Journal of Chemical Technology and Metallurgy, 58, 5, 2023, 897-905

THERMODYNAMIC STUDY FOR THE REMOVAL OF Ni^{2+} BY LIQUID-LIQUID EXTRACTION IN THE PURIFICATION OF EFFLUENT

Amel Aidi[1,2], Hanane Rehali[1,2], Djamel Barkat[1,3]

[1]Department of Industrial Chemistry
Faculty of Science and Technology
University of Biskra, 07000Biskra, Algeria
[2]Laboratory of LARGHYDE, University of Biskra
Bp 145 RP, Biskra 07000, Algeria
[3]Laboratory of Molecular and Environment Chemistry
Biskra University, 07000 Biskra,Algeria.
E-mail: h.rehali@univ.biskra.dz

Received 01 September 2022
Accepted 18 November 2022

ABSTRACT

The recovery of Ni^{2+} from aqueous solutions is very important for environmental protection. The objective of this work is to study the influence of pH, concentration of the extractant, nature of diluents, and temperature on the solvent extraction of Ni^{2+} ions, which is a highly toxic metal ion that is readily encountered in the environment. The liquid-liquid extraction of Ni^{2+} from sulfate medium of constant ionic strength ($I = 1.0$ mol kg^{-1}) with salicylideneaniline (HL) in cyclohexane at 10, 20, 30, 40, and 50°C has been investigated. By using the slope analysis method, the stoichiometry of the extracted organometallic complex was determined. At the end of this research, we have found that stoichiometry of Ni^{2+} complex is of the type NiL_2. The extraction of this metal increases with increasing temperature. The values of the equilibrium constant have been calculated as well as the values of the thermodynamic parameters $\Delta H°$, $\Delta S°$ and $\Delta G°$.

Keywords: liquid-liquid extraction, environmental, transition metal ions, temperature effect, thermodynamic parameters.

INTRODUCTION

Water pollution is a global problem that threatens the entire biosphere and affects the lives of many millions of people around the world. Water pollution is not only one of the most important global risk factors for disease and death but also contributes to the continual reduction in available drinking water around the world [1]. This pollution is due to contaminants such as pharmaceuticals, dyes, metals and pesticides, fertilizers; and so, on coming from domestic, industrial, or agricultural sources poses significant environmental concerns [2]. Heavy metals are, in fact, highly toxic species above a certain concentration. They have the ability to concentrate along the food chain and accumulate in certain organs of the human body. It is therefore essential to completely eliminate the heavy metal ions present in the different industrial effluents or to reduce their quantity below the admissible thresholds defined by standards [3]. Many methods and techniques of pollution control have been developed in recent years. Among these techniques are: flocculation, ion exchange, electrolysis, membrane processes, adsorption and extraction. Solvent extraction is among the most common separation techniques, which constitutes a method of choice allowing the exploitation of poor ores and the recovery of various metallic elements, the quantitative extraction of heavy metal micropollutants as well as the detoxification of wastewater effluents. This technique remains the most widely used, thus covering a field of very important industrial and analytical applications [4 - 6]. Taking into account the prolixity of works and publications reported in this field, the main part of the work carried out aims at the development of this technique by the optimization

of the parameters which govern it such as the pH, the concentration, and the solvent as well as the development of new extractant molecules. Several organic extractants have been developed and their extracting properties have been evaluated for different metal ions. Particular attention is paid to the Schiff family of bases, which have proven to be excellent extractants against a large series of metal ions in recent years [7 - 11]. The choice of a solvent is one of the important matters in solvent extraction. The most important factor in choosing a solvent is the extractability of the elements involved. From this point, cyclohexane has frequently been used as the most useful solvent in solvent extraction. In this context, we have undertaken in this work the study of the extraction of Ni^{2+} in sulfate medium by salicylideneaniline (HSA). The aim is to determine the main extraction parameters for this metal. The determination and improvement of these parameters will be done by the variation of the pH, the concentration of the extractant and the variation of the temperature.

EXPERIMENTAL

The condensation of aniline on salicylic aldehyde has enabled us to develop a Schiff base of the N-(2-hydroxybenzylidene) aniline [salicylideneaniline (HAS)] type, according to the following procedure [10, 12]. Equimolar quantities of salicylic aldehyde and aniline are dissolved in the minimum amount of pure ethanol is placed in a two-necked flask fitted with a condenser and a graduated thermometer. The whole is kept at reflux and stirred for about two hours. The mixture is then cooled to room temperature and then concentrated by removing the solvent using evaporation. The solid product obtained is then filtered and then recrystallized from a minimum of pure ethanol.

The determination of concentration on Ni^{2+} in the aqueous phase was carried out using a visible spectrophotometer. The variation in the pH of the aqueous phase was monitored using a pH meter of the PHS-3E type (Fig 1).

