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PURIFICATION OF TRI-*n*-OCTYL PHOSPHINE OXIDE BY EXTRACTION AND PRECIPITATION. EXTRACTION OF Zn, Mo AND Fe IN ACID MEDIUM

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Abstract: The aim of this work was a process of purification of tri-*n*-octyl phosphine oxide (TOPO) based on extractability properties. In this context, the extraction parameters (acid concentration, volume ratio of the phases, mixing time) were optimized. The extraction operation was followed by the precipitation of the formed complex. This purification technique made it possible to increase the TOPO purity from 27.8% to 92%. The liquid–liquid extraction of Zn, Mo and Fe was carried out using the purified TOPO, starting from the aqueous solutions of hydrochloric acid. It was carried out under various operating conditions including the variation of the HCl concentration, the molar ratio [TOPO]/[Zn], the volume ratio of the phases (organic/aqueous) and the contact time between phases.

The best extraction yields were obtained for the concentrations of HCl varying between 3 – 7 mol/L, for the contact times varying from 5 – 20 minutes and the volume ratios of phases between 1 and 4, according to studied metal. For a molar ratio [TOPO]/[Zn] > 10, the value of extraction yield of Zn by TOPO is doubled.

Keywords: *TOPO, solvent extraction, zinc, molybdenum, iron, chromatography.*

INTRODUCTION

Processes of metal recovery and purification by liquid - liquid extraction are highly used in hydrometallurgy. The development of these processes on an industrial scale demands a continuous requirement in powerful and pure organophosphorus extractants [1-3].
The present study considers the purification of the gross product of synthesis of the organophosphorus extracting agent namely: tri-*n*-octyl phosphine oxide (TOPO), under optimal conditions. This compound is known in literature as being a solvating agent of metal ions [4-6]; consequently, the method developed at the point in this work is based on the extraction of iron by TOPO followed by a precipitation of the formed complex.
Previous works concerning the extraction of metals such as iron, molybdenum, cobalt, copper, zinc and others whose state of oxidation is III, IV, V, VI by diverse extractants already demonstrated the influence of the concentration, nature of the used acid and the phases volume ratio on the extraction yield [7-10]. In the present article, we report the combined effects of the concentration of hydrochloric acid, the contact time of the phases and volume ratio organic/aqueous phases on the extraction of zinc, molybdenum and iron by the TOPO in cyclohexane.

EXPERIMENTAL

Before setting in motion this procedure of purification of TOPO based on the extraction, we considered necessary to optimize three highly significant parameters in the liquid – liquid extraction: concentration of the acid medium, the volume ratio of the phases and the agitation time.

Influence of the hydrochloric acid concentration

For this study, various samples of various concentrations of hydrochloric acid were prepared. The same volume of solution of $FeCl_3$ / H_2O (2.10^{-2} M) was added to each acid solution. Each one of these solutions was put in contact with an organic solution containing TOPO dissolved in cyclohexane to 1 $mmol.L^{-1}$. The acid concentrations vary between 1 and 9M, the time of agitation was fixed at 35 min and the volume ratio of the phases is one.

Influence of the agitation time

In order to determine the optimal agitation time, we have proceeded in the same way than above mentioned, while varying the agitation time from 10 to 60 min and fixing the volume ratio of the phases to 1 and the acid concentration to 7.5 M.

Influence of volume ratio of the phases

In this case, the ratio of the phases is varied from 1/4 to 4; the agitation time and the concentration of acid are fixed at 35 min and 7.5 M respectively.

Determination of the formula of the formed complex

In order to determine the number of ligands (stoechiometric coefficient) of the complex TOPO : $FeCl_3$ while following Job's methodology **[11].** To such an end, several tests were carried out varying the ratio of the concentrations of $FeCl_3$ / TOPO. The formed complex of yellow color was titrated by UV/visible spectrophotometry using a Perkin Elmer Lambda 800. The maximum wavelength was fixed at 316 nm.

