIBK. The mixture was shaken for 15min. this time was sufficient since the equilibrium was reached rapidly and then both phases were separated by gravity. The pH was adjusted by adding a few drops of 0.2 moldm^{-3} NaOH. After the two phases were separated completely, the metal ion concentrations were determined in aqueous phase photometrically at 720 nm using photoLab® 6100 VIS. The metal ion concentrations in the organic phase were calculated from the difference between the metal ion concentrations in the aqueous phase before and after extraction.

3. Results and discussion

3.1. General treatment of extraction equilibrium of nickel(II) with HSA

The overall reaction in the extraction of nickel(II) with chelating extractant (HSA), in chloroform from sulphate aqueous medium of ionic strength I=1.0 mmol g^{-1} ($[Na_2SO_4] = 0.33$M), may be expressed as

$$Ni^{2+} + (n+m)HL_{org} \overset{Kex}{\leftrightarrows} NiL_n(HL)_{m\,org} + nH^+$$

Where the subscript org correspond to the organic phase. The distribution ratio D of nickel is defined as

$$D = \frac{\left[Ni^{2+}\right]_{org}}{\left[Ni^{2+}\right]} \quad \text{(Eq1)}$$

The extraction constant, K_{ex}, is defined as equation (2) and it can be rewritten as equation (3) by using the distribution ratio, D, of the metals.

$$K_{ex} = \frac{\left[NiLn(HL)_m\right]_{org}\left[H^+\right]^n}{\left[Ni^{2+}\right]\left[HL\right]_{org}^{n+m}} \quad \text{(Eq2)}$$

$$\log D = \log\frac{\left[Ni^{2+}\right]_{org}}{\left[Ni^{2+}\right]} = \log K_{ex} + (n+m)\log\left[HL\right]_{org} + npH \quad \text{(Eq3)}$$

Equation (3) show that the function log D=f(pH) at a constant $[HL]_{org}$ or logD=f($[HL]_{org}$) at a constant pH, should yield a straight line with a slope of n and n+m, respectively.

The efficiency of extraction of metals E % in the case where the volumes of the two phases are equal (A/O) = 1, is defined as follows (Eq 4)

$$E\% = 100\frac{D}{D+1} \quad \text{(Eq 4)}$$

3.2. Extraction of nickel (II) with HSA alone:

Preliminary experiments led to the following observations. Virtually no nickel was extracted from sulfate medium into MIBK alone. Therefore we will base, in our study, on the extraction of the Ni (II) by HSA.

The extraction of nickel by HSA was accompanied by a slow development of green color in the organic phase. The intensities of the colors were qualitatively observed to peak at six hours over a wide pH range 6-8. When nickel (I1) were extracted at pH > 8, third phase was detected at the boundary of the aqueous and organic phases. Extensive studies have been conducted on the third phase formation systems, which have been reviewed in detail (21, 22). It is the splitting of organic phase into two phases with the heavier one, rich in metal–solvate and the lighter phase rich in diluent (23). In various extraction systems the third phase formation is troublesome to the operation of the reprocessing processes. For example, it may change the mass transfer and phase separation, and reduce the extraction efficiency.

The formation of the third phase in our system, which decreases the extraction of Ni (II) by HAS, may be due to the hydrolysis of NiSO4, which occurs in this pH range.

S.A. Berger (24) has studied the solvent extraction of nickel (II) with Chlorendic Acid. The author has observed that the slopes of the plots of log D vs. pH, yield fractional values lower than the normally expected integral values of 1.0 or 2.0 for ions of Nickel in the oxidation state of +2. This value depends upon the existence of complexation in the aqueous phase.

Several authors have observed for the extraction of metals using carboxylic acid extractants, the maximum efficiency occurs at pH values just below that for the precipitation of their metal hydroxides (25-27). and it has attributed the lower of the extraction to the existence of a partially hydrolyzed metal species or the presence of other anionic complexing agents which react with the metal in the aqueous phase (28,29) which would form such species as $[M(II)(OH)]^{+1}$ and $[M(II)(X)]^{+1}$.

The stoichiometry of the extracted species in the pH rang 6-8 was determined by analyzing the experimental data by the use of the slope analysis method.

Figure 2 show the results obtained for the extraction of nickel (II) with solutions of various concentration of HSA.

The degree of extraction of Ni(II) (figure 3) increase with increase in pH and the concentration of extractants. The plots of the logD versus pH for Ni cation and for various concentrations of HSA are linear with a slope equal to 2 (n=2), this suggesting exchange of two protons between the metal cation and the extractant by his phenolate group.

According to equation (3), the number of HSA molecules involved in the extracted species can be determined from the slope of the plots of logD=f([HL]) at constant pH. The plots of logD versus log $[HL]_{org}$ at constant pH values are also linear with slopes equal to 2 (as shown in figure 4).

These results give n=2 and m= 0 which are readily replaced in equation (5). This means that the complex extracted is NiL_2 into chloroform.

$$Ni^{2+} + (2)HL_{org} \leftrightarrows NiL_2 + 2H^+ \quad \text{(Eq 5)}$$

The extraction constant obtained is $\log K_{ex}$= -14.75. The structures of the extracted species may be proposed as follows (figure 5).

The complex formed has a structure of an adduct, in which particular places in the coordination sphere of nickel ion is occupied in total by two molecules of extractant.