In a thermoregulated glass cell at 25°C, 40 mL of an aqueous solution containing Ni^{2+} of concentration ($6.8.10^{-3}$ M) stirred with 40 mL of organic solvent containing 0.01; 0.02 and 0.04 M HSA. Stirring of the phases is ensured by a magnetic stirrer of constant speed and a temperature of 25°C. The pH of the aqueous phase is varied by adding 0.2 M sodium hydroxide of the same ionic strength to the system. After 20 minutes, the extraction equilibrium being largely reached, samples of the aqueous phase are taken for the assay and the determination of the distribution coefficient of the metal at the pH considered. The concentration of Ni^{2+} in the organic phase was calculated from the difference between the concentrations of the metal in the aqueous phase before and after extraction. Ni^{2+} absorbs and $\lambda max = 720$ nm.

RESULTS AND DISCUSSION

The extraction is obtained with a good yield of 80 %. The infrared analysis spectrum of the different adsorbents of the salicylideneaniline is shown in Fig. 3.

The study of the extraction of a metallic species M^{n+} from a sulfate medium by HSA in less polar solvents (cyclohexane, toluene, chloroform) is described by the following equilibrium:

$$M^{n+} + (n+m)HL_{org} \underset{}{\overset{K_{ex}}{\rightleftharpoons}} ML_n(HL)_{m\,org} + nH^+$$

Which has for constant:

$$K_{\alpha} = \frac{[M_n(H)_m]_{org}[H^+]^n}{[M^{n+}][H]_{org}^{n+m}} \quad (1)$$

The distribution coefficient of the metal is defined by:

$$D = \frac{[M_n(H)_m]_{org}}{[M^{n+}]_{aqu}} \quad (2)$$

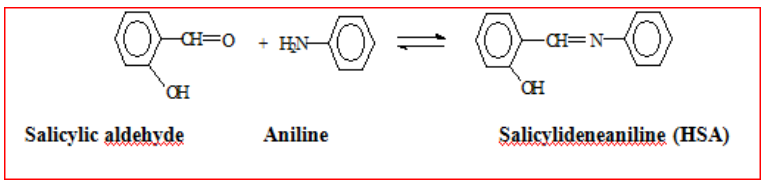


Fig. 1. Schematic representation of salicylideneaniline synthesis.

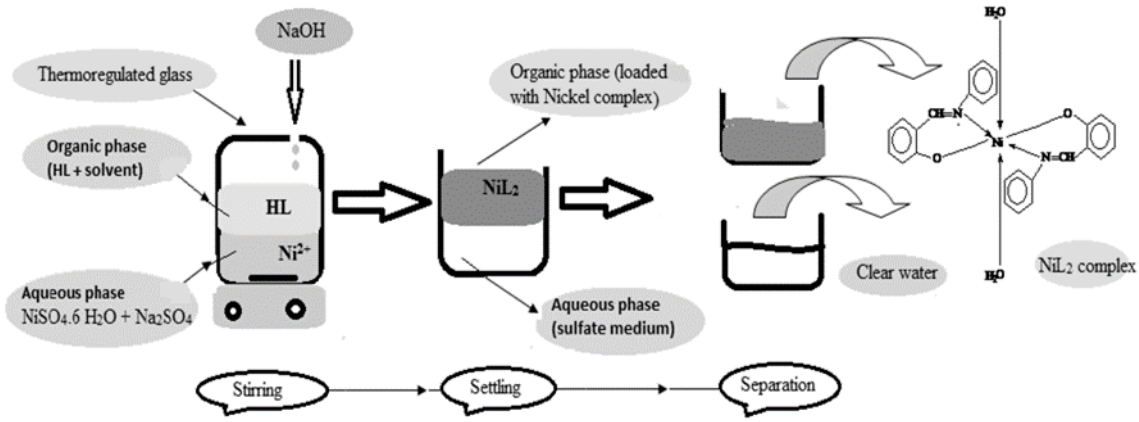
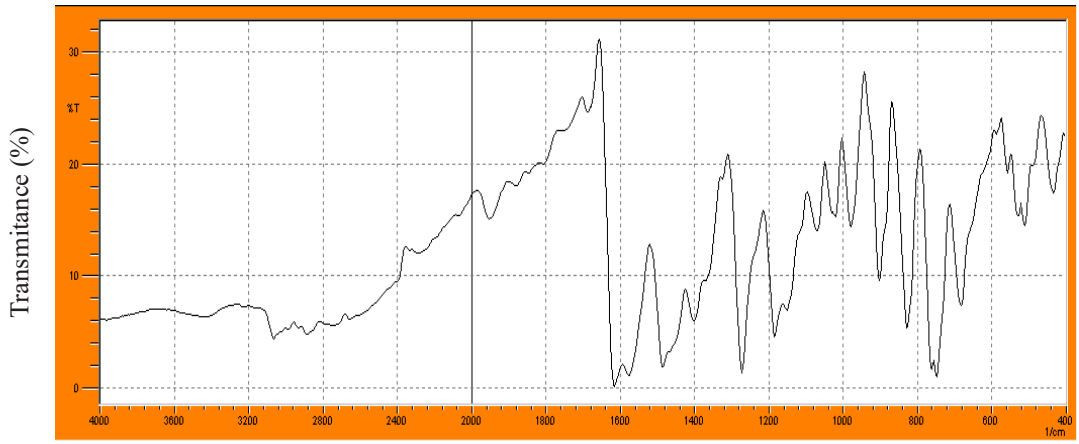


