

Extraction of Zn (II) in acetate medium by 8- Hydroxyquinoline.

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Abstract –The objective of this work is the liquid-liquid extraction of Zn (II) in an acetate medium by the 8-hydroxyquinoline quinoline compound known by these chelating properties, with respect to heavy divalent metals, as well as these important biological and pharmacological properties. Various parameters have been optimized such as contact time, concentration of aqueous phase, mass of extractant, pH effect and salt effect. The thermodynamic study showed that the extraction process is spontaneous ($\Delta G < 0$) and exothermic ($\Delta H < 0$). On the other hand, the extractant forms a yellow solid complex of structure $M(C_8H_7NO)_2$ confirmed by IR analysis.

Keyword-The 8-Hydrox quinoléine, Environnement, Zinc, Extraction liquid – liquid

1. INTRODUCTION

8-Hydroxyquinoline (8HQ), a derivative of the original quinoline, has been used as an agricultural fungicide and a preservative in the textile, wood and paper industries, 8HQ is a powerful chelant that can restore balance of metals and be useful for the treatment of metal-related diseases[1-7].

8-Hydroxyquinoline (1-8-HQ) (or quinolinol) is a non-specific ligand chelating a large variety of metal ions[8-9]. 8-Hydroxyquinoline is able to chelate essential metallic ions for metabolism of bacteria and fungi, so 8-HQ derivatives are used as antibacterial and antifungal. 8-HQ complexes of Zn or Mn can be also used for such applications[10-14].

Metal complexes of 8-hydroxyquinolines were used in supramolecular chemistry as luminescent or fluorescent solids [4].

The objective principles of this work fall within this framework. We propose to study the liquid-liquid extraction of zinc (II) in an acetate medium

by 8'-hydroxyquinoline and to determine the optimum conditions for extraction.

II. MATERIALS AND METHODS

All commercial reagents were purchased from Prolabo or Aldrich, and were used as received without further purification.

Spectro201plusUV-VISIBLE spectrophotometer and a consort C831 PH meter with combined glass electrode were used for concentration and Ph measurement

The FTIR spectrum was recorded on a Bruker Vector 22 spectrophotometer

Processing of extraction

8-HQ, which is soluble in ethyl acetate and chloroforme, was taken as the organic solvent throughout this study. Equal volumes of organic and aqueous phases (5 mL) were agitated for 30 min (enough for equilibrium) at 22°C under the desired experimental conditions. The two phases were then separated by decantation and assayed by taking known aliquots from the aqueous phases. The zinc concentrations in the aqueous phase were determined, before and after extraction spectrophotometrically.

III. RESULTS AND DISCUSSION

A. *The contact time determined by a kinetic extraction study of Zn (II)*

The contact time is 30 minutes for chloroform and 45 minutes for ethyl acetate.

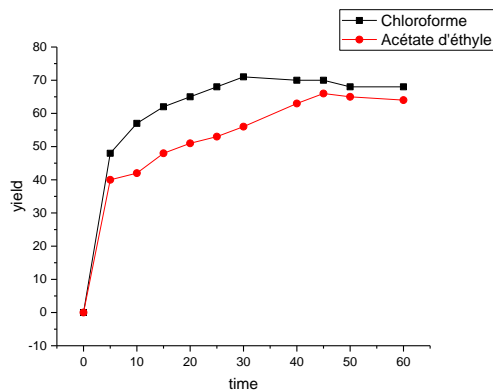


Figure 1: Kinetic of extraction of Zn (II) $pH_i = 4,5$ $T^\circ = 20C$
 $[Zn(II)] = 10^{-2}M$ $[8HQ] = 10^{-2}M$

B. Volume ratio

The ratio Q between the volume of the organic phase and the volume of the aqueous phase is very important in a liquid-liquid extraction

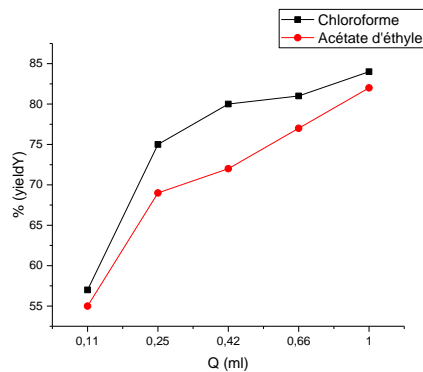


Figure 2: Effect of volume ratio $pH_i = 4,5$ $T^\circ = 20C$ $[Zn(II)] = 10^{-2}M$ $[8HQ] = 10^{-2}M$ $Q=1$