3.2.1 Electronic spectra

Based on the electronic spectral data, nickel (II) complex, (Figure 6), has the octahedral geometry with its characteristic features. The electronic spectrum of the organic phase showed in addition to the band associated with the transfer of charge occurs at 420 nm which is corresponding to the $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) transition, two author bands. One occurs at 620 nm, which is corresponding to $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) electronic transition and the other located at 950 nm corresponding to the $^3A_{2g} \rightarrow {}^3T_{2g}$ electronic transition. The three transitions are consistent with a distorted octahedral geometry with two water molecules at an axial position of the complex. (30)

3.2.2 IR spectra and mode of bonding

In order to study the binding mode of the ligand with the metal ions, a comparison was made between the IR spectra of the free ligands with that of the complex extracted in the organic phase as showed in figure 7. The data (table 1) revealed that the complex formed showed a broad band in the range 3440 cm^{-1} assignable to ν(OH) of the coordinated or uncoordinated water and/or alcohol molecules associated with the complex. In addition, the band at 1615.27 cm^{-1} assigned to ν(C=N) in the free ligand was shifted to lower wave number in the complex, indicating the participation of the azomethine nitrogen in chelation. The band at 1453 cm^{-1} assigned to ν(C–O) in the free ligand was shifted to 1445.47 cm^{-1} in the complexes and the intensity of the band has decreased showing the involvement of the phenolic oxygen in coordination. The new bands observed at 569.92 and 877.75 cm^{-1} are respectively assigned to ν(M-O) and ν(M-N) (Metal-Ligands) stretching bands. (31-33)

3.2.3 DFT studies

In order to gain further insights on the Ni-HSA bonding, we have carried out a theoretical investigation with the density functional theory. The calculated geometrical parameters of the complex found to be in good agreement with the experimental values obtained from the electronic study (Table 2). According to those bond lengths, the structure shown a distorted octahedral geometry involving two bidentate (SA^-), The O-Ni and N-Ni distances are found to be 1.84021 Å and 1.9013 Å, respectively. The H_2O-Ni distances are 3.1145 Å indicate the repulsion between the Ni^{2+} and two water molecules situated at an axial position of the complex. The association energy of this complex is 79.74 kcal/mol.

3.2.4 X-ray diffraction studies

Single crystal of the complex could not be prepared to get the XRD and hence the powder diffraction data were obtained for structural characterization and In order to test the degree of crystallinity of the synthesized metal complex. Powder X-ray diffractograms of free Schiff base ligand and Ni(II) complex show sharp peaks which indicate their crystalline nature. By comparing the X-ray diffractogram of free Schiff base ligand (HL) with its Ni(II) complex, as show in figure 9, the Ni(II) complex shows few new peaks which suggest the formation of metal chelates. X-ray diffraction analysis of the nickel (II) complex confirm the Monoclinic crystal system with Space group P21. Complex has unit cell dimensions a = 7,3080 Å, b =11,0930 Å, c = 12,2380 Å et α =90,0000°, β = 98,0970°, γ= 90,0000°. The crystal of the ligand retained its orthorhombic crystal structure with lattice dimensions a = 27.971Å, b = 5.939Å, c = 12.879Å and $\alpha = \beta = \gamma = 90°$ with non-centro symmetric space group F_{d2d}. (34).

3.3. Synergistic extraction of nickel(II) with HSA and MIBK:

In the synergistic extraction of nickel (II) with a mixture of HSA and methyl-isobutyl ketone (MIBK), the extraction equilibrium and the synergistic extraction constant K_{syn}, can be expressed by

$$M^{n+} + (n+m)(HL)_{org} + p(MIBK)_{org} \leftrightarrows ML_n(HL)_{m,\ org}(MIBK)_{p,\ org} + nH^+ \quad \text{(Eq 6)}$$

$$K_{syn} = \frac{\left[ML_n(HL)_{m,org}(MIBK)_{P,org}\right]\left[H^+\right]^n}{[M^{n+}]\left[(HL)_{org}\right]^{(n+m)}\left[(MIBK)_{org}\right]^p} \quad \text{(Eq 7)}$$

The equation (7) shows that the plots of log D against pH at constant $[(HL)_{org}]$ and constant $[(MIBK)_{org}]$ should consist of straight lines with slope 2. Typical plots for the extraction of nickel(II) from 0.33M sodium sulfate solution by mixture of HSA and methyl-isobutyl ketone in chloroform are shown in figure 6. The slopes obtained 2.00 confirm the expected second-order dependence of metal distribution upon pH.

As illustrated in figure 6, the addition of methyl-isobutyl ketone causes an enhanced extraction of nickel (II) for all MIBK concentration; this means that MIBK gives a synergistic effect for these concentrations.

The addition of MIBK to the solvent leads to a synergistic enhancement and improvement of the extraction of Ni(II). However, no formation of third phase was observed.

$\Delta pH_{1/2}$ Values was determined from extraction isotherms in figure 10, using equation (8) :

$$\Delta pH_{1/2} = pH_{1/2}(HSA) - pH_{1/2}(HSA + MIBK \quad \text{(Eq 8)}$$

It can be seen from table 3, that $\Delta pH_{0.5}$ is significantly higher when using a mixture of HSA and MIBK compared to HSA alone. The most selective extraction results can be achieved by HSA to MIBK concentration ratio of 0.4 M/5M (HSA/ MIBK) in which the $\Delta pH_{1/2}$ increases from 0.15 for 0.4 M HSA to more than 1. Figure 11 illustrates the effect of adding MIBK as synergist on $pH_{1/2}$. It is observed that $pH_{1/2}$ values decreases with increasing MIBK concentration added to HSA. In addition, it can be inferred from figure 11 that the extraction efficiency was higher with MIBK concentration equal to 5M.

