RECOVERY OF HEAVY METALS FROM WASTES WATERS BY SOLVENT EXTRACTION USING THE PHOSPHORIC ACID (D2EHPA)

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ABSTRACT

The solvent extraction of metallic cations by di(2-ethylhexyl)phosphoric acid (D2EHPA), diluted in n-heptan, is discussed in a way of the extraction efficiency. The solvent extraction was carried out starting from an acetate aqueous solution.

By study of the acetate aqueous phase containing metal to be extracted (volumetric analysis) and while varying the following conditions: Q, $[(D2EHPA)_2]$, volumes ratio aqueous to organic (V_w/V_{org}), we could :

- To optimize the extraction yield of each metal ion taken separately,
- To establish a equilibrium mechanism of extraction for each metal,
- To establish an order of selectivity, during the extraction starting from synthetic mixture of the metallic cations and show the synergy effect, during the extraction with extractants mixture (D2EHPA + TBP).

Keywords: Copper Nickel Separation, Solvent Extraction, D2EHPA, Synergy Effect

INTRODUCTION

The phosphorus chemistry offers broad fields of scientific and technological applications. The organophosphorus compounds are excellent metal ions extractants because are chelating agents; this is why they are frequently employed in the solvent extraction process. In particular, they are used for the purification of the liquid effluents who can contain heavy metals **[1,2]**.

Among the commercial phosphoric acid extractants, di(2-ethylhexyl)phosphoric acid (abbreviated as D2EHPA or simply HR) has been extensively studied as an extractant reagent in hydrometallurgical processes for the separation and purification of a number of metals. It can extract heavy metals such as copper, cobalt, nickel and zinc **[2,3]**.

Di(2-ethylhexyl)phosphoric acid continues to be studied in the solvent extraction process, for the separation and the purification of the metal liquid effluents **[3,4]**. The solutions of D2EHPA in organic solvents can be charged strongly by the divalent metal ions, without the formation of a third phase and viscosity becomes inaccessible when the moles number ratio of ligand /metal = 2 (Q) is held in account.

Many studies treat solvent extraction of nickel and copper in aqueous mediums such as sulphate, chloride and nitrate but our work was based on the choice of an acetate medium.

EXPERIMENTAL

1. Realization of the extractions

Each experimental point was obtained by magnetic shaking of extract aqueous phase (10 cm^3) and extracting organic phase (5 cm^3) in funnels separating, followed by a separation. The shaking time, in each case, determined from experiments and was chosen largely higher than time necessary to reach the extraction equilibrium. In all the cases, thirty minutes of stirring appeared sufficient. The variations of volume were supposed to be negligible and all experiments were carried out at ambient temperature (20 °C).

2. Reagents and produced

The aqueous solutions were prepared with distilled water and the following reagents were used: copper acetate (II), nickel acetate (II), murexide ($C_8O_6N_5H_5$) and 1-[pyridyl-(2)-azo]-2-naphtol ($C_{15}H_{11}N_3O$) (PAN) provided by MERK, ethylen diamine tetraacetic bisodium acid ($C_{10}H_{14}N_2Na_2.2H_2O$), (EDTA) provided by FLUKA.

The organic phase is made up:

The n-heptan diluent and di(2-Ethylhexyl)phosphoric acid (D2EHPA) extractant provided by FLUKA of which the proportion in D2EHPA / M2EHPA is 60 / 40. %

3. Analytical methods

During this work, we were brought for determine the copper and nickel concentrations in the aqueous solutions. For this reason, the following analytical methods were used:

- pH-metric analysis of D2EHPA,
- Volumetric analysis of Cu (II) and Ni (II).

RESULTS AND DISCUSSION

The D2EHPA being a mixture of mono and di- phosphoric acids, we takes 10 ml of D2EHPA diluted in the n-heptan (10^{-3} M) to which we adds 20 ml of distilled water, follow-up of a strong stirring and phases separation, in order to check if the monophosphoric acid remained or not in organic phase. We analyze a well defined volume of the organic phase (after separation of the two phases) by NaOH 5 x 10^{-2} N.

Figure 1 shows only one turn, which confirms that all the M2EHPA passes in the aqueous phase and only the D2EHPA ensures the extraction of the metal ions.