The results for the two solvents show that the best yield is obtained from a volume ratio equal to 1, so to carry out this extraction it is necessary to take the same volume of the organic and aqueous phase

C. Effect of the initial Zn (II) concentration of the aqueous phase

The effect of the concentration of the aqueous phase on the extraction yield was examined in the following concentration range: $[Zn^{2+}] = 10^{-3}$ to $0.005M$

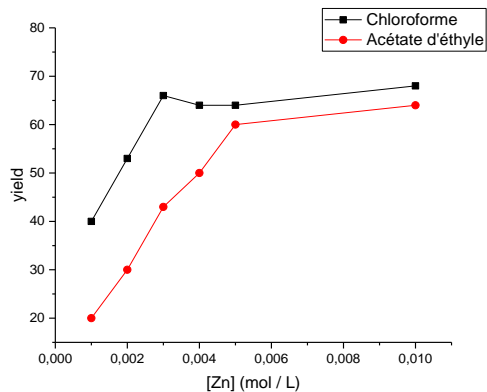


Figure 3: Effect of the concentration of Zn(II) on the extraction yield of Zn(II) $pH_i = 4 - 5$ $T^\circ = 20C$ $[Zn(II)] = 10^{-2}M$ $[8HQ] = 10^{-2}M$

According to this result the optimal concentration of the feed phase will be taken equal $10^{-2}M$.

D. Effect of the initial pH of the aqueous phase

The study of the influence of the initial pH of the aqueous phase on the extraction yield was examined by adding suitable quantities of hydrochloric acid

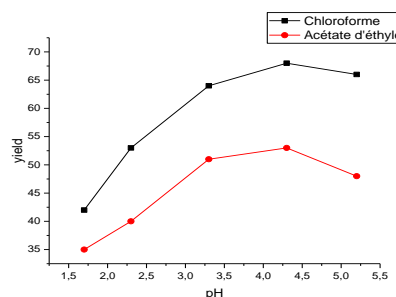


Figure 4: Effect of pH_i on extraction yield of Zn(II) $[Zn(II)] = 10^{-2}M$ $T^\circ = 20^\circ C$ $V_{aq}/V_{org} = 1$ $[8HQ] = 10^{-2}M$

From the figure it can be seen that the extraction efficiency decreases with the increase in the acidity of the medium, this result shows that the extraction of metal is carried out by proton exchange with the aqueous phase. The progress of the extraction reaction increasingly enriches the aqueous phase with H^+ . Therefore, in order to carry out the extraction in good yield, it must work in the less acidic medium possible, in order to avoid the formation of precipitates $Zn(OH)_2$, $Zn(OH)_4^{2-}$

E. Effect of the extractant mass on the extraction of Zn (II)

We conclude from the optimal mass of the extractant is of the order 0.2 g for the two solvents

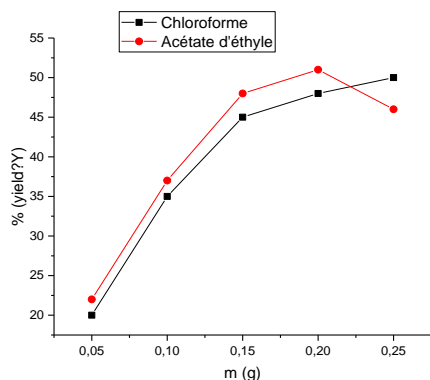


Figure 5: yield of extraction on fonction weight of extractant $pH_i = 4,5$ $T^\circ = 20C$ $[Zn(II)] = 10^{-2}M$

F. Effect of salt

We tried in this study to see the effect of addition of CH_3COONa salt at different concentrations on Zinc (II) extraction yields.