The number of MIBK molecules involved in the extracted species can be determined from the slope of the graph log D against $\log[MIBK]_{org}$, at constant pH and [(HL)]. As figure 11 shows, the plot yielded a straight line with a slope of 2.00. Thus, the number of MIBK involved in the extracted complex is two. There is, therefore, a complex extraction of type $NiL_2(MIBK)_{2org}$. From above results, the equation for the synergistic extraction equilibrium of nickel(II) is considered to be

$$Ni^{2+} + 2(HL)_{org} + 2(MIBK)_{org} \leftrightarrows NiL_2(MIBK)_{2org} + 2H^+ \quad \text{(Eq 9)}$$

The extraction constant obtained is $\log K_{syn} = -13.51$. The formation of $NiL_2(MIBK)_{2org}$ is due to the replacement by MIBK of two water molecules at an axial position of the Ni-complex (figure 12).

The synergistic enhancement coefficient SC, was calculated by the following equation (Eq. 10). [35]

$$SC = \log\left(D_{mix} / \left(D_{HSA} + D_{MIBK}\right)\right) \quad \text{(Eq 10)}$$

where D_{HSA}, D_{MIBK} and D_{mix} represents distribution coefficients of the nickel with the two extractants HSA and MIBK obtained separately and with their mixture.

Table 4 shows the values of SC at different concentrations of MIBK for 6.99 pH value. At the constant pH, SC was increased with increasing in MIBK concentrations. The largest synergistic coefficient was 16.49 for (0.4 M HSA/5 M MIBK) system. Therefore, in the extractant mixture, the mixed-ligand complex of Ni(II) with HSA and MIBK contributed to the increased extraction of Nickel compared to the complex of Nickel with HSA alone.

K. K. Sahu et al. (36) reported the extraction of iron (III) from acid chloride solutions with methyl isobutyl ketone (MIBK), tri-n-butyl phosphate (TBP) and di(2-ethylhexyl) phosphoric acid (D2EHPA). On comparing the extraction of iron (III) with mixed and individual extractant, it was found that both D2EHPA-MIBK and D2EHPA-TBP mixtures exhibit synergism, the latter having better extraction ability. An increase in the concentration of MIBK and TBP in the mixed organic resulted in higher synergistic coefficient. Stripping of iron (III) from D2EHPA-MIBK loaded solvent is better than D2EHPA-TBP. The study shows the incorporation of one molecule of MIBK in the iron (III) species extracted from D2EHPA-MIBK system, and the extracted species was $ClFeR_2 . L_{(org)}$.

According to the study of the electronic absorption spectral for the complex in the presence and absence of MIBK (figure 14), the nickel extracts are octahedral coordination compounds. The complex shows two weak bands in the regions 907–946 and 617–650 nm, in addition to ligand bands (37). The positions of these bands suggest that these complexes have distorted octahedral stereochemistry . T. ZHU (38) explains the existence of much large number of Ni(ll) octahedral coordination compounds compared to its other configuration complexes. Moreover, it has been confirmed by many authors that certain quantity of water always extracted with nickel (39-41). Thus, nickel (II)-HSA complex in chloroform is characterized by distorted octahedral structure involving two bidentate (SA^-) with two water molecules at an axial position.

It is found by Preston [42] that during the extraction of nickel with organophosphorous acids, the extraction was enhanced by the addition of isodecanol or nonylphenol to xylene diluent. This is in agreement with the present study in that the diluent substitutes with a water molecule in the complex.

The synergic extraction of metal chelates has been mostly explained by an increase in the hydrophobicity of extracted chelates by this replacement reaction of water molecules bound to the central metal ion by basic neutral organic molecules, such as Methyl-Isobutyl Ketone (MIBK).

4. Conclusion

The solvent extraction of nickel(II) from sulphate medium with N -(2-hydroxy-benzylidene)aniline (HL) in chloroform in the absence and presence of methyl-isobutyl ketone (MIBK) in chloroform was studied and the following information was obtained. In the absence of the synergic agent MIBK, the extracted species is NiL_2, and in its presence, the extracted species is $NiL_2(HL)_2(MIBK)_{2org}$. The addition of MIBK to the system of extraction of nickel leads to a synergistic enhancement and no formation of third phase was observed. The increase in the hydrophobicity of extracted chelates by the replacement of water molecules by MIBK, has been taken into account to explain the synergic effect.

References

[1] M. H. Youcef, D. Barkat, T. Benabdellah. J. Saudi Chem. Soc., Vol. 10, No.1, pp. 15-20 (2006).

[2] Y. Boukraa, D. Barkat, T. Benabdellah, A. Tayeb and M. Kameche. Physics and Chemistry of Liquids., Vol. 44, No. 6, 693-700(2006).

[3] D. Barkat and M. Kameche. Physics and Chemistry of Liquids., Vol. 45, No. 3, 289-293(2007)..

[4] A. Aidi, D. Barkat. Journal of Coordination Chemistry., Vol. 63, No. 23, 4136- 4144 (2010).

[5] J. Stary, The Solvent Extraction of Metal Chelates, Pergamon Press, Oxford, (1964).

[6] Y. Marcus, A.S. Kertes, Ion Exchange and Solvent Extraction of Metal Complexes , Wiley London, (1969).

[7] T. Sekine, Y. Hasegawa, Solvent Extraction in Chemistry, Marcel Dekker, New York, (1977).

[8] G. Henrici-Olive, S. Olive, The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide, Springer, Berlin, (1984).

[9] H. Dugas, V. Penney, Bioorganic Chemistry, Springer, New York, 1981.

[10] J.D. Margerum, L.J. Miller, Photochromism, Interscience, Wiley, NewYork, (1971).

[11] W.J. Sawodny, M. Riederer, Addition compounds with polymeric chromium(II)– Schiff bases complexes, Angew. Chem. Int. Ed. Engl. 16 (12) (1977) 859–860.

