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Article

Tantalum and Niobium Selective Extraction by Alkyl-Acetophenone

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Abstract: A study has been carried out on Ta and Nb recovery by liquid-liquid extraction process using 4-methylacetophenone (4-MAcPh) as organic phase. The 4-MAcPh was compared to methylisobutylketone (MIBK) with respect to extraction efficiencies (k_D values) at different concentrations of H_2SO_4 in the aqueous phase. The results showed a similar extraction of Nb for both solvents. However, for Ta extraction efficiency is increased by a factor of 1.3 for 4-MAcPh. In addition, the MIBK solubilized completely after 6 mol L^{-1} of H_2SO_4 against only a loss of 0.14 to 4% for 4-MAcPh between 6 and 9 mol L^{-1} of H_2SO_4. The potential of 4-MAcPh has also been studied to selectively recover Ta from a model capacitor waste solution. The results showed a selectivity for Ta in the presence of impurities such as Fe, Ni, Mn. The 4-MAcPh also presents the advantage of having physicochemical properties adapted to its use in liquid-liquid extraction technologies such as mixer-settlers.

Keywords: 4-Methylacetophenone; Refractory metals; Solvent extraction; Selective recovery

1. Introduction

During the last thirty years, the demand for metals has increased in volume but has also changed in nature. The number of elements of the periodic table used by the global industry has increased significantly, each having its physico-chemical specificity adapted to the desired application.

- Between the 1980s and the end of the 2000s, the number of chemical elements used to produce computers increased from about fifteen to about sixty.

- From 1990 to 2005, the world production of rare earths increased from 400 to 1400 t, mainly due to their increasing use in electronics, energy and lighting.

- From 1993 to 2007, global production of germanium doubled until 90 t to cope with its growing use for optical fiber production, for information transport, for infrared and photovoltaic devices (USGS source).

- From 2007 to 2015, the European consumption of tantalum (metal and oxide) quadrupled, from less than 100 t to 380 t, the use of this metal being in full swing in superalloys for aerospace, automotive or stationary turbines, as well as in components carbide for cutting tools, but especially in miniaturized capacitors (60% of current consumption) for mobile electronics (phone, laptops, tablets…) [1] [2].

Thus, the annual consumption of refined tantalum is around 2000 tons per year worldwide, with the supply exclusively resulting from mining, concentrated on 3 continents, Australia (40 %) Brazil (17%) and the Great Lakes region in Africa (23%). On the other hand, with very similar chemical properties, tantalum (Ta) and niobium (Nb) occur naturally in the same ores, especially tantalite and columbite (Table 1).

Table 1. Main economical minerals for Ta [1].

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Mineral	General formula	Ta_2O_5 (%)	Nb_2O_5 (%)
Tantalite	$(Fe,Mn)(Ta,Nb)_2O_6$	40-80	2-30
Columbite	$(Fe,Mn)(Ta,Nb)_2O_6$	1-40	30-75
Wodginite	$(Ta,Nb,Sn,Mn,Fe,Ti,Mn)_{16}O_{32}$	45-70	1-15
Microlite	$(Ca,Na)_2, (Ta,Nb)_2(O,OH,F)_7$	50-79	1-10
Stueverite	$(Fe,Mn)(Ta,Nb,Ti)_2O_6$	5-26	7-17
Euxenite	$(Y,Ca,Ce,U,Th)(Ta,Nb,Ti)_2O_6$	2-12	22-30
Samarskite	$(Fe,Ca,U,Y,Ce)_2(Ta,Nb)_2O_6$	15-30	49-55

Whereas less popular than tantalum, Niobium is an essential metal for some industries. Thereby, it is involved in the manufacture of microalloyed steels for pipelines, stainless steels for the automotive industry as well as in the production of alloys and superalloys for the aerospace industry, the nuclear industry, petrochemicals and some medical devices such as nuclear magnetic resonance equipment [3].