Precipitation of the complex TOPO / Fe formed in the organic phase

This study consists at determining the best conditions of precipitation of the complex formed after extraction. Hence, the organic phase recovered after extraction under the optimal conditions was treated with ammonia solutions with various concentrations (0.1 – 7 M). Subsequently, each of the recovered organic phases was mixed with a in each case given volume of lead nitrate ($Pb(NO_3)_2$ to 0.05 M). After agitation, a precipitate appears at the interface of the phases. The recovered precipitate by filtration was then washed alternatively with the much diluted acid then hexane. The organic phase (hexane) was dried by distillation; the obtained product was analyzed by gas chromatography on a Perkin – Elmer chromatographic apparatus, equipped with PE-1, 100% methylsilicone 25m length, 320 mm diameter capillary tube and the carrier gas pressure of (N_2) is fixed at $6.9.10^4$ Pa; and by ^1H NMR spectrometry on a Fourier spectrometer Bruker AC 250 multinuclear. Commercial TOPO was purchased from Fluka.

Extractions tests

Aqueous solutions of Zn, Fe and Mo of concentration 1 mmol.L^{-1} were prepared by respective dissolution of sodium molybdate ($Na_2MoO_4 \cdot H_2O$), iron chloride ($FeCl_3$) and zinc chloride ($ZnCl_2$) in hydrochloric acid.

The experiments were carried out as follows: a first series concern the influence of the concentration of the hydrochloric acid and the molar ratio [TOPO]/[Zn]; to such end, two concentrations of $ZnCl_2$ are selected: 10 and 1 mmol/L, the concentration of the acid is varied from 2 to 10M, the contact time and the volume ratio of the phases (org / aq) are fixed respectively at 30 min and 1 min .

The second series of experiments refer to the effect of the contact time that is varied from 5 to 60 min; the volume ratio and the concentration of the acid are fixed respectively at 1 and 6 mol/L. The third series deal with the effect of the volume ratio of the phases that varies from 0.5 to 6, the contact time and the concentration being fixed respectively at 20 min and 6 mol/L.

Each solution thus prepared (Zn: 1 mmol/L; Mo: 1 mmol/L; Fe: 1 mmol/L) was put in contact with an organic solution of TOPO at 10 mmol/L in cyclohexane in a separatory funnel of 100 mL. Agitation was made in an apparatus of the type Jank Kunkel HS 500 IKA-WERK, at a speed of 90H ub / min.

After each extraction, the metal concentration was determined using an atomic absorption spectrophotometer Perkin Elmer A Analyst 300 and a pH-meter of type Tacussel Mini-80 was used for pH measurement.

RESULTS AND DISCUSSION

Influence of the concentration of the hydrochloric acid on the extraction of iron by TOPO

The extraction yields in function of HCl concentration are given by the curve (figure 1). According to the tracing of the curve, the maximal yields are between 6.5 and 8M.

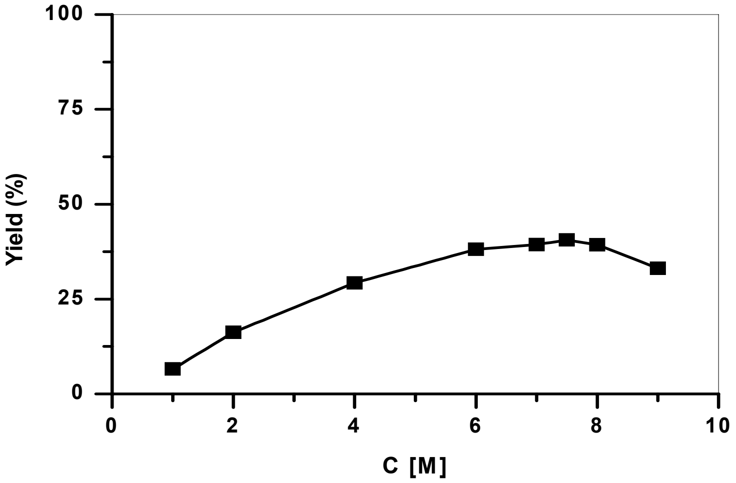

Figure 1. *Effect of HCl concentration on the extraction yield*
[TOPO]= 1.0 mmol.L^{-1}, [Fe^{3+}] = 20 mmol.L^{-1}, Vaq / Vorg = 1, T = 20 °C.

Influence of the agitation time

The presentation of the extraction yield in function of the agitation time is given in figure 2. According to the shape of the curve, the yield increases up to the value of 35 min, after which the formation of the complex is stabilized.