[12] K.H. Chu, M.A. Hashin, J. Ind. Eng. Chem. 9 (2003) 163.

[13] T.Y. Kim, S.J. Kim, J.H. Yang, S.Y. Cho, J. Ind. Eng. Chem. 10 (2004) 201.

[14] C. Jeon, S.H. Yeom, J. Ind. Eng. Chem. 12 (2006) 362.

[15] A. Suresh, C. V. S. Brahmananda Rao, K. N. Sabharwal, T. G. Srinivasan, P.R. Vasudeva Rao, Third phase formation in the extraction of Nd(III) by octyl (phenyl)-N,N-diisobutyl carbamoyl methylphosphinoxide (O_CMPO), Solvent Extr. Ion Exch. 17 (1) (1999) 73–78.

[16] T. Sekine and Y. Hasegawa, “Solvent Extraction Chemistry”, (1977), Marcel Dekker, Inc., New York andB asel.

[17] S. Katsuta, Bunseki Kagaku, (1995), 44, 1001.

[18] Gaussian 09 program, Gaussian Inc., Wallingford, CT, 2009.

[19] (a) M.A.D. Becke, Phys. Rev. A 38 (1988) 3098; (b) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785

[20] D. M. Hurwitz, US Patent 2,582,128, Jan. 8, Chem. Abstr., 46, 8146 (1952).

[21] Rao, P.R.V.; Kolarik, Z. (1996) A review of third phase formation in extraction of actinides by neutral organophosphorus extractants. Solvent Extr. Ion Exch, 14 (6): 955–993.

[22] Testard, F.; Bauduin, P.; Zemb, T.; Berthon, L. (2010) Third-phase Formation in Liquid=Liquid Extraction: A Colloidal Approach. In: Ion Exchange and Solvent Extraction, Moyer, B.A. eds.; CRC Press: Boca Raton, FL; Vol. 19, 381–428.

[23] P.R. Vasudev Rao, Z. Kolarik, A review of third phase formation in extraction of actinides by neutral organophosphorus extractants, Solvent Extr. Ion Exch. 14 (6) (1996) 955–993.

[24] S. A. Berger, The Liquid-Liquid Extraction of Nickel(II) and Cobalt(II) with Chlorendic Acid, Mikrochimica Acta, (1982) II, 125--132

[25] A. W. Fletcher and D. S. Flett, J. Appl. Chem. 14, 250 (1964).

[26] A.W. Fletcher and D. S. Flett, Carboxylic Acids as Reagents for the Solvent Extraction of Metals, presented at the International Conference on the Chemistry of the Solvent Extraction of Metals, Harwell, England, (1965).

[27] A. W. Ashbrook, Carboxylic Acids as Extractants for the Separation of Metals in Commercial Solvent Extraction Operations, Annual Meeting of the AIME, San Francisco, 22, (1972).

[28] A. M. Poskanzer and B.M. Foreman, J. Inorg. Nucl. Chem. 16, 323 (1961).

[29] 9 y. Marcus and S. Kertes, Ion Exchange and Solvent Extraction of Metal Complexes, New York: Wiley. (1970). p. 454.

[30] Maria Atanassova and Ivan Ljubomirov Dukov, Synergistic Solvent Extraction of Trivalent Lanthanoids with Mixtures of 1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone and Crown Ethers, *Acta Chim. Slov. (2006), 53, 457–463.*

[31] G. G. Mohamed, Z. H. Abd El-Wahab, Salicylidene-2-inobenzimidazole Schiff Base Conmplexes of Fe(III), Co(II), Ni(II), Cu(II),Zn(II) AND Cd(II), J. Ther Analy Calo, (2003) 73 347.359.

[32] R.A. Lal , S. Choudhury , A. Ahmed, M. Chakraborty, R. Borthakur and A.

Kumar, Journal of Coordination Chemistry Vol. 62, No. 23, (2009), 3864–3874

[33] T. ZHU, Min. Pro. En . Met. Rev.. Vol. 21. pp. 1-24.

[34] J. R. Dyer, Applications of Absorptions Spectroscopy of Organic Compounds; Prentice-Hall of India, New Delhi (1984); A. C. Hiremath, Z. S. Qureshi, K. M. Reddy and M. B. Halli, Indian J. Chem. Soc., Sec. A, 30 (1991) 293.

[35] R. Destro, A. Gavezzotti, M. Simonetta, Salicylideneaniline, Acta Crystallo- gr. B 34 (1978) 2867–2869.

[36] K. K. Sahu, R. P. Das, Mixed solvent systems for the extraction and stripping of iron (III) from concentrated acid chloride solutions. Metallurgical and Materials Transactions B, (2000) 31 (6). 1169-1174.

[37] J. A. Dean, Lange`s Handbook of Chemistry: 14th Edition, McGraw-Hill, New York (1992).

[38] H.F. Al-amary, Synthesis, investigation of some mixed ligand chelates and their biological activity. M.Sc. Thesis, Benghazi: Garyounis University (2004).

[39]Yuan Chcnye, Xu Qingren, Yuan Shengang, Long Haiyan, Feng Hanzhen. Wu Fubing and Chen Wuhua (1988). Solvetlr E.vrra. Ion Exch., 6(3), 363-416.

[40] Danesi, P. R., Reichley-Yinger. L., Kaplan, M. L., Horwitz, E. P. and Diamond, H. (1985). Solvenr Elrrr. Ion E.~ch., 3(4), 435-452.

[41] Zhou Naifu, Wu Jinguang, Sarathy, P. K., Liu Fuan and Neuman, R. D., Solvenr Esrraction Proc. ISECPO, Kyoto, Ed. Sekine T., Part A, Elsevier, (1990), pp. 165-170.