Fig. 2. Process of extraction liquid-liquid to removal Ni^{2+}.



Wavenumber (cm^{-1})

Fig. 3. Infrared spectrum of salicylideneaniline.

Table 1. Physical characteristic and infrared spectroscopy of salicylideneaniline.

Appearance and color	Melting temperature (°C)	Spectroscopy R. ν (cm^{-1})			
Yellow crystals	50	C=N	OH	C=C	C-H
		1618	3440	1500-1600	750–686

The distribution coefficient of the metal is defined by:

$$\log D = \log K_{ex} + (n+m)\log[HL]_{org} + n\ pH \qquad (3)$$

To determine the stoichiometric coefficients of the organometallic complex extracted in the organic phase, we used the slope method which consists in plotting the logarithm of the distribution coefficient of the metal as a function of the pH of the aqueous phase and as a function of the logarithm of the concentration of extracting it. The slopes of the lines obtained, we will allow to deduce the stoichiometry of the extracted species.

The logD = f(pH) extraction curves at 25°C for nickel in sulfate medium (ionic strength I = 1), for various concentrations of HSA in cyclohexane, toluene and chloroform are shown in Fig. 4. In all cases, it is observed that when the concentration increases, the extraction of Ni^{2+} increases. The study of the effect of pH on the liquid-liquid extraction of Ni^{2+} leads to the formation of a third phase when the concentration of Ni^{2+} exceeds $3{,}4.10^{-3}$ M for cyclohexane; $2{,}4.10^{-3}$ M for toluene and 2.10^{-3} M for chloroform in the organic phase [13]. The curves obtained are straight lines with a slope close to 2, so n = 2. This indicates that two protons are

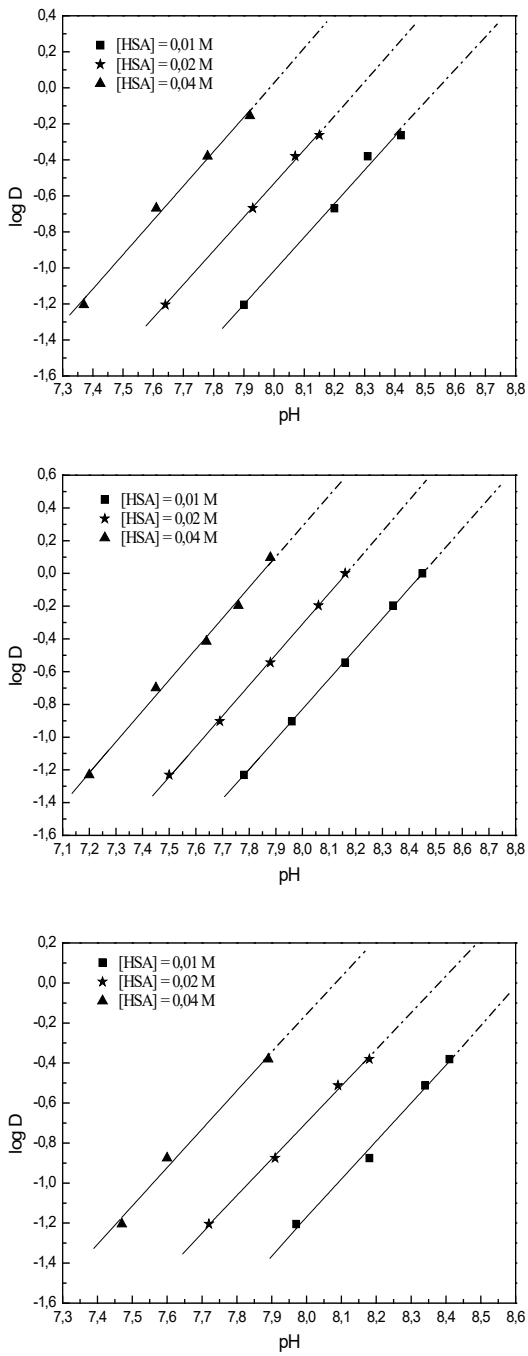


Fig.4. Influence of pH on the extraction of Ni^{2+}. Organic phase HSA in: a)cyclohexane; b) toluene; c) chloroform.

exchanged between the metal cation and the extractant.