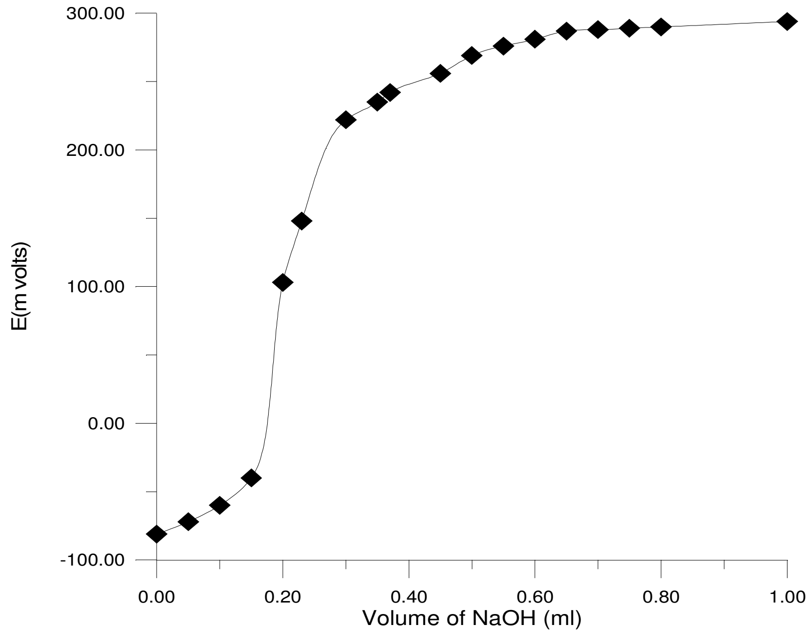

Fig. 1: Potentiometry curve of D2EHPA

I. EXTRACTION OF COPPER BY THE D2EHPA

The concentration of the cupric ions after extraction was determined by volumetric analysis in the presence of indicator "PAN" (twice to recristallize in ethanol to 96 %, pH ≤ 5). The results are presented in Fig. 2, which shows an extraction yield maximum of 94 %.

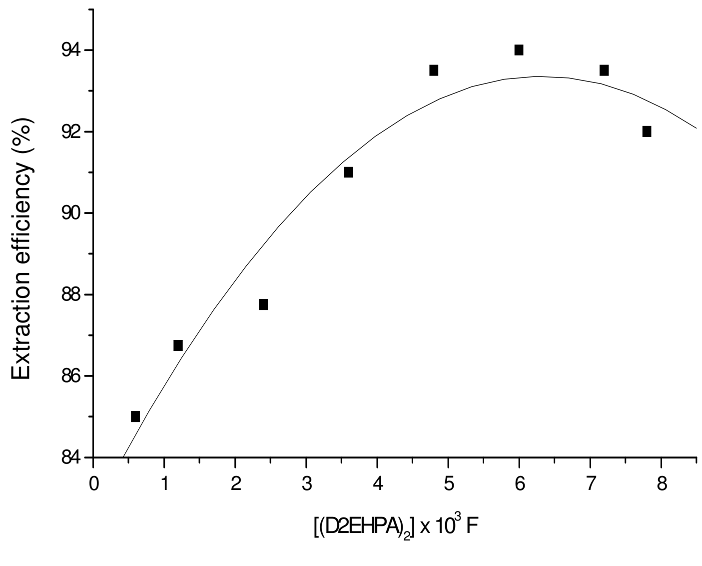

Fig. 2: Effect of D2EHPA concentration on extraction efficiency of copper, $[Cu^{2+}]_i = 10^{-3}$ M, pH= 6.17

The extraction of copper (II) by D2EHPA, diluted in n-heptan can be expressed by the general equation (1) **[5-7]**.

$$M_w^{n+} + (x+n)/2\ (\overline{H_2R_2}) \longleftrightarrow \overline{MR_n.xHR} + n\ H_w^+ \quad (1)$$

The corresponding equilibrium constant is:

$$K_x = \overline{[(MR_n.xHR)]}[H^+]^n[M^{+n}]^{-1}[(\overline{H_2R_2})]^{-(n+x)/2} \quad (2)$$

The distribution ration of copper is given by:

$$E = C_{M,org}/C_{M,w} = [\overline{(MR_n\,xHR)}]/C_{M,w} \quad (3)$$

$$E = K_x[(\overline{H_2R_2})]^{(n+x)/2}[H^+]^{-n}\ \alpha_{(M)}^{-1} \quad (4)$$

$\alpha_{(M)}$: is the coefficient, which takes account of the secondary reactions due to the hydrolysis and the formation of metal complexes in the aqueous phase **[8]**.

$$R = (C_8H_{17}O)_2P(O)O^-$$

M^{n+}_w = metal ion extracted of load n^+ in aqueous phase
$\overline{H_2R_2}$ = dimerous form of D2EHPA in organic phase
HR = monomeric form of D2EHPA

From equation (4), distribution ratio depends on the pH and the extractant concentration. The logarithmic plots of the distribution ration according to each variable of the equation (4) by maintaining the others constant, give an estimate of the stoechiometries values x and n. A plot of log E vs. log [H^+] gives a straight line with a slope of 0.83 i.e., n = 1. The experimental results are shown in Fig. 3. Figure 4 shows a straight line between log E and log $[\overline{H_2R_2}]$ with a slope of 0.96 i.e., x = 1.