[42] J. S. PRESTON, SOLVENT EXTRACTION OF COBALT AND NICKEL BY ORGANOPHOSPHORUS ACIDS, I. COMPARISON OF PHOSPHORIC, PHOSPHONIC AND PHOSPHINIC ACID SYSTEMS; Hydrometallurgy, 9 (1982) 115-133.

Table 1: Vibration spectral data for free ligand (HSA) and the Ni/complex in KBr disk (cm^{-1}).

	O-H	**C=N**	**C-O**	**M-O**	**M-N**
Ligand seul	3448. 2	1615.27	1453	-	-
Nickel/ligand	3440	1606	1447.47	569.92	877.75

Table 2: Selected bond lengths (angstroms) for nickel complex.

C-N1	C-O	M-N1	M-O	M-OH$_2$(1)	M-OH$_2$(2)
1.30354	1.31431	1.90133	1.84021	3.1145	3.1126

Table 3: pH1/2 value in the extraction of nickel for different mixtures of HSA and MIBK at 25°C.

Molar ratio of HSA/MIBK	**$PH_{1/2}$**	**Δ $PH_{1/2}$(HSA-mixture)**
0.4	7.72	0.00
0.4/0.4	7.57	0,15
0.4/0.8	7.4	0,32
0.4/1.6	7.32	0,4
0.4/2	6.99	0.73
0.4/5	6.55	1.17

Table 4: Values of the synergistic coefficients ([HSA]=0.4 M) for different MIBK concentrations at pH value equal 6.99

[MIBK]	**SC**
0.4	0,26872
0.8	0,55219
1.6	0,69403
2	1,2598
5	2,10115

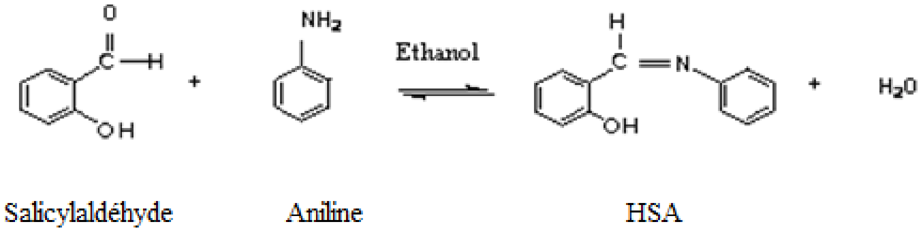


Figure 1: Schematic of the synthesis reaction of the Schiff Bases.

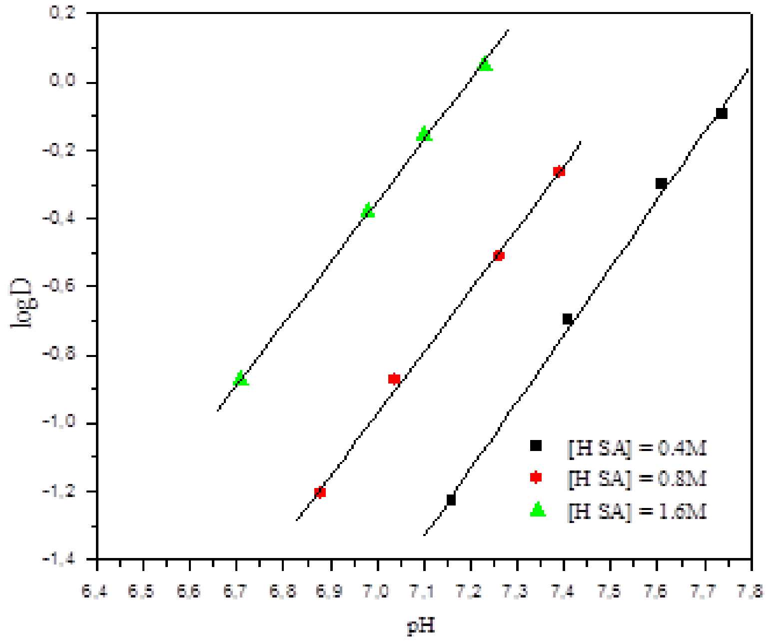


Figure 2: pH effect on the Ni^{2+} extraction with HSA, in chloroform.