To study the influence of the HSA concentration, we followed the variations of log D as a function of log $[HL]_{org}$ at constant pH of the extraction of the metal from the sulphate medium of unit ionic strength in these different diluents. In Fig 5, we represent the variations of log D = f (log $[HL]_{org}$) at different pH values on the extraction of Ni^{2+} by HSA in cyclohexane, toluene and chloroform. The curves obtained for the three solvents are straight lines with a slope close to 2 therefore n + m = 2 (m = 0), this confirms that two HL molecules participating in the coordination of the organometallic species extracted in the organic phase which has for stoichiometry NiL_2. The overall equilibrium of the extraction can be formulated as follows:

$$Ni^{2+} + 2HL_{org} \overset{K_{ex}}{\rightleftharpoons} NiL_2 + 2H^+$$

The log K_{ex} extraction equilibrium constant calculated from the following relation:

$$\log K_{ex} = \log D - 2\,pH - 2 \log [HL]_{org} \quad (4)$$

The establishment of the final stoichiometry of this organometallic species was confirmed by the realization of the electronic spectrum of the organic phase during the operation of extraction of Ni^{2+} by HSA. Electronic spectra of the complex of Ni^{2+} with the HSA ligand were performed in cyclohexane, toluene and chloroform (Fig. 6). The observed absorption bands are all analogous and agree with an octahedral surround around Ni^{2+}. A wide band observed at λmax = 975 nm, corresponds to the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition and a weak band observed in the 760 - 810 nm region corresponds to the theoretically forbidden transition $^3A_{2g} \rightarrow {}^1E_g$. The third band centered at λmax = 620 nm probably corresponds to the $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) transition. The $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) transition not observed in this complex would be masked by the excessively high intensity of the charge transfer bands in the neighboring UV regions. The octahedral structure of the NiL_2 extracted complex would be constituted by the two molecules of organic ligand ligand the metal in equatorial position while the axial positions are occupied by two molecules of water (Fig. 7). These results are similar to those already carried out during the study of the structure of the complexes extracted from Ni^{2+} by a mixture of Schiff bases N-(2-hydroxy-1-naphthylidene)-2,6-diisopropylaniline (HL_1) and N-(2-hydroxybenzylidene)-2,3-dimethylaniline (HL_2) [14], and on the synergistic extraction of nickel(II) from sulfate medium by a mixture of N -(2-hydroxybenzylidene)aniline and methyl-isobutyl keton

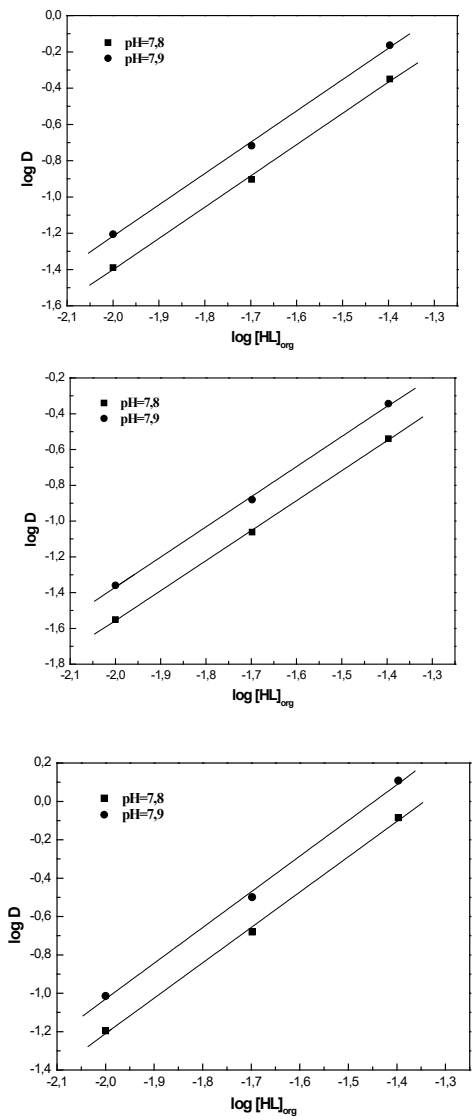


Fig. 5. Influence of HSA concentration on Ni^{2+} extraction. Organic phase HSA in: a) cyclohexane; b) toluene; c) chloroform.