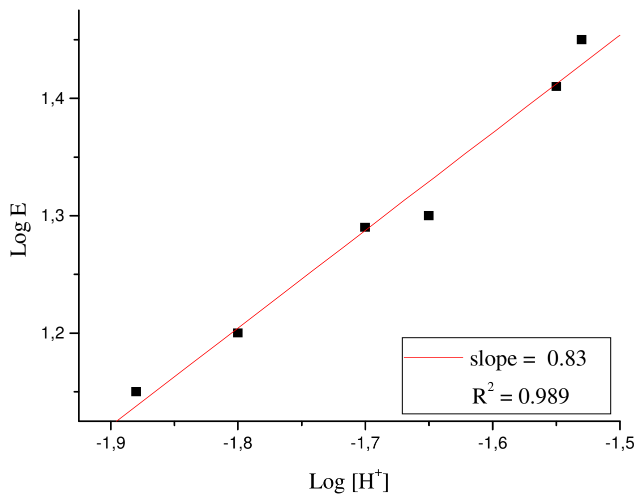

Fig. 3: Plots of log E vs. log [H^+] at extraction equilibrium of copper, $[Cu^{2+}]_i = 10^{-3}$ M.

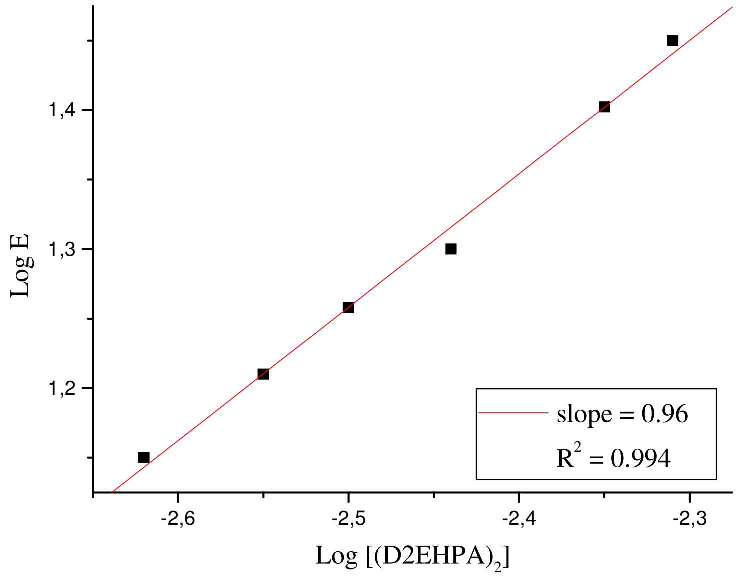

Fig. 4: Influence of D2EHPA concentration on distribution ratio of copper, $[Cu^{2+}]_i = 10^{-3}$ M.

The values obtained (x and n) shows that the extraction equilibrium of Cu^{+2} in acetate medium by the D2EHPA, diluted in n-heptan obeys at following equation:

$$CuCH_3COO^+_w + (\overline{H_2R_2}) \longleftrightarrow \overline{CuCH_3COOR.HR} + H^+_w \qquad (5)$$

The suggested structure of the formed complex, in the organic phase during the extraction, is given by Fig.5.