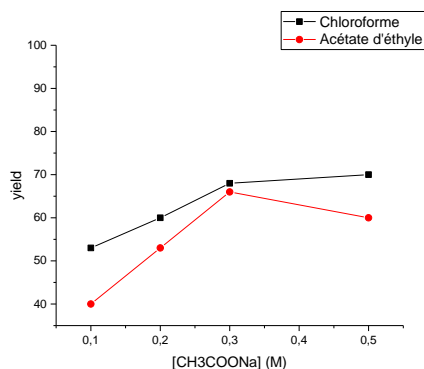


Fig.6: Effect of the addition of Sodium Acetate on the extraction yield of Zn(II)

According to the figure in note the increase yield is due to the increase in ionic strength and then decreases due to the competition of Sodium with the Zinc during the extraction which makes the zinc more accessible to the interface of the extractant.

G. Effect of temperature:

The effect of temperature on Zinc extraction has been studied at different temperatures from $22^\circ C$ (295K) to $60^\circ C$ (333K) by heating in a water bath.

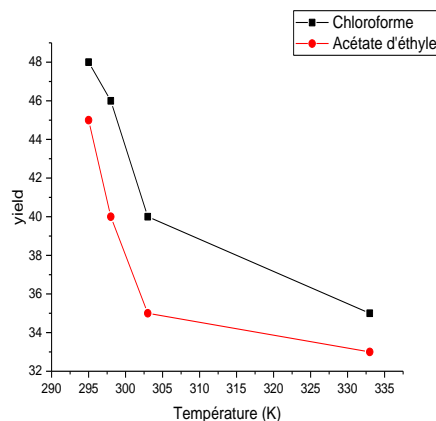


Figure7: Effect of temperature on the yield of extraction $pH_i = 4,5$ $T^\circ = 20C$ $[Zn(II)] = 10^{-2}M$ $[8HQ] = 10^{-2}M$

According to the figure, a temperature increase of the extraction in the range (295a3330k) decreases the extraction yield.

H. Study of thermodynamic parameters

The study of the temperature effect also made it possible to determine the thermodynamic parameters of the extraction, in our operating conditions, such that free enthalpy (ΔH), entropy (ΔS) and free enthalpy (variation in the Gibbs function) (ΔG). These thermodynamic parameters are calculated using the following equations:

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ = \Delta H - T \Delta S$$

From these two equations we derive the following equation, which will allow us to calculate ΔH and ΔS by plotting the curve which gives the evolution of the constant K as a function of the temperature.

$$\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

K, T and R are respectively: the partition coefficient of Zn (II) between the two equilibrium phases, the temperature and the perfect gas constant ($R = 8.314 \text{ J. mol}^{-1} \text{ K}^{-1}$).

The partition coefficient is defined by the following expression:

$$K = \frac{[Zn(II)]_{org}}{[Zn(II)]_{aq}}$$

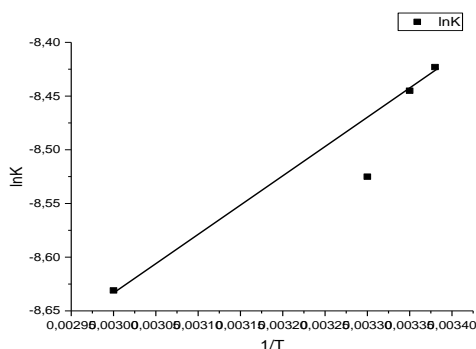


Figure 8: Variation of $\ln K$ in function of $1/T$

The calculated values of ΔH , ΔS and ΔG are summarized in the following table1:

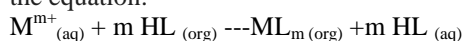
Table 1: Evolution of thermodynamic parameters as a function of temperature

T en K	ΔG (KJ/mol)
295	-3,44
298	-3,41
303	-3,37
333	-3.1

The calculation of ΔH shows that: - The extraction process is exothermic ($\Delta H < 0$). The extraction process is spontaneous ($\Delta G < 0$).