Since 1957, liquid-liquid extraction has replaced the Marignac process, a crystallization process less efficient, discontinuous and time-consuming for the production of Ta and Nb [4]. All commercial liquid-liquid extraction processes are carried out in the presence of fluorine and often with a second mineral acid such as sulfuric or hydrochloric acid.

Ta and Nb can reach several oxidation states such as +5, +4, +3, +2, +1 but only Ta^{5+} and Nb^{5+} are the most stable states in aqueous solutions [5]. Ta^{5+}reduction does not occur even in the presence of powerful reducers like Al, Zn, Cd. More reactive, Nb^{5+} is reducible to Nb^{3+} in acidic medium since it forms anionic complexes such as $(NbCl_6)^{3-}$ or $(Nb(SO_4)_3)^{3-}$ in hydrochloric (HCl) and sulfuric (H_2SO_4) solution respectively. However, the reduced Nb^{3+} is unstable and can rapidly be oxidized to Nb^{5+} in the presence of oxygen in the atmosphere [6].

In hydrofluoric medium, Ta^{5+} and Nb^{5+} are very stable monomeric complexes, each of them forming two types of complexes such as TaF_7^{2-}, TaF_6^- and $NbOF_5^{2-}$, NbF_6^- [7]. The equilibrium between complexes is governed by the concentration of HF and elements (Ta or Nb) and it can be described as follows:

For the Ta: $TaF_7^{2-} + HF \leftrightharpoons TaF_6^- + HF_2^-$,

And for the Nb: $NbOF_5^{2-} + 3HF \leftrightharpoons NbF_6^- + H_2O$

The predominance domains of these complexes in the Ta_2O_5 / Nb_2O_5 - HF - H_2O system is described elsewhere [7].

Also with the presence of second mineral acid, HSO_4^-, Cl^-, NO_3^-, there may be a possibility of formation of mixed fluoro-bisulfate, fluoro-chloride or fluoro-nitrate complexes [8].

Figure 1 presents a process scheme for Ta and Nb production. The ore containing at least 25% of Ta and Nb is dissolved in the binary $HF+H_2SO_4$ [9]. After dissolution residues removal by filtration, Ta (TaF_7^{2-} , TaF_6^-) and Nb ($NbOF_5^{2-}$,NbF_6^-) are selectively extracted by contacting with a solvent. Here, two different routes are typically used [9]. One consists of a first Ta and Nb co-extraction from an aqueous phase at acidity more than 9 $mol\ L^{-1}$ followed by a selective separation of both elements at low acidity. The other method is to selectively extract one after the other Ta and Nb elements from aqueous solution by changing the acidity. In both cases (grouped or sequential extraction), Ta and Nb are stripped from solvent by ammonium fluoride or water.

In this process, several solvents were studied for the extraction of Ta and Nb namely bis-(2-ethylhexyl) phosphoric acid (DEHP) [10], trioctyl-phosphine oxide (OPO) [11], dibenzo-18-crown -6 (B18C6) [12], tri-n-butyl phosphate (TBP) [13], ketones such as diisopropyl ketone, diisopropyl butyl ketone, n-butyl ethyl ketone [14, 15], methyl isobutyl ketone (MIBK) [16] and cyclohexanone [13], amides such as dimethylheptylacetamide [17] and bis-2-ethylhexylacetamide [18], secondary and tertiary amines [19 , 20] such as tri-n-octylamine [21], Alamine™®336 and tri-n-decylamine, quaternary ammonium salts [10] such as tri-n-octylmethylammonium, tri-n-octylpropylammonium and ethylbenzyldimethylammonium

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chlorides, tetrahexylammonium iodide, tri-n-octylmethylammonium hydroxide, bis-tri-sulfate n-octylmethylammonium, bistetrahexylammonium sulphate and tri-n-octylmethylammonium nitrate as well as long chain alcohols such as 1-octanol, 2-octanol [9, 15] and isoamyl alcohol [5, 17].