[13]. This same type of octahedral entourage has already been observed around Ni^{2+} during complexation with substituted Schiff bases [15].

The effect of diluent on the extraction of Ni^{2+} by salicylideneaniline is studied using chloroform, toluene and cyclohexane as diluents. In Fig.8, we show the variations in log D as a function of pH during the extraction of Ni^{2+} by HSA in the diluents mentioned above.

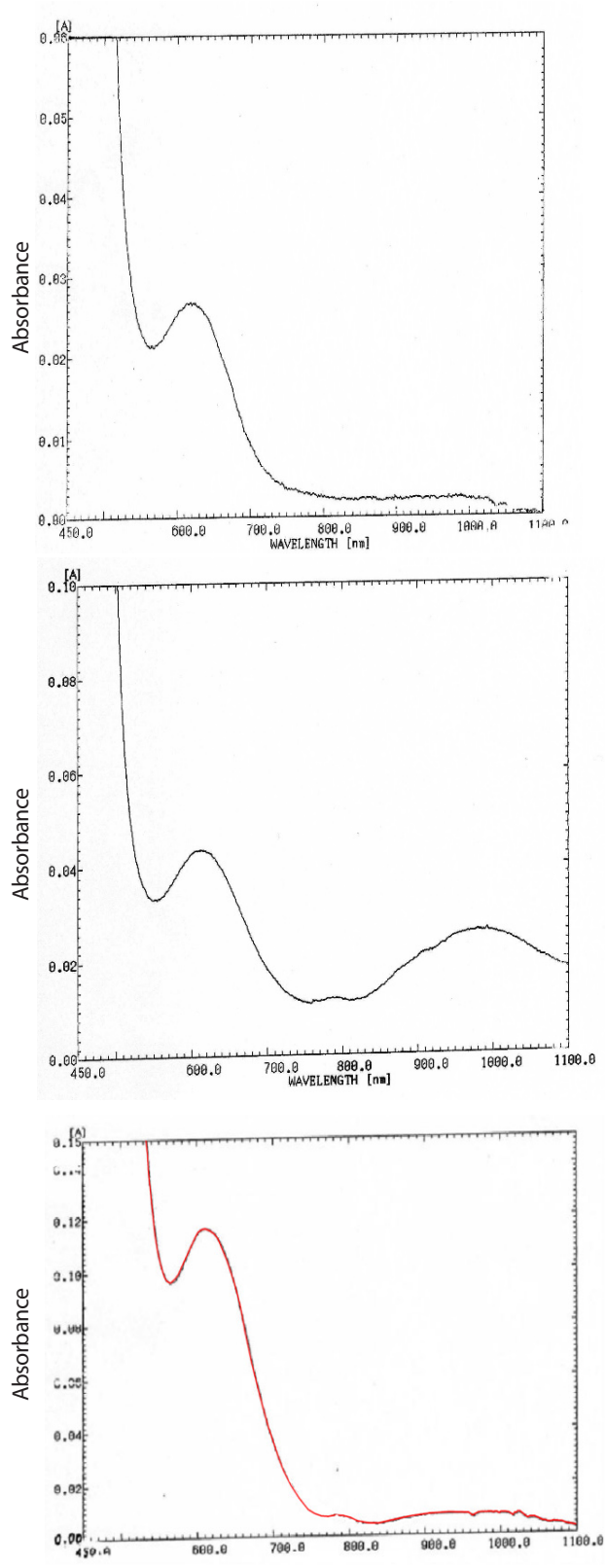


Fig. 6. Electronic spectra of the nickel complex with HSA in: A - cyclohexane; B - toluene; C - chloroform.

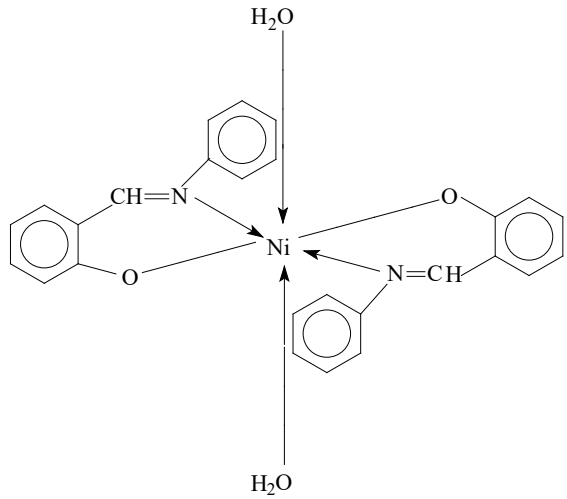


Fig. 7. Scheme of the proposed structure of the NiL_2 complex.