I. Extraction mechanism:

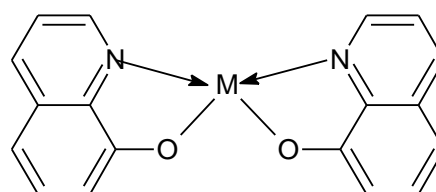
The complexing character of 8HQ is explained by the fact that it creates coordination with O-OH of OH in the formation of water-insoluble complex theoretically the complex formed is of the form $M [C_9H_6ON]_n$ or n the number of charge of the metal in our case $n = 2$ Thus, extraction is carried out by simple proton exchange of the extraction against the divalent cation of the aqueous phase to form a yellow-colored organosoluble complex according to the equation:



J. Spectral study:

In order to confirm the complexation of our metal, we performed ligand IR spectroscopy analysis before and after extraction. The complex is a yellow solid, water-insoluble and soluble in chloroform. The characteristic infrared bands for the 8-hydroxyquinoline ligand (Oxine) and the complex form are shown in fig.10-11 and in table 2.

The band located at 3236.3cm^{-1} characterizing the OH group. The band 1504 cm^{-1} characterizing the CN bond. The band 1629 cm^{-1} characterizing the CH of the aromatic ring. The band 2856.4 characterized OH group around two aromatic rings. Then, in the spectrum fig.11 which corresponds to the complex 8HQ-Zn one observes the displacement and disappearance of certain bands and the appearance of new bands, for example the appearance of the characteristic band Zn-N and Zn-O, namely $505.3 - 644.2\text{ cm}^{-1}$. By virtue of these results it is concluded that 8HQ contains two electron donor sites located at the nitrogen atom of the aromatic ring and the atom of oxygen of the second aromatic ring. And the structure of the 8HQ-Zn complex takes the following form:



M= Zn

Figure 9: Structure of complex M-8HQ

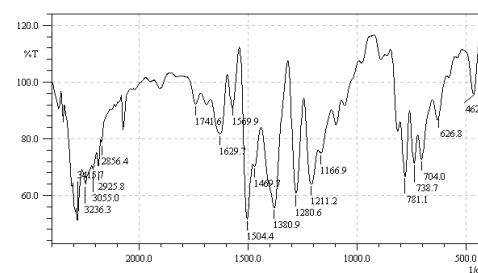


Figure 10: Infrared spectrum of the 8-HQ

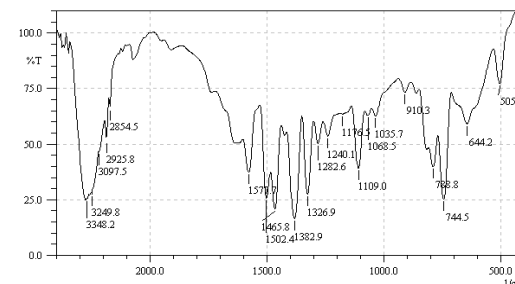


Figure 11: Infrared spectrum of the complex [Zn (8-HQ)]

Table 02:

Compound	ν (CH)	ν (OH)	ν (C-N)	ν (C-O)	ν (Zn-N)	ν (Zn-O)
Oxine (8HQ)	1629	3236.3 2856.4	1504	1280	----- -----	----- --
Zn (oxine) ₂	1577	3348	1465.8	1326.9	505.3	644.2

IV. CONCLUSION

The 8-hydroxyquinoline obtained exhibited high efficiency for the uptake and removal of zinc in water and the recovery is quantitative ($\approx 100\%$). The best performance is achieved from a molar ratio equal to 1.. The extraction yield (99.4%) was found to be higher at slightly acid pH. At equilibrium, the extraction yield with chloroform solvent was higher than with ethyl acetate . the thermodynamic parameters showed that the extraction process is exothermic ($\Delta H < 0$) and spontaneous ($\Delta G < 0$). IR spectroscopy confirms the complexation of Zn (II) 8HQ \rightarrow 8HQ forms a stable solid complex of yellow color, and of following structure
 $Zn [C_9H_7NO]_2$