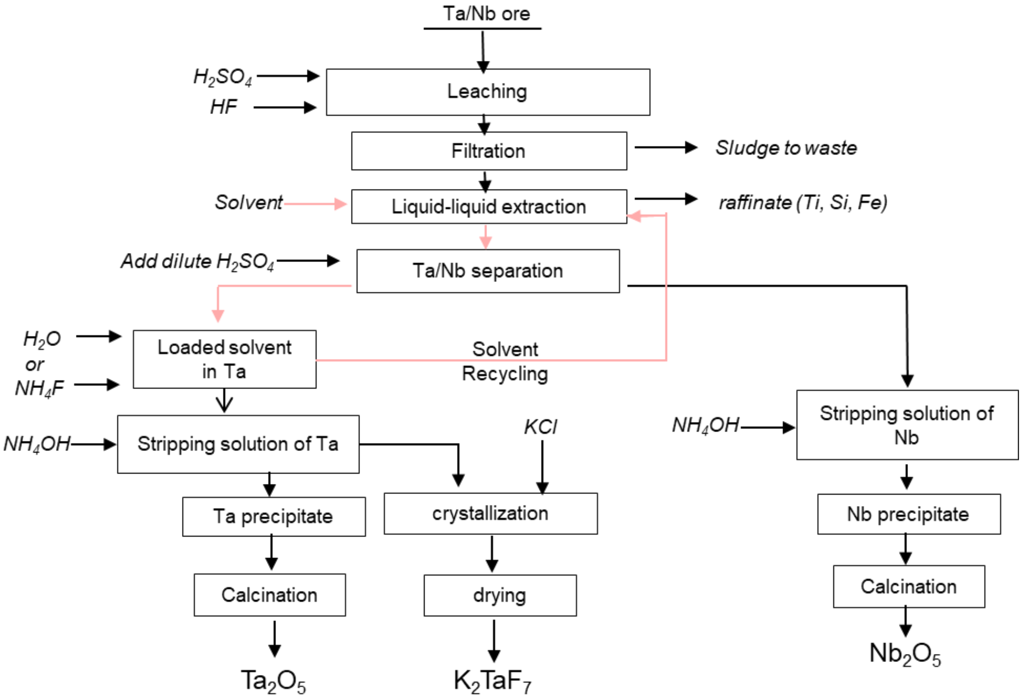

Figure 1. Process scheme for Ta and Nb production [4]

Among these solvents, only MIBK, TBP, cyclohexanone and 2-octanol are used industrially. However, despite their implementation in well-tried and effective processes for the production of Ta and Nb, some issues inherent in their use are observed.

Actually, the MIBK, which is the most widely used in the world, has a relatively high solubility in water (of the order of 2% w) [5], a high volatility and a low flash point (14 °C). Therefore, the MIBK display safety problems since the mixers-settlers and the pumps which are used to recover Ta and Nb on industrial scale must be able to operate in explosive atmosphere.

TBP, which is more used in Russia and India, has a relatively low solubility in water (0.6%w) and a high flash point (193 °C) [5]. However, it is unstable in highly concentrated acidic solutions, especially in the presence of hydrofluoric acid and its hydrolysis products, such as phosphorus (V), which has the consequence of decrease the purity of Ta and Nb obtained [22].

Cyclohexanone has a very high solubility in water (16%w), which justifies its weak use.

Finally, 2-octanol has a very low solubility in water (<0.1%w), a relatively high flash point (71°C). This makes its use less hazardous than that of the MIBK. Nevertheless, it presents the double drawback of having a relatively high viscosity (8 mPa.s) and a low extraction performance for Ta and Nb [5].

Considering the limitations associated to the physico-chemicals properties of the previous solvents we explore the potential of methylacetophenone (MAcPh, Figure 2) as solvent for the competitive extraction and purification of Ta and /or Nb. The para-substituted derivative 4-methyl-acetophenone (4-MAcPh) was selected which highlight interesting physico-chemicals properties such as a very low solubility in water (< 0.2%w), a relatively high flash point (85.1 ± 8.8 ° C), a moderate viscosity (1.88 mPa.s).