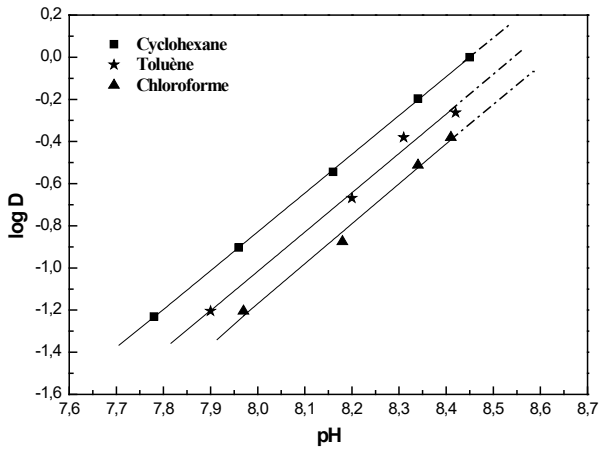


Fig. 8. Effect of pH on the extraction of Ni^{2+} in different solvents and [HSA] = 0.01 M at 25°C.

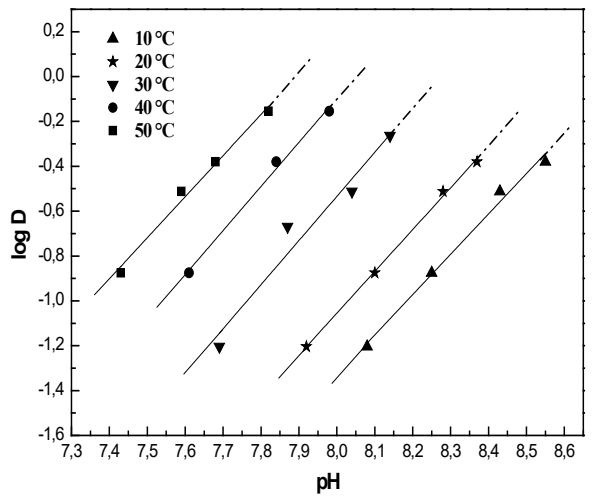


Fig. 9. The effect of temperature on the extraction of Ni^{2+} in sulfate medium by HSA.

Table 2. Log Kex values of Ni^{2+} extraction for 0.01 M HAS in 0.33 M sulfate medium at 25°C.

Diluent	log K_{ex}	Extracted species
Cyclohexane	-12.85	NiL_2
Toluene	-13.04	NiL_2
Chloroform	-13.19	NiL_2

The logarithmic values of the extraction constants (log Kex) obtained in the different solvents are given in Table 2.

The effect of the diluent on the liquid-liquid extraction of Ni^{2+} follows the following order: cyclohexane > toluene > chloroform.

When we take cyclohexane as a solvent, the extraction is significantly improved. Note for this purpose the particularly high value of the extraction constant of Ni^{2+} in cyclohexane, this is explained by the fact that the complex formed is less hydrated and this leads to the reduction of the formation of a film which constitutes a third interfacial phase rich in metal, a phenomenon which makes extraction difficult to achieve.

A study of the variation of log D as a function of pH at constant $[HSA]_{org}$ in cyclohexane was carried out at different temperatures 10, 20, 30, 40 and 50°C. In Fig. 9 we represented the variations of log D = f(pH) at $[HSA]_{org}$ = 0.01 M at different temperatures. From Fig. 9, we notice that the curves are straight lines of slopes 2, and that the temperature variation has no influence on the slope of these extraction curves.

In addition, the curves indicate that the extraction of Ni^{2+} increases with increasing temperature. The overall equilibrium of the extraction of Ni^{2+} in cyclohexane can be formulated as follows:

$$Ni^{2+} + 2HL_{org} \overset{K_{ex}}{\rightleftharpoons} NiL_2 + 2H^+$$

The values of log Kex are determined from the equation which relates pH with log D (relation 5):

$$\log K_{ex} = \log D - 2\ pH - 2\log [HL]_{org} \quad (5)$$

For this metal, we notice that the values of the extraction constants increase with the rise in temperature. To calculate the values of the enthalpy and the entropy

Table 3. log K_{ex} values of Ni^{2+} extraction with [HSA] = 0.01 M at different temperatures.

T(°K)	log $K_{ex[Ni(II)]}$
283	-13,39
293	-13,07
303	-12,53
313	-12,09
323	-11,74

Table 4. Thermodynamic parameters of extraction of Ni^{2+} by HAS in cyclohexane.