REFERENCES

[1]. Albrecht M, Fiege M, Osetka O. 8-Hydroxyquinolines dans la chimie metallosupramoleculaire. *Coord Chem Rev.* 2008; 252 (8-9): 812-824.
 [2] a) M. Albrecht, O. Blau. Synthesis of Ethylene-Bridged Bis(8-hydroxyquinoline) Derivatives: New Building Blocks for Metallo Supramolecular Chemistry. *Synthesis.* 1997, 28, 213-216. b) M. Albrecht, K. Witt, R. Fröhlich, O. Kataeva; Inter- and intramolecular hydrogen bonding in amid- and arene-substituted 8-hydroxyquinoline derivatives, *Tetrahedron*, 2002, 58, 561-567.
 [3] B. Erdem, A. Özcan, A. Safa Özcan. Adsorption and solid phase extraction of 8-hydroxyquinoline from aqueous solutions by using natural bentonite. *Applied Surface Sci.* 2010, 256, 5422-5427
 [4] I. Garcia-Santos, J. Sanmartin, A. M. Garcia-Deibe, M. Fondo, E. Gomez. Structural and photophysical studies on a linear trinuclear zinc complex of 2-[(2-hydroxyethylimino) methyl] quinolin-8-ol. *Polyhedron.* 2009, 28, 3055-3059.
 [5] L. E. Sarmiento, M. Rodriguez, L. Echevarria, V. Lubes. Speciation of the Vanadium (III) Complexes with 1, 10-phenanthroline, 2,2'-bipyridine, and 8-hydroxyquinoline. *J. Sol. Chem.* 2010, 39, 1484-1491.

[6] S. Rubbo, A. Albert, M. Gibson. The influence of chemical constitution on anti-bacterial activity. 5. The anti-bacterial action of 8-hydroxyquinoline. *Br. J. Exp. Pathol.* 1950, 31, 425-441.
 [7] National Toxicology Program (NTP) Technical report on the toxicology and carcinogenesis studies of 8-hydroxyquinoline in F344/N rats and B6C3F1 mice, NTPTR276, US. 1985 Department of Health and Human Services.
 [8] S. Madonna, C. Beclin et al. Structure-activity relationship and mechanism of action of antitumor bis 8-hydroxyquinoline substituted benzylamines *European J. Med. Chem.* 2010, 45, 2, 623-638..
 [9] a) Q. Zhang, D. Wu, B. Bao. Synergistic extraction of praseodymium with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester and 8-Hydroxyquinoline. *J. Shanghai Univ (Engl Ed)* 2009, 13 (1) 72-75, b) C. Wang, Dean; Martin. Cloud-point extraction of chromium(III) ion with 8-hydroxyquinoline derivatives *J. Environmental Sci. and health. Part A, Environmental science and engineering.* 1999, 34 705 - 719. c) T. Moeller. Extraction and Colorimetric Estimation of Certain Metals as Derivatives of 8-Hydroxyquinoline. *Ind. Eng. Chem. Anal. Ed.*, 1943, 15 (5), 346-349.
 [10] a) B. Himmi, Banacer, J. P. Joly, F. Hlimi, M. Soufiaoui, S. Kitane, A. Bahloul, A. Eddaif, A. Sebban. Synthesis of novel 5, 7-substituted 8-hydroxyquinoline. *J. Heterocycl. Chem.* 2008, 45, 4, 1023-1026. b) B. Himmi, B. Messnaoui, S. Kitane, A. Eddaif, A. Bouklouz, M. Soufiaoui Study of Zn (II) extraction by 5-azidomethyl-8-hydroxyquinoline: Experiment and modelling. *Hydrometallurgy.* 2008, 93, 39-44.
 [11] K. Gloe, H. Stephan, T. Krüger, A. Möckel, N. Woller, G. Subklew, M. J. Schwuger, Neumann, E. Weber. Solvent extraction of toxic heavy metal ions with 8-hydroxyquinoline extractants from effluents. *Progress. Colloid. Polym. Sci.* 1996, 10, 145-148.
 [12] L. Li, B. Xu, Synthesis and characterization of 5-substituted 8-hydroxyquinoline derivatives and

their metal complexes *.Tetrahedron*. **2008**, 64, 10986-10995.

[13] D. Wu, Q. Zhang, B. Bao, Solvent extraction of Pr and Nd(III) from chloride-acetate medium by 8-hydroxyquinoline with and without 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester as an added synergist in heptanes diluent *.Hydrometallurgy* **2007**, 88, 210-215.

[14] F. Zaoui • M.A. Didi • D. Villemin Investigation of 7-((dioctylamino)methyl)quinoline-8-ol for uptake and removal of uranyl ions. *J Radioanal Nucl Chem* (**2013**) 295:419–424. DOI 10.1007/s10967-012-1789-8