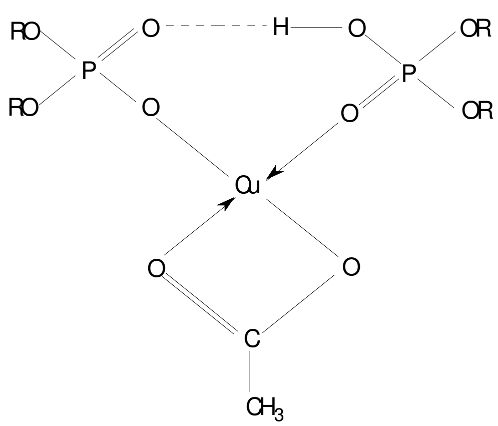

Fig. 5: Schematic representation of Cu-D2EHPA complex

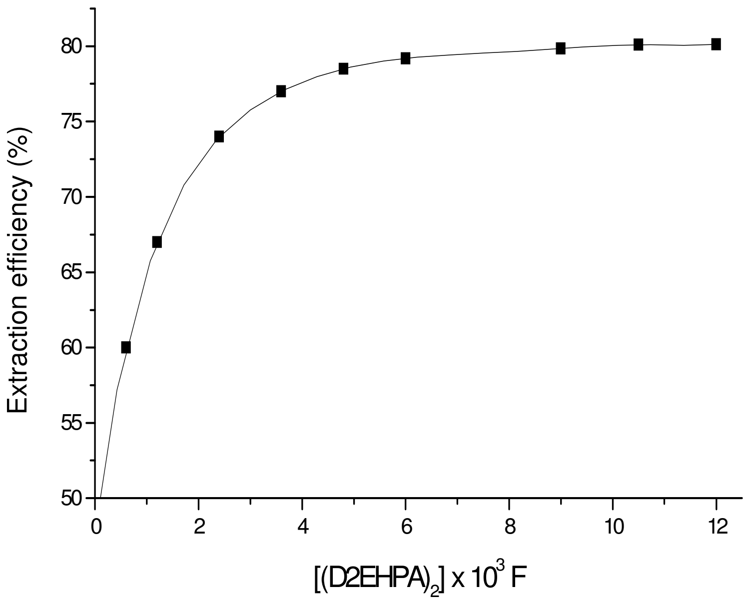

Fig. 6: Influence of D2EHPA concentration on extraction efficiency of nickel, $[Ni^{+2}] = 10^{-3}$ M

However, it should be announced that the hydrolysis product of copper (II) is the dimerous species $(Cu_2(OH)_2)^{2+}$ **[9,10]**. A series of monomolecular species: $Cu(OH)^+$, $Cu(OH)_2$, $Cu(OH)_3^+$, can also be formed but are formed in considerable proportions only in the solutions very diluted between pH 7 and 12.

II. EXTRACTION OF NICKEL BY D2EHPA

The extraction of nickel (II) by the D2EHPA, diluted in the n-heptan, is carried out in neutral medium with a volumes ratio ($V_w/V_{org} = 2$). It takes place in an engine stirred perfectly until equilibrium reached (t = 30 min). One separates the two phases using a funnel of separation. A volume of 4 ml taken of the aqueous phase is titrated. The results are represented in Fig. 6. The choice of n-heptan is that it presents a synergy effect toward the metal, because according to the principle of **Taube** the molecules of the thinner do not block extractant. Then the D2EHPA preserves its extractive character.

By observing Fig. 6, one notices that the extraction yield of nickel increases with the concentration of extractant dimerous until becoming constant by reaching the maximum value of 80 %.

The stoechiometries coefficients of the extraction equilibrium equation of nickel (II) by the D2EHPA, in neutral medium are deduced from the slopes of logarithmic plots. One distinguishes that the nickel is chelated by the half of dimer.

Firstly: when extractant is in its monomeric form, equilibrium is written:

$$NiCH_3COO_w^+ + 2H_2O + (\overline{HR}) \longleftrightarrow \overline{NiCH_3COO.(H_2O)_2R} + H_w^+ \qquad (6)$$

The structure of complex is represented as follows (Fig. 7):

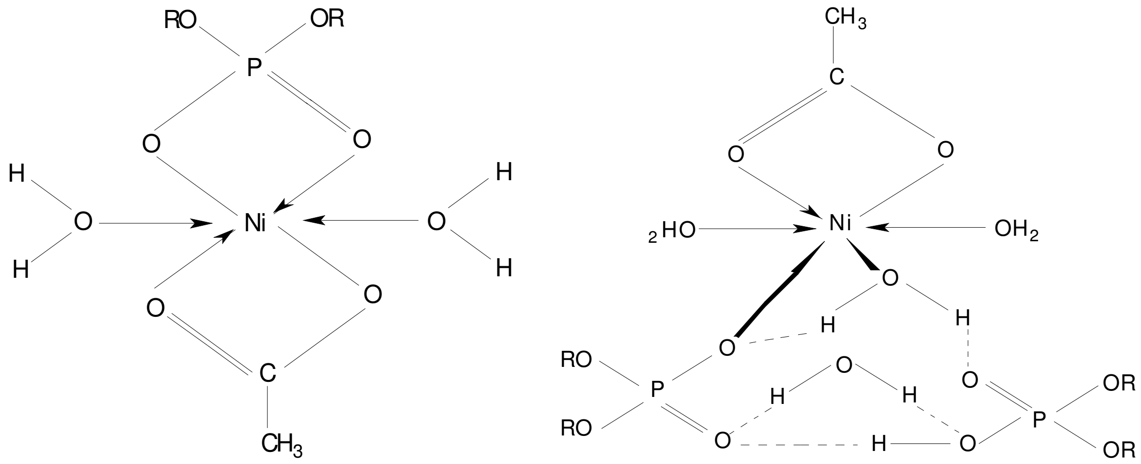

Fig. 7: Schematic representations of Ni-D2EHPA complexes

<u>Secondly</u>: when extractant is in its dimeric form, equilibrium is written:

$$NiCH_3COO_w^+ + 3H_2O + \tfrac{1}{2}(\overline{H_2R_2.2H_2O}) \longleftrightarrow \overline{NiCH_3COO.(H_2O)_4.R} + H_w^+ \qquad (7)$$

Dimer H_2R_2 is related to two water molecules because of the great solubility of water in the D2EHPA (0.051 mol.l^{-1} at 20°C). Structure of complex is represented by Fig. 7.

III. SELECTIVE EXTRACTION OF COPPER BY D2EHPA

III. 1. Calibration curves

The calibration curves of nickel, copper and their mixture were carried out starting from the aqueous acetate solutions.

For each solution one takes a volume of 2.5 ml, titrated by the EDTA (5×10^{-3}M) in the presence of the indicator "meruxide". The results are deferred in the Fig 8.

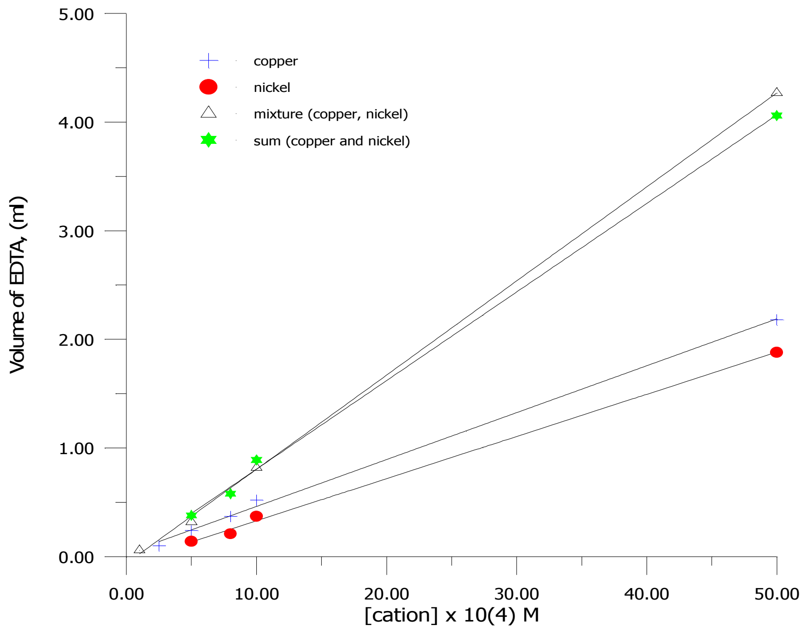

Fig. 8: Calibration curves of Cu^{+2}, Ni^{+2} and their mixture, pH = 6

From Fig. 8, one notices that beyond the concentration 1.5 x 10^{-3}M in copper and nickel, the titrated volume of the two mixed cations is slightly higher than the sum of titrated volume of each taken cation separately (relative error equalizes to 5%).

III. 2. Selective extraction of copper in neutral medium

The extractions were carried out starting from an initial aqueous solution 10^{-3} M in copper and nickel. The concentrations of extractant are selected in such way that the difference between the extraction yield of each cation taken separately is highest (maximum for copper and minimum for nickel). The others conditions of extraction like the equilibrium time = 30 min, V_w/Vorg = 2 and T = 20°C, were maintained. From aqueous phase recovered after extraction, a volume equal to 2.5 ml is titrated by the EDTA (5 x 10^{-3} M) in the presence of meruxide. The results are gathered in Figs. (9-12) and Table (1).