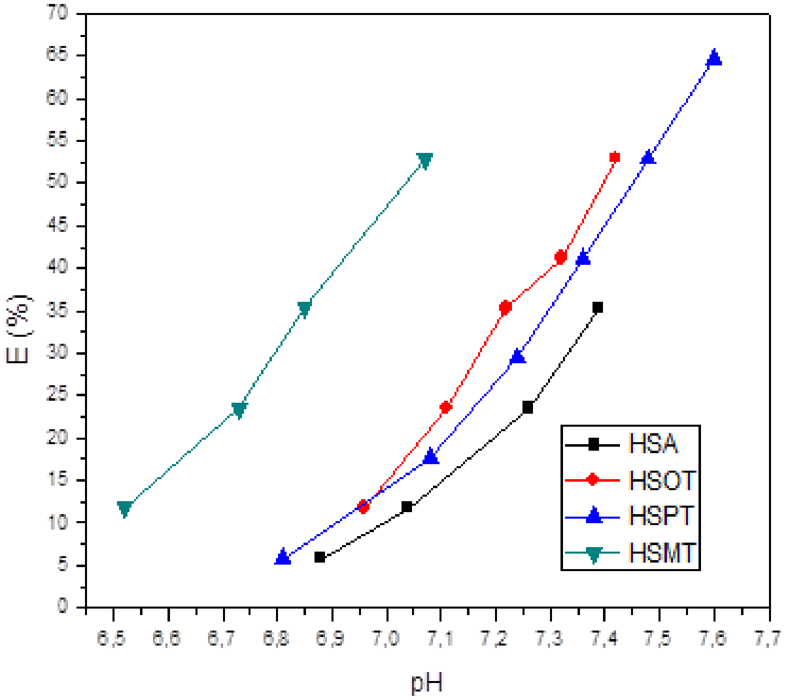


Figure 3: The efficiency of extraction of Ni(II) with HSA, in chloroform

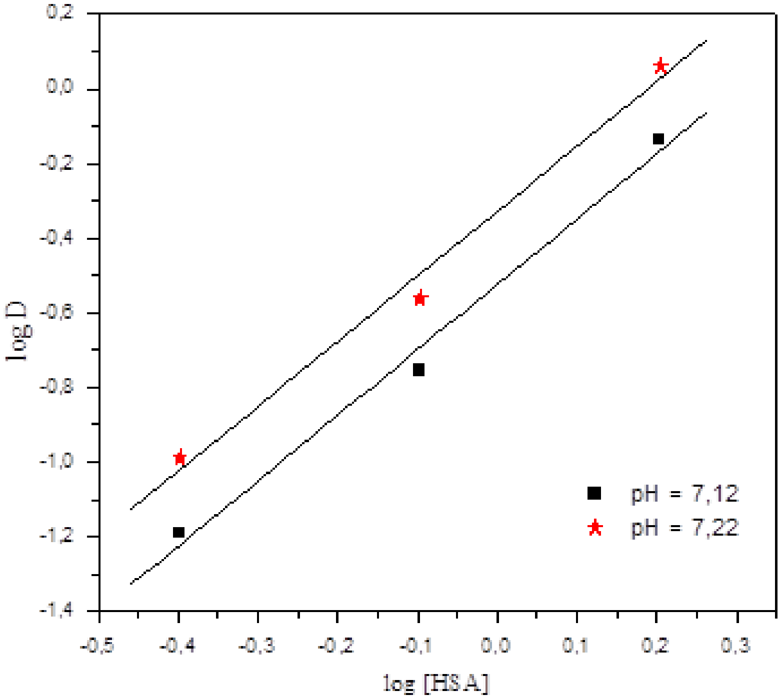
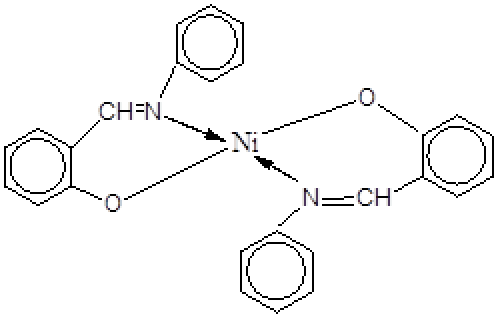


Figure 4: Concentration effect of HSA in chloroform on the Ni^{2+} extraction.



NiL$_2$

Figure 5: Structures of the Ni-complexes of HAS

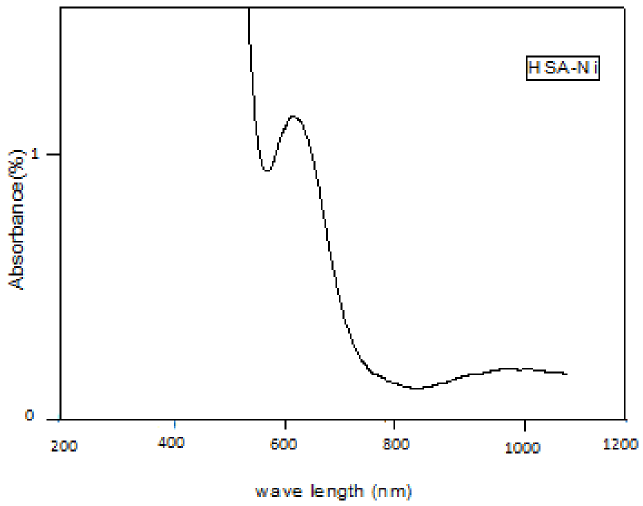


Figure 6: UV-Vis spectra of Ni complex.