Metallic ion	Ni^{2+}
ΔH° (kJ mol^{-1})	71.22
ΔS° (J mol^{-1} K^{-1})	-48.25
ΔG° (kJ mol^{-1})	72.79

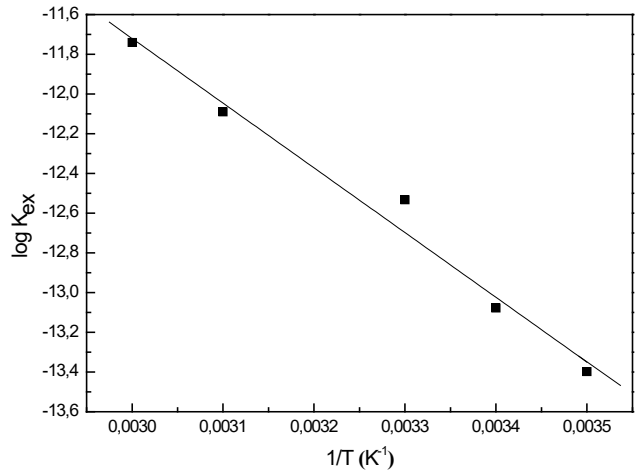


Fig. 10. Influence of temperature on the extraction of Ni^{2+} by HSA in cyclohexane.

of extraction of Ni^{2+} we used the relation which links **1/T** and these thermodynamic parameters, according to the equation of Gibbs Helmholtz [16].

$$\log k_{ex} = -\frac{\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303R} \qquad (6)$$

where : ΔS°- metal extraction entropy; ΔH° - enthalpy of extraction of the metal; T - temperature in K; R = 8.314 $Jmol^{-1}.K^{-1}$.

The variation of log K_{ex} as a function of (1/T) gives a straight line of slope

$$-\frac{\Delta H^\circ}{2.303R}$$,

and the intersection of the line with the log axis K_{ex} gives

$$\frac{\Delta S^\circ}{2.303R}$$ (Fig.10).

The value of the free energy (ΔG°) is calculated from the following expression:

$$\Delta G^o = -2.303\ RT\ \log K_\alpha \qquad (7)$$

The thermodynamic parameters of Ni^{2+} extraction are shown in Table 4.

The results collated in Table 4 show that the process of extraction of Ni^{2+} by HSA in cyclohexane is endothermic. Negative values of ΔS° imply that the degree of order in the organic phase increases, this increase created by the new strong metal-ligand bonds. The positive values of ΔG° calculated for each metal show that the reaction is not spontaneous. The values of the thermodynamic parameters ΔH°, ΔS° and ΔG° are in favor with those published by the following authors: The positive value of ΔG° (ΔG° = 42.3 kJ mol^{-1}) implies that the reaction of the extraction is not spontaneous. The negative value of ΔS° (ΔS° = -20.3 J $mol^{-1}.K^{-1}$) shows that the degree of order of the extracted complex increases [17]. E. O. Otu et al.[16] studied the extraction of Ni^{2+} from aqueous nitric acid medium by mono-2-ethylhexyl phosphoric acid (H2MEHP) dissolved in o-xylene. The aggregation of the extractant was studied as a function of the temperature between 25 and 60 °C. These authors have shown that the process of Ni^{2+} extraction is not spontaneous (ΔG° = 0.2 kJ mol^{-1}). The negative value of ΔS° (ΔS° = -75.4 J $mol^{-1}.K^{-1}$) implies that the degree of order of the extracted complexes increases in the organic phase. In the same context, Al-Sabti observed during the study of the liquid-liquid extraction of nickel (II) and cobalt (II) by o-diphenylamino benzoic acid in chloroform at 293°K and 318°K that the values of ΔG° for the two metals are successively:

$\Delta G^\circ_{(Co)}$ = 47.47 kJ mol^{-1} and $\Delta G^\circ_{(Ni)}$ = 49.54 kJ mol^{-1} at 293 °K.

$\Delta G^\circ_{(Co)}$ = 51.82 kJ mol^{-1} and $\Delta G^\circ_{(Ni)}$ = 53.76 kJ mol^{-1} at 318 °K [18].

CONCLUSIONS

The extraction of Ni^{2+} by salicylideneaniline has been studied according to the pH and the concentration of the extractant. The study of the effect of pH on the liquid-liquid extraction of Ni^{+2} by salicylideneaniline led to the formation of a third phase in cyclohexane. The stoichiometry of the complex extracted for this metal was determined by the bi-logarithmic slope method, it is a NiL_2 type complex. The electron spectroscopic study showed that: The shape of the geometry of the complex is octahedral. We are also interested in studying the effect of temperature on the liquid-liquid extraction of Ni^{2+} in cyclohexane. This study showed that the extraction of this metal increases with increasing temperature. The thermodynamic parameters such as enthalpy, entropy and free energy of extraction of this metal have been determined.

• The positive value of $\Delta H°$ for this metal shows that the extraction process with salicylideneaniline is endothermic.