Table. 1: Influence of extractant concentration on Hydrogen ion concentration at extraction equilibrium of metal

	Cu (II)	Ni (II)	
$[(D2EHPA)_2]$ x 10^3 F	PH	pH	ΔpH^*
0.6	3.88	1.84	2.04
1.2	3.1	1.7	1.4
2.4	1.88	1.64	0.24
4.8	1.53	1.53	0

where ΔpH^* = pH(Cu) - pH(Ni)

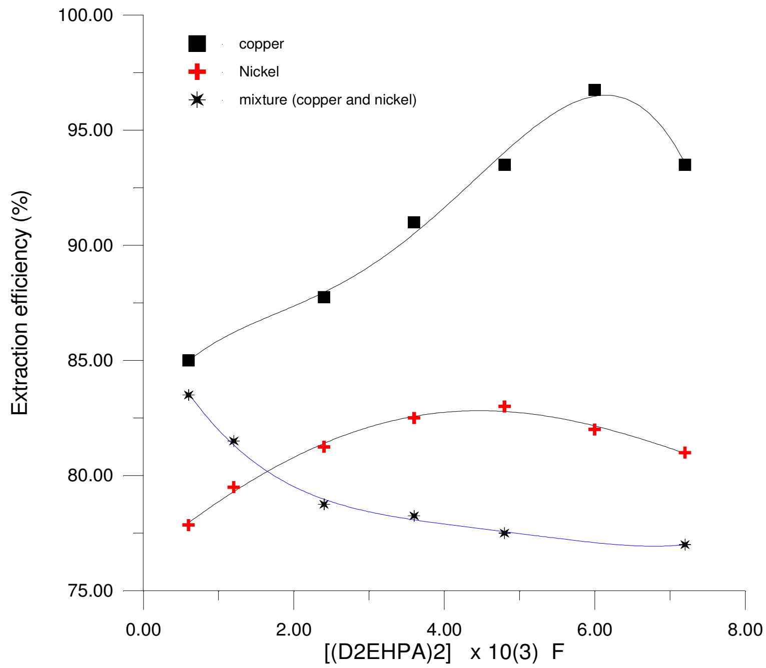

Fig. 9: Influence of D2EHPA concentration on extraction efficiency of copper, nickel and their mixture, pH = 6.

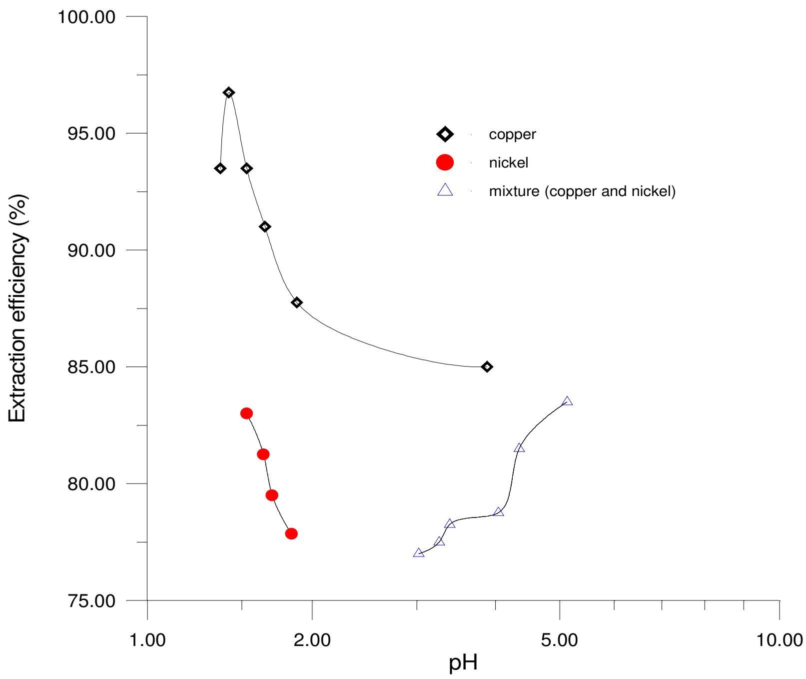

Fig. 10: Variation of extraction efficiency of copper, nickel and their mixture with pH of equilibrium

At a concentration of D2EHPA equal to 4.8 x 10^{-3} F, we obtain under the same experimental conditions the same pH of equilibrium for both cations (Table 1). The extraction yields of copper and nickel which results from this, show a good extrability of copper (93.5 %) compared to nickel (83%) (Fig. 10). In the order, we have the extrability of Cu (II) is higher than Ni (II). This result was obtained by **Yukio Nagaosa** and **al [11]** in sulphated medium. For the extraction of the mixture (Cu^{+2}, Ni^{+2}), the yield decreases with the increase in the extractant concentration (Fig. 9).