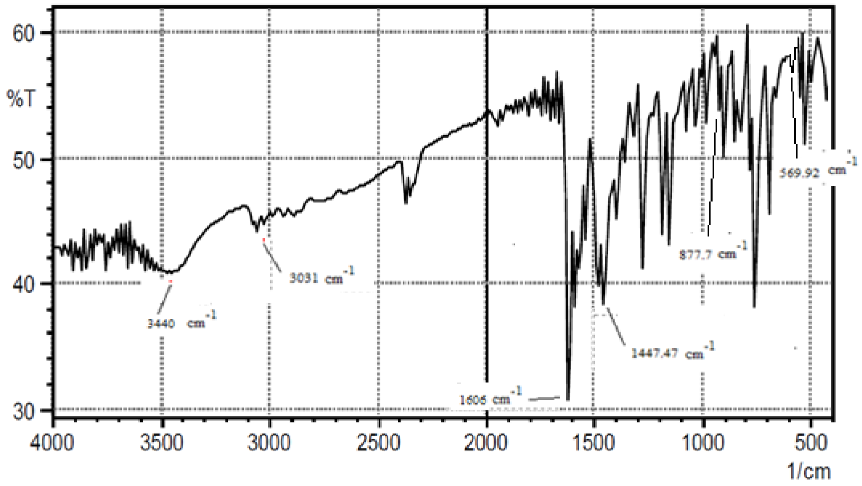
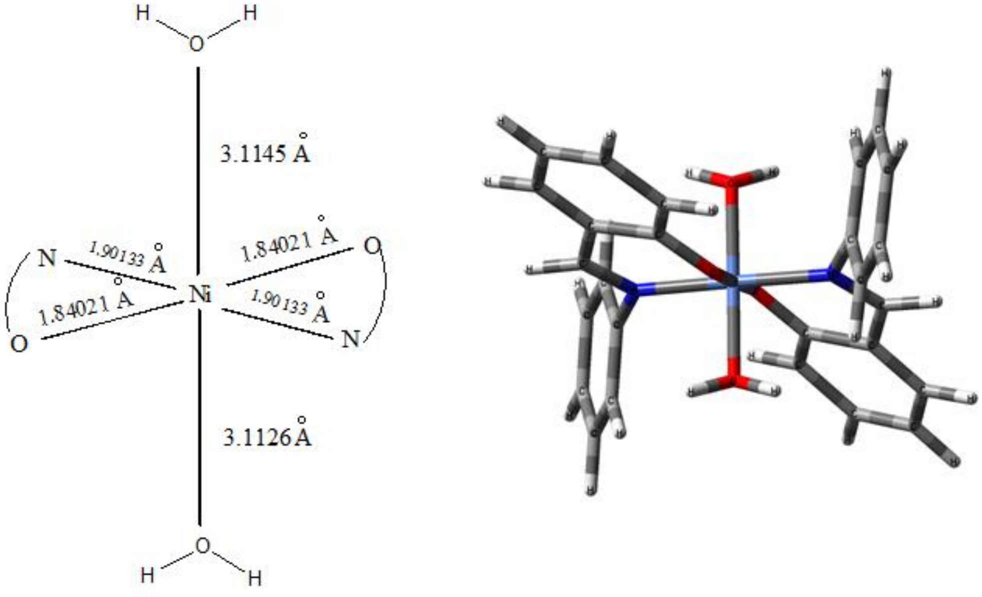


Figure 7: IR spectra of Ni complex.



$NiL2(H_2O)$

Figure 8: Optimization of the geometry of Ni-complex performed with B3LYP 6-311G(d,p).

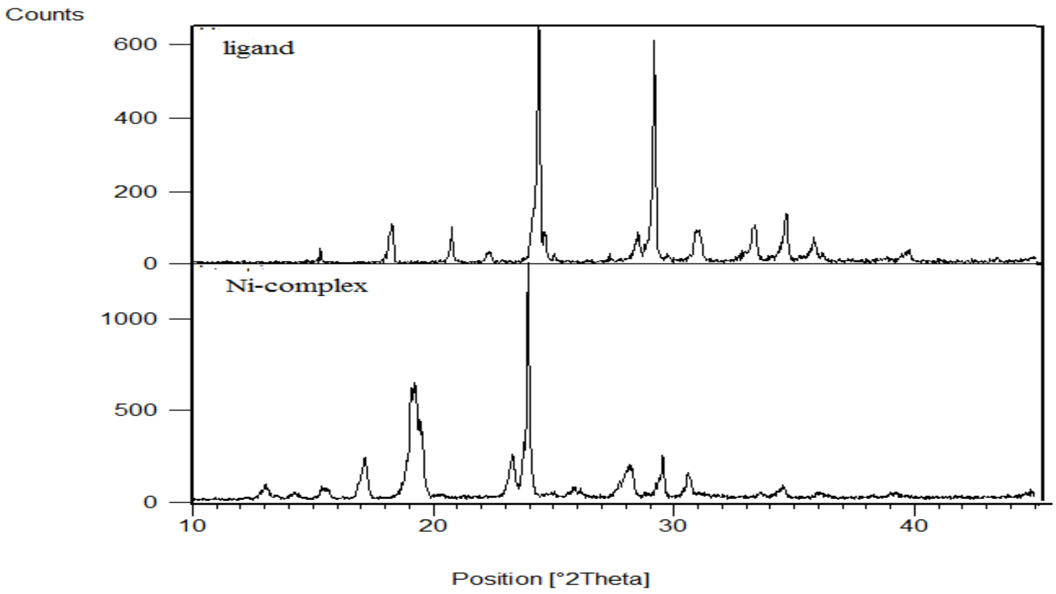


Figure 9: XRD spectrum of HSA crystal and its nickel complex.

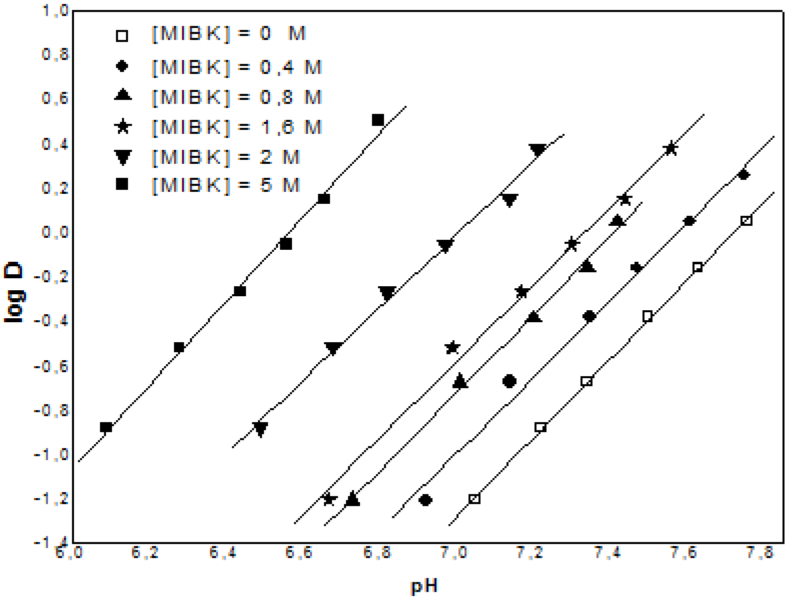


Figure 10: Synergistic effect of MIBK in the extraction of nickel with HSA in chloroform.