• The negative value of $\Delta S°$ calculated for this metal implies that the degree of order of complex, extracted increases in the organic phase.

• The positive value of $\Delta G°$ calculated for this metal shows that the reaction is not spontaneous.

REFERENCES

1. S. Bolisetty, M. Peydayesh and R. Mezzenga, Sustainable technologies for water purification from heavy metals, review and analysis.Chem, Soc. Rev. 48, 2, 2019, 463-487.
2. Y. Yang, G. Zeng, Recent advances in application of graphitic carbon nitride- based catalysts for degrading organic contaminants in water through advanced oxidation processes beyond photocatalysis, Water Research, 184, 2020.
3. E.A. Pazou yehouenou, A. Soton, D.azocli, H. Acakpo, M. Boco, L. Fourn, D. Houinsa, J-C. keke et Benjamin Fayomi, Contamination du sol, de l'eau et des produits maraîchers par des substances toxiques et des métaux lourds sur le site de Houéyiho (Cotonou) en République du Bénin, Int. J. Biol. Chem. Sci., 4, 6, 2010, 2160-2168
4. A. Guerdouh, D. Barkat, Experimental study of the extraction of chromium(III) from nitrate medium by lauric acid, Metallurgical and Materials Engineering, 24, 3, 2018, 189-197.
5. F. Ghebghoub, D. Barkat, Solvent Effect on the Extraction of Cobalt(II) Using Bis(2-ethylhexyl) Phosphoric Acid, TACL, 9, 1, 2019, 104-112.
6. A. Guerdouh, D. Barkat, Influence of the solvent on the extraction of copper (II) from nitrate meduim using salicylideneaniline, J. Dispers. Sci. Technol., 38, 7, 2017, 930-934.
7. Y. Kouadria, S. Almi, D. Barkat, The Improvement of Copper (II) Extraction by Nitro Substitution on Schiff's Bases Derived from Salicylaldehyde, Anal. Chem. Lett, 11, 3, 2021, 343-353.
8. S. Almi, M. Bouzgou, F. Adjel, D. Barkat, Methyl-isobutyl ketone and 1 octanol as synergistic agents and phase modifiers in solvent extraction of cobalt(II) by the N-(2-hydroxybenzylidene)aniline from sulfate medium, Inorganic and Nano Metal Chemistry, 50, 1, 2019, 8-15.
9. M.F. Cheira, A.S. Orabi, M.A. Hassanin, S.M. Hassan, Solvent extraction of thorium (IV) from chloride solution using Schiff base and itsapplication for spectrophotometric determination, Chemical Data Collections, 13, 14, 2018, 84-103.
10. D. Barkat, M. Kameche, Liquid–liquid extraction of Copper(II) wit Schiff's Bases derived from Salicylaldehyde, Physics and Chemistry of Liquids, 43, 2007, 289-293.
11. Z. Benfettouma, M. HadjYoucef, H.Reffas, T.Benabdallah, H, Reffas, Extraction study on recovery of nickel (II) from concentrated chloride medium with N,N′-bis(salicylaldeyde) ethylenediimine in the presence of CTAB and Brij® 35 , Journal of Dispersion Science and Technology, 42, 13, 2021, 1912-1925.
12. M.D. Hurvitz, US Parent 2,582,128, Chem. Abstr. 46, 1952, 8146.
13. S. Almi, F. Adjel, D. Barkat, 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, 47, 11, 2017, 1577-1584.
14. K.A. Mapari, K.V. Mangaonkar, Synthesis, Characterization and Antimicrobial Activity of Mixed Schiff Base Ligand Complexes of Transition Metal(II) ions, Chem Tech Research, 3, 2, 2011, 636-641.

15. A.A. Ahmed, S.A. BenGuzzi, A.A. EL-Hadi, Synthesis and characterization of Divalent Transition Metals Complexes of Schiff bases derived from O-Phenylenediamine and Benzoylacetone and Related species, Journal of Science and Its Applications, 1, 1, 2007, 79-90.
16. M.M. Huff, E.O. Out, Thermodynamics of the Extraction of Lead, Copper, Cadmium, Cobalt, and Nickel with Mono-2-ethylhexyl Phosphoric Acid, Solvent Extraction and Ion Exchange, 22, 4, 2004, 695-712.
17. A. Aidi, D. Barkat, Thermodynamics of the extraction of Cu(II) with capric acid in cyclohexane, Courrier du Savoir, 26, 2018, 23-28.
18. M.D. Sabti. Effect of Temperature on The Solvent Extraction of Cobalt(II), Nickel(II), and Copper(II) Metal Ions by o-diphenylamino Benzoic Acid, Eng Tech, 26 (5), 2008, 496-500.