Influence of the volume ratio of the phases

The representative curve of the extraction yield in function of the volume ratio is given by figure 3.

According to the curve, one notes that for the values of the volume ratio of phases superior or equal at 4, the quantity of extractant is sufficient to complex the majority of the molecules of $FeCl_3$.

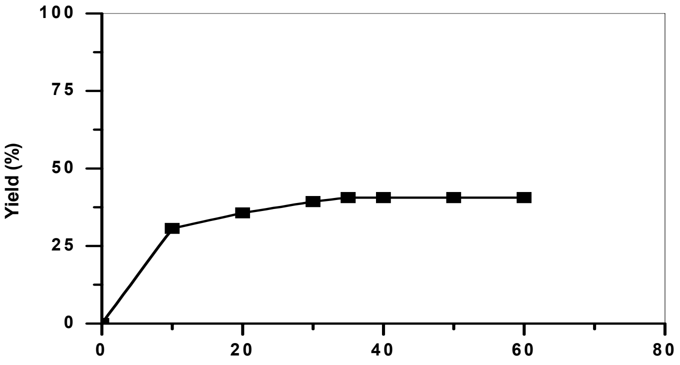

Figure 2. *Fe(III)yield extraction kinetics.*
[TOPO]= 1.0 mmol.L^{-1}, [Fe^{3+}] = 20 mmol.L^{-1}, Vaq / Vorg = 1, [HCl] = 7.5 M, T = 20 °C.

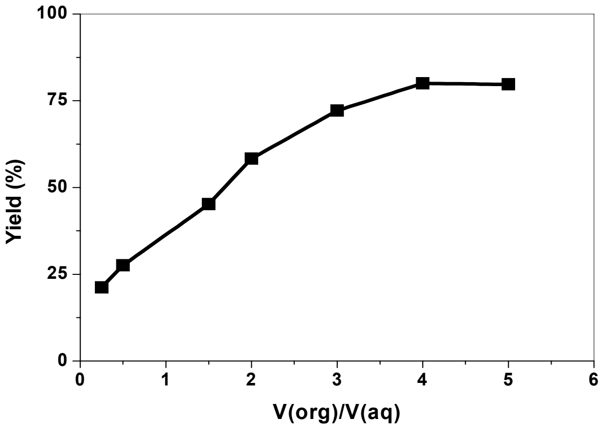

Figure 3*. Effect of volume ratio on extraction yield of Fe (III)*
[TOPO]= 1.0 mmol.L^{-1}, [Fe^{3+}] = 20 mmol.L^{-1}, [HCl] = 7.5 M, t = 35 min, T = 20 °C.

Determination of the number of extracted ligands

The number of ligands was determined starting from the curve representing the optical density in function for the concentrations ratio of $FeCl_3$ on TOPO. The optical densities were recorded to the maximum wavelength of the complex which is $\lambda = 316$ nm.
Figure 4 represents the optical density in function of the concentration ratio of $FeCl_3$on TOPO.
According to the curve, the number of ligands has the value of 1. Therefore the formula of complex is: [TOPO·$FeCl_3$], according to the Job's method [11]. The extraction follows the equation:

$$\left[\mathrm{Fe}^{3+} + 3\mathrm{Cl}^{-}\right]_{aq} + \left[\mathrm{TOPO}\right]_{org} \Leftrightarrow \left[\mathrm{FeCl}_3 \cdot \mathrm{TOPO}\right]_{org} \qquad (1)$$

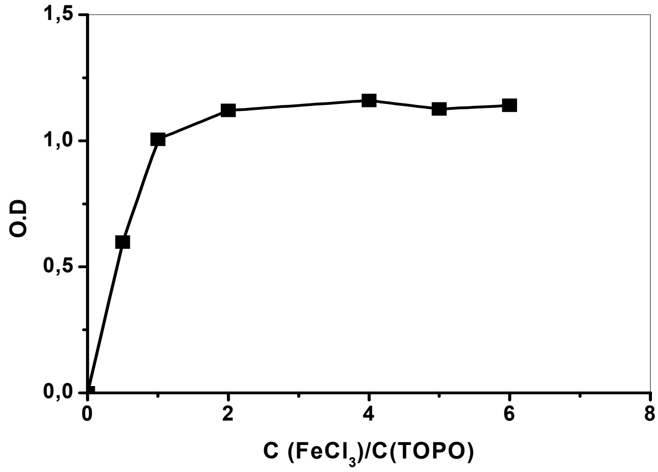

Figure 4. *Optical density in function of the ligands number*
$[Fe^{3+}]$ = 20 mmol.L^{-1}, Vaq / Vorg = 4, [HCl] = 7.5 M, t = 35 min, T = 20°C.