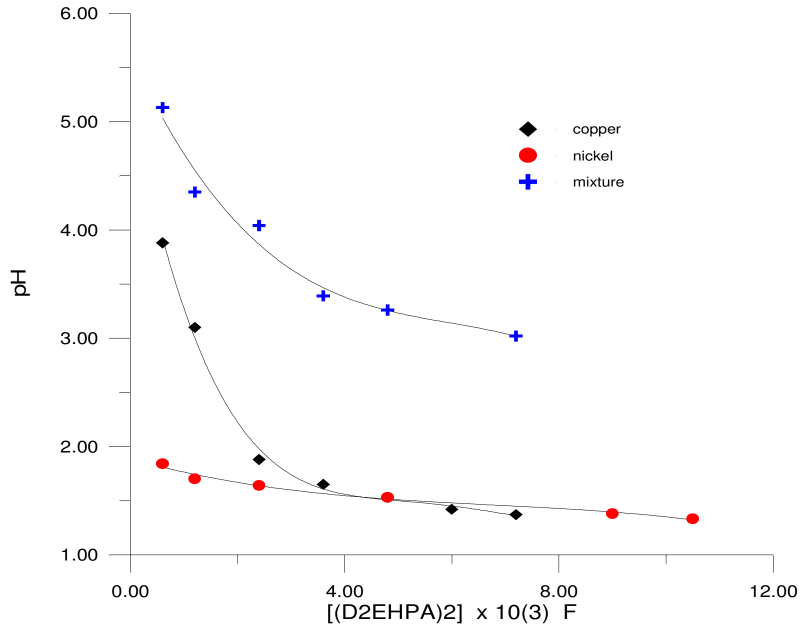

Fig. 11: Variation of pH at the extraction equilibrium of copper, nickel and their mixture with the extractant concentration

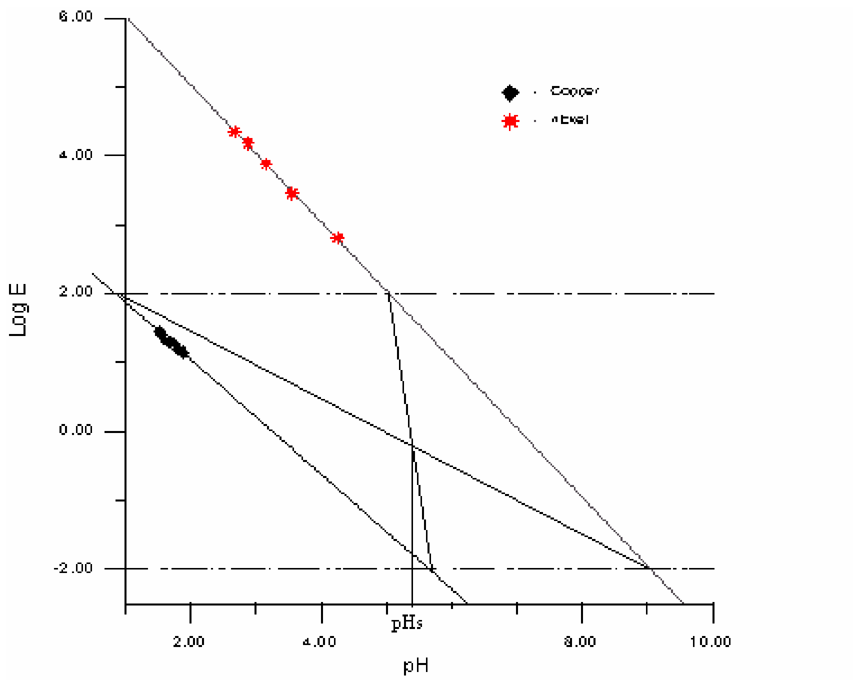

Fig. 12: pH of separation for both metal-ions at one stage

From Table (1) and Figure 11, the values of pH of extraction equilibrium for the metal ions decrease with the increase in the extractant concentration. In the range 0.6 x 10^{-3} F at 8 x 10^{-3} F, the values of pH change as follows:

Cu (II) (range of pH = 2.35) > Ni (II) (range of pH = 0.31).

The value of ΔpH^* indicates that the effectiveness of copper separation decreases when the extractant concentration increases.

The separation process for both ions is discussed in a way of distribution ratio for each one of these two metals, under the conditions identical to those of their mixture, by:

$$SF = E_{Cu+2} / E_{Ni+2}$$

where E_{Cu+2} : Distribution ratio of copper extraction
E_{Ni+2} : Distribution ratio of nickel extraction

This method is valid only when two metals have the same oxidation step. The two plots log E vs. pH of equilibrium have slopes equal to 1 for Cu^{2+} and Ni^{2+} respectively. We can separate both ions in an extraction at only stage by determining of pH_s (pH of extraction at only stage), with log E = +2 for copper and log E = -2 for nickel.