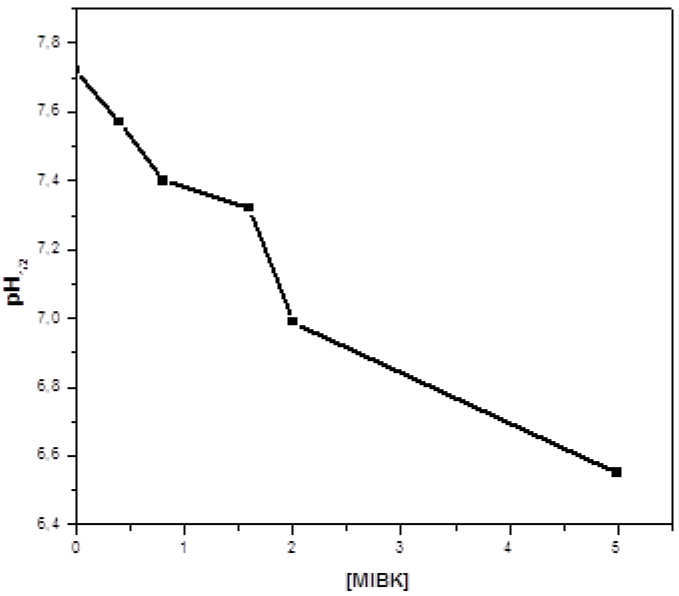


Figure 11: Effect of MIBK concentration on the $pH_{1/2}$

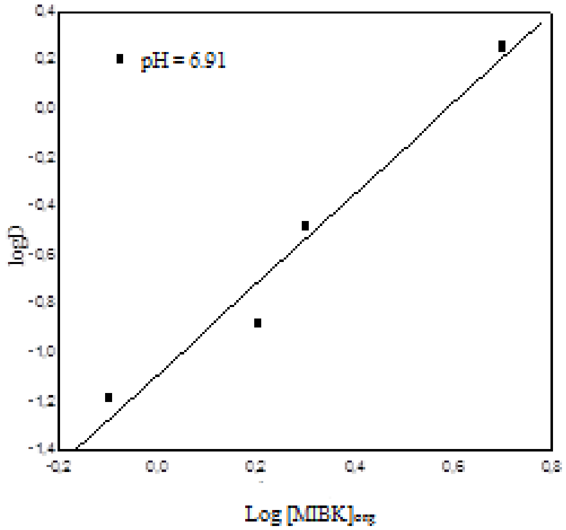


Figure 12: Determination of the number of MIBK's involved in the extracted species.

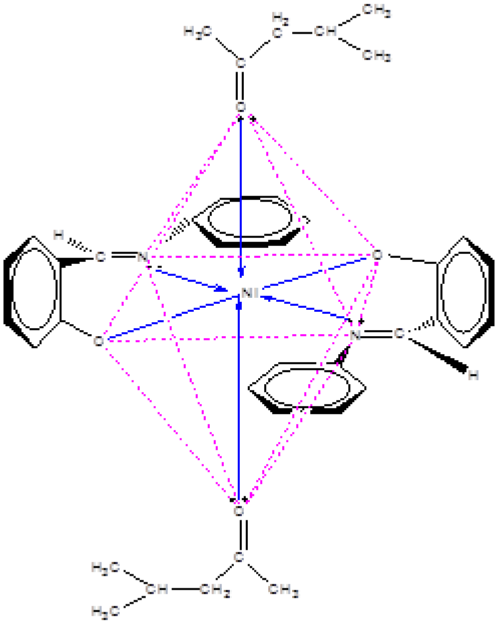


Figure 13: octahedral coordination compounds of Ni(II) in presence of MIBK.

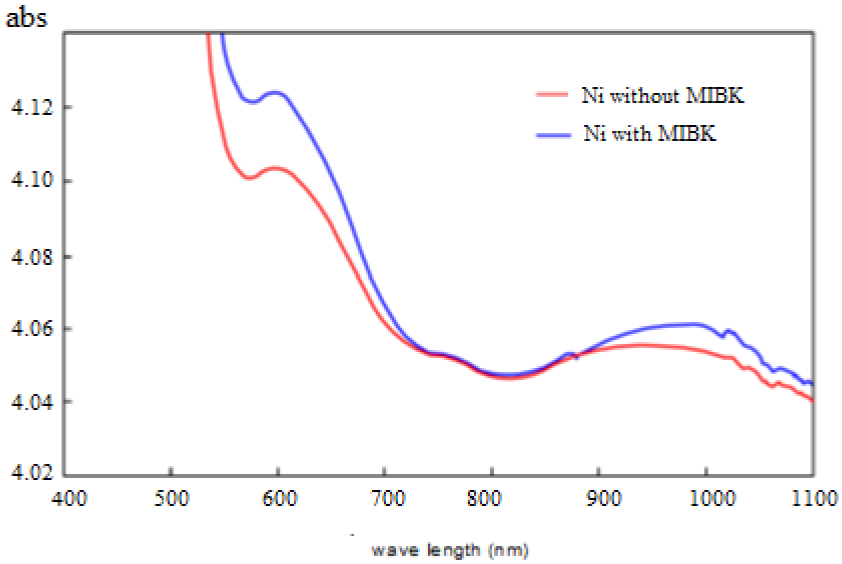


Figure 14: UV-Vis spectra of Ni complex with and without MIBK..