Precipitation of the formed complex

Precipitation is carried out after one has determined the conditions giving the best yields of extraction which are: acid concentration = 7.5M, agitation time = 35 min and the volume ratio of the phases = 4. The best precipitation is given for an ammonia concentration of 0.18M. The precipitate is isolated by filtration and then washed with water or with very diluted acid and hexane. The organic phase which comprises hexane and TOPO is subjected to a distillation to remove the solvent. The recovered product is analyzed by CPG and ^1H NMR (δ (ppm)= 0.85 (t, CH_3), 1.3 (m,CH_2), 1.6 (m, CH_2)). Figure 5 represents the chromatogram of commercial TOPO dissolved in hexane and figure 6 of commercial TOPO (dissolved in hexane) after treatment by the precipitation method.

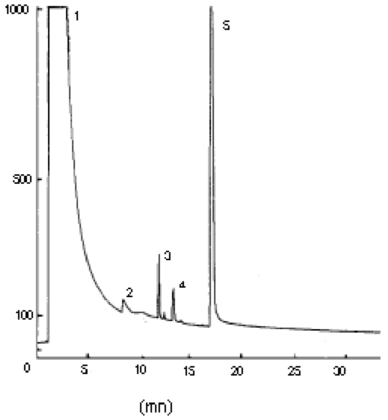

Figure 5. *Chromatogram of untreated TOPO (1: hexane;2, 3 and 4: impurities; 5: Commercial TOPO)*

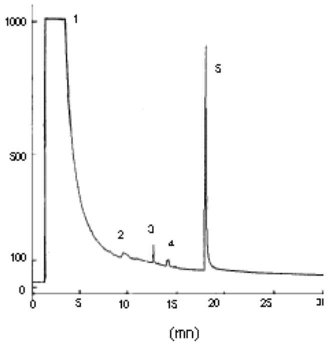

Figure 6. *Chromatogram of treated TOPO (1:hexane; 2, 3 and 4:impurities; 5: Commercial TOPO)*

According to the two figures, the hexane appears at the retention time (r.t.) 1.60 min, followed by impurities at 9.6 min, 12.33 min and 14.2 min. TOPO appears finally at 17.4 min. One notes that after purification the peaks of the impurities disappeared almost entirely (Figure 6) which demonstrates the efficacy of such a method.

Application of the method to the unfinished product of TOPO synthesis

After having determined the conditions of purification by using commercial TOPO, the procedure was applied to the gross product of synthesis of TOPO after having analyzed it by the CPG. In consequently and following the method described above the obtained precipitate was washed with water and hexane. After hexane removal, the obtained product was analyzed by CPG. Figure 7 represents the chromatogram of the gross product of synthesis, and figure 8 that of the obtained product after purification.
According to the two figures, the peak corresponding to hexane is located at r.t. = 1.75 min. The impurities appears at retention times of 3.7 min, 8.03 min, 12.73 min and the peak of TOPO is at r.t. = 17.5 min. The effectiveness of the procedure of purification is clearly stated by comparing these two figures. Indeed, the peaks of the impurities clearly decreased (Fig. 8).