The separation minimum of these two plots should be equal to 4/n. As n=1 (number of protons exchanged during the copper or nickel extraction) then there is 4/n = 4 from where one finds pH_S = 5.71 (Fig. 12). At this pH, the D2EHPA concentration must be lower than 0.5 x 10^{-3} F.

III. 3. Effect of extractants mixture on the selective extraction of copper

The mixture of two extractants, one cationnic (D2EHPA) and the other neutral (TBP), produces one of the two effects:

- synergy effect or
- antagonism effect.

Effect of the TBP (tri-butylphosphate) is discussed of its action capacity on the copper selective extraction. The extractions have been carried out on the mixture (Ni^{2+}, Cu^{2+}) in neutral medium (pH = 6.24). Concentration of TBP was constant and equal at 3.676 x 10^{-3} M throughout our experiments, only the concentration of D2EHPA varies. Mixture was prepared in the n-heptan. The experimental conditions are maintained, identical to those of the preceding experiments (T= 20°C, V_w/V_{org} = 2, stirring time = 30 min, $[Ni^{2+}]_i = [Cu^{2+}]_i = 10^{-3}$M, $[(D2EHPA)_2]$ = 0.6 x 10^{-3} F at 7.2 x 10^{-3} F). Extraction results of Cu^{2+} and Ni^{2+} by the D2EHPA in the presence of TBP are presented in Fig. 13.

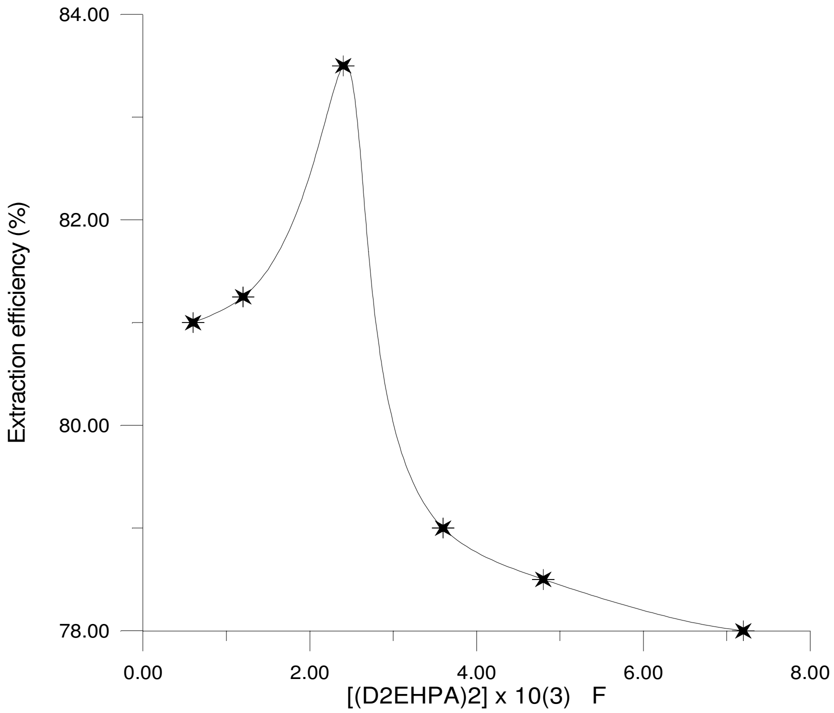

Fig.13: Influence of concentration of extractants mixture on selective extraction efficiency of copper

Result obtained shows that when the percentage of TBP in the extractants mixture is lower than 0.76%, we have an increase in the extrability due to the solvatant character of the TBP. While, when the percentage of TBP is higher than 0.76%, we have a decrease in the extrability due to the polar character of the TBP and chemical reaction between D2EHPA and TBP which lowers the free D2EHPA concentration.

CONCLUSION

The solvent extraction of various metal ions (copper and nickel), starting from the aqueous solutions containing the organic ion (CH_3COO^-) using an organophosphorus acid (D2EHPA) diluted in n-heptan, gave us a maximum yield of 94 % for copper and 80 % for nickel. Our experimental study enabled us to determine the extrability order from where we found that the extrability rate of copper (93.5%) is higher than nickel (83%). These last results were given when the metal ions are together.

It is necessary to use an optimal concentration of D2EHPA lower than 0.5×10^{-3} F to extract copper instead of nickel. Moreover, synergy effect was observed with 0.76 % of the TBP in the extractants mixture (D2EHPA + TBP).

In this present work, we used simple means and a traditional method which is the solvent extraction. The organophosphorus acid agents showed their effectiveness in the depollution of contaminated waters by heavy metals. Two successive extractions are sufficient to purify an industrial or urban liquid wastes containing copper, nickel or both at the same time.

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