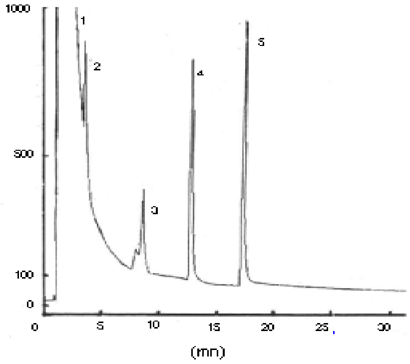

Figure 7. *Chromatogram of the synthesized TOPO before purification (1 : hexane ; 2, 3 et 4 : impurities ; 5 : TOPO synthesized)*

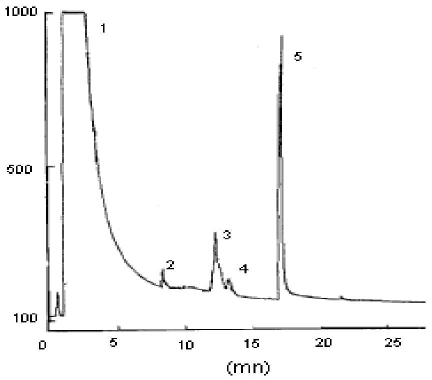

Figure 8. *Chromatogram of the synthesized TOPO after purification (1 : hexane ; 2, 3 et 4 : impurities ; 5 : TOPO synthesized)*

Calculation of the purity of the product before and after purification

The purity of the product was given by establishing a calibration curve (figure 9) which gives the concentrations of TOPO in its rough mixture and purified. The calibration curve was plotted starting from surfaces of the peaks according to various concentrations of TOPO in hexane. The coefficient "a" (slope) was determined by the least squares method (a = 699.54 $mol^{-1}.L^{+1}$).

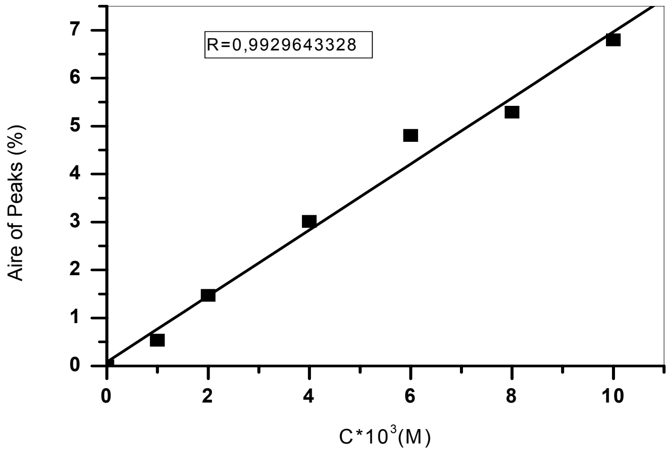

Figure 9. *Calibration curve of TOPO by CPG*

According to the curve, the peak surface of TOPO in the rough mixture of synthesis corresponds to a concentration of $9.88.10^{-3}$ M, for a mass of gross product equal to 0.5 g dissolved in 40 mL of hexane; the peak surface of purified TOPO correspond to a concentration of $9.31.10^{-3}$ M, however, for a mass of analyzed product equal to 0.20 g. The purity of the gross product increased therefore from 27.8 to 92 %.

Applications of TOPO in the liquid-liquid extraction

The applications of TOPO in the liquid-liquid extraction are discussed in terms of extraction yield which is defined as:

$$R(\%) = \frac{[M^{n+}]_i - [M^{n+}]}{[M^{n+}]_i} \times 100 \qquad (2)$$

$[M^{n+}]_i$: initial metal concentration in the aqueous phase,
$[M^{n+}]$: metal concentration in the aqueous phase after extraction.

Effect of the concentration of the acid and the molar ratio **[*TOPO*]/[*Zn*]**

The variation of the concentration of $ZnCl_2$ solution in function of its acidity is determined as a first step (figure 10). According to the graph, the pH is inversely proportional to the $ZnCl_2$ used amount; which could be explained in terms of conversion of $ZnCl_2$ to the equivalent hydroxide, according to:

$$ZnCl_2 + 2H_2O \rightarrow Zn(OH)_2 + 2HCl \qquad (3)$$

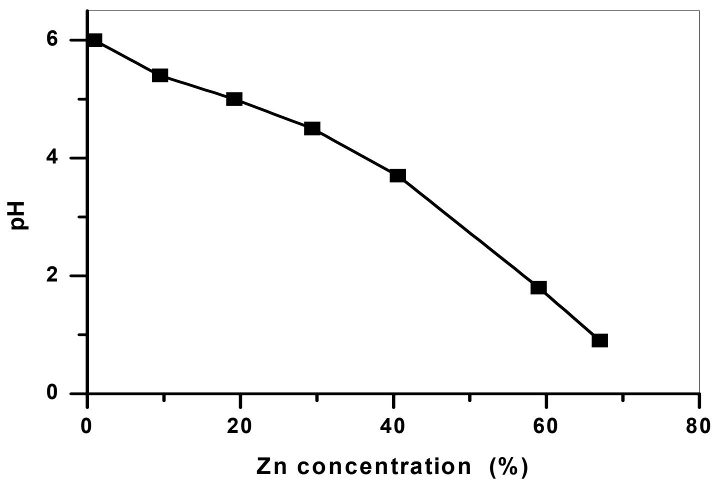

***Figure 10**. pH function of the amount of $ZnCl_2$ in water*

Two concentrations of zinc chloride were tested to check the influence of the acid concentration on the extraction of Zn by the TOPO in cyclohexane.

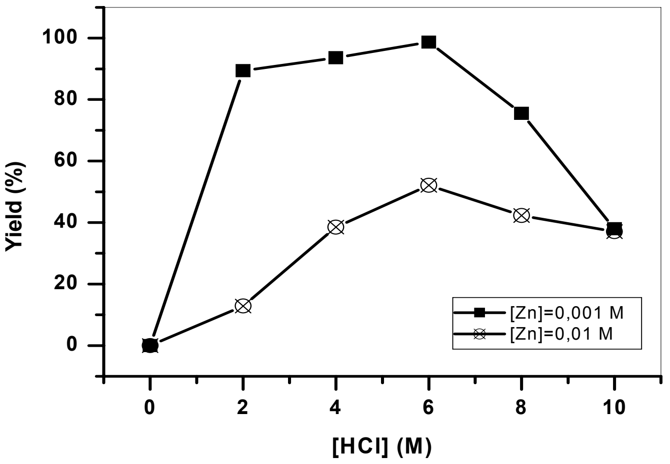

***Figure 11.** Effect of HCl concentration on the extraction yield of Zn(II)*

Thus, according to the curve shown in Figure 11, one notes that the concentration of $ZnCl_2$ does not impact the domain of acidity of the extraction medium. Indeed, the best extraction yields are at the domain 3 – 7 mol/L of hydrochloric acid concentration.
Nevertheless, the effect of the Zn concentration is noticed the yield value; for a molar ratio TOPO/Zn = 10 and a HCl concentration of 6 $mol.L^{-1}$, the yield is 98.7% and for the same concentration in acid and a molar ratio of 1, the yield decrease to 52.1%, which is probably due to the very strong acidity of the medium subsequent to the dissociation of zinc chloride in solution.

Effect of the contact time of the phases

Figure 12 shows the influence of the contact time of both the aqueous and organic phases on the extraction yield.

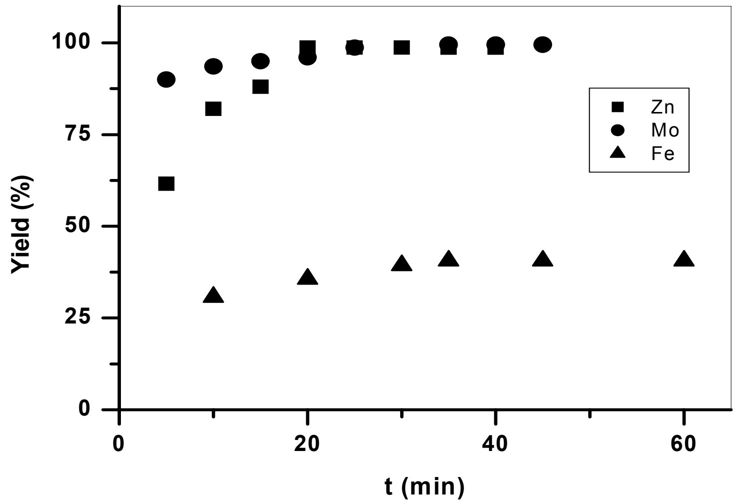

Figure 12. *Extraction kinetics yield of Zn(II), Mo(III) and Fe(III)*
[HCl]= 6 mol/L, $V_{org}/V_{aq} = 1$, *T = 20°C.*

It is observed that for an agitation time of 5 to 10 min, the yields approaches 99% for Mo and Zn. For Fe however, the yield is very different, approaching the 40% after 20 min; the extraction is stabilized after this contact time.

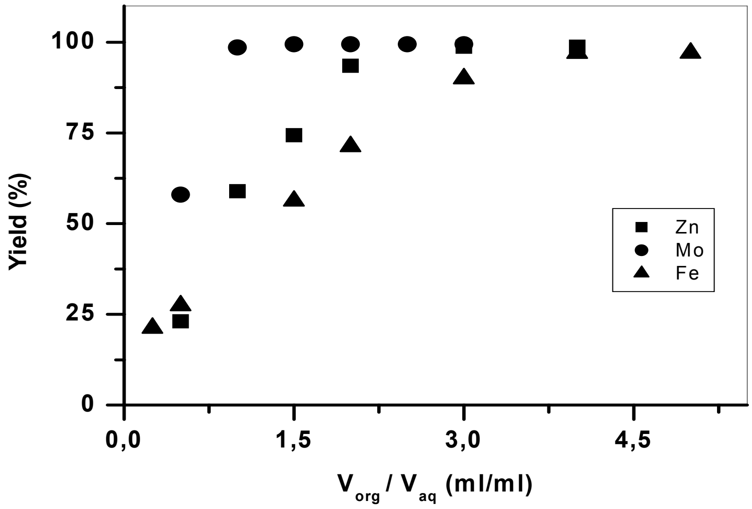

***Figure 13**. Effect of volume ratio on the extraction yield of Fe(III), Mo(III) and Zn(II)*
t = 20 min, C = 6 mol/L, T = 20°C

Effect of the volume ratio of the phases (Vorg / Vaq)

Figure 13 shows the influence of the volume ratio of the phases on the extraction yield. The yields are best beyond the value (Vorg / Vaq) = 2 for Zn, (Vorg / Vaq) = 1 for Mo and (Vorg / Vaq) = 4 for Fe. For this latest, one may observe that the value of the yield has practically doubled (> 98%).
In theory, the volume ratio of the phases (Vaq / Vorg) is inversely proportional to the yield $\{R\ (\%) = 100 \cdot D/[D + (Vaq/Vorg)]\}$; consequently, the more Vorg / Vaq increases, the better is the yield. Starting from a certain value of the ratio, the yield is stabilized, according to studied metal; for Mo from 1, for Zn from 2.5 and for Fe from 4.

CONCLUSION

This work allowed us the determination of the optimal conditions ([HCl] = 7.5M, t = 35 min and *R* = 4) of iron extraction, as well as the determination of the formula of the complex [Fe.TOPO].
The addition of an ammoniacal solution 0.18M and lead nitrate to the organic solution containing Fe.TOPO complex allowed the formation of an easy collectible precipitate through filtration.
Gas chromatography allowed the identification and titration of TOPO in its reactional mixture. Its purity determination was consequently achieved.
This technique of purification made it possible to increase the purity of TOPO from 27.8 % to 92 %. Therefore, this work represents an upgrade in the purification process.
It emerges from this study that several factors can influence the extraction yield of metal by TOPO; namely the nature of the medium (concentration and type of acid), the molar ratio: solvent / metal, the contact time and the volume ratio of the organic and aqueous phases.
Concerning the nature of the medium, an average acidity of 3 - 7mol/L is recommended in the extraction of the three studied metals; the contact time must be > 5 min and the volume ratio of the phases between 1 and 2 so as to have a yield of extraction > 97% for Mo and Zn.
The concentration of zinc chloride must be at least 10 times weaker than that of TOPO. Like it was noted, the elevated concentrations of $ZnCl_2$ increase the acidity of the medium and lead to the risk of trespassing of the domain of medium acidity recommended for the extraction of Zn.
In the case of Fe, one notes that the increase in the volume ratio beyond 4, leads to a clear increase in yield; with the domain of acidity favorable to the extraction of three metals (3-7M) and for a contact time of 20 min, the value of the extraction yield of Fe more than doubled (from 40 to 99%) by increasing the volume ratio.

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