In a similar approach, Kasikova et al. [23, 24] proposed a solvent mixture of acetophenone (30-50%) and triisooctylamine (20-40%) diluted in an inert diluent for Nb isolation from concentrated hydrochloric acid solutions (9 and 10 mol L-1) containing Ta and Ti as impurities.

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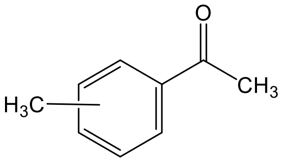

Figure 2. General structure of methylacetophenone molecules

In the same goal, and also in concentrated hydrochloric medium between 8 and 10 mol L-1, Gibala et al. [24] described a mixture of acetophenone and benzaldehyde. However, these methods do not allow the extraction of Ta but rather of Nb, with precisely 4.4% of Ta extracted with acetophenone compared to 92.4% of Nb from a hydrochloric acid solution initially containing 0.43 g L-1 of Ta and 4.1 g L-1 of Nb. It is also mentioned a drawback related to an insufficient density difference between pure acetophenone (1.028 g/cm3) and hydrochloric solutions concentrated in Nb, Ta and Ti for application in current mixers-settlers type technologies.

A first step of our study was focused on the comparison of 4-MAcPh with MIBK in term of the selective extraction of Ta and Nb in the binary HF+H2SO4 system. The second part of the procedure was dedicated to the study of the ability of 4-MAcPh to selectively extract Ta from a model solution that mimics acidic leach solutions from capacitors waste.

2. Materials and Methods

To evaluate the selective properties of 4-MAcPh, experiments were performed under batch conditions. For this purpose various ratio organic (O) over aqueous phase (A) were studied with 4-MAcPh as organic phase and aqueous acidic stock solution of cations.

Ta(V) and Nb(V) stock solutions (1 - 10 g.L^{-1}) were prepared at the desired acidity (H_2SO_4 1–9 M) from 10.000 mg L^{-1} ICP standard from SCP Science (aqueous solution of NH_4TaF_6 or NH_4NbF_6 with 1% fluorhydric acid). For the aqueous solution with competitive cations Fe, Mn and Ni were introduced by dissolving their corresponding sulfate salts. The initial concentrations of metals were measured by inductively coupled plasma/optical emission spectrometry (ICP/OES SPECTRO ARCOS)

The two phases were mixed and stirred for 30 minutes at room temperature (22 ± 3 ° C), kinetic experiments confirmed that the equilibrium was reached. After separation by centrifugation (3000 rpm for 5 minutes), the aqueous phases were collected and analyzed.

From the results obtained by ICP-OES, the distribution coefficient for each species were determined at equilibrium as follow (1):

$$k_D = \frac{[M]_{org}^{eq}}{[M]_{aq}^{eq}} \tag{1}$$

where $[M]_{org}^{eq}$ is the metal concentration in solvent and $[M]_{aq}^{eq}$ is the metal concentration in aqueous phase.

The separation factor ($SF_{M1/M2}$) is given by equation (2):

$$SF_{M1/M2} = \frac{k_{DM1}}{k_{DM2}} \tag{2}$$

where k_{DM1} and k_{DM2} are the distribution coefficients of the metal M1 and M2 ions, respectively.

The extraction percentage (E) is defined in relation to the distribution ratio k_D as given by equation by (3):

$$E(\%) = \frac{(100 \times [M]_{org}^{eq})}{([M]_{org}^{eq} + [M]_{aq}^{eq})} = \frac{(100 \times D)}{(D+1)} \tag{3}$$

From the results obtained by Total Organic Carbon (TOC) using a Shimadzu TOC-VCSH analyser based on a 680ºC combustion catalytic oxidation/NDIR method the loss by solubility of the solvent (S) was evaluated as follows:

$$S(\%) = \frac{TOC}{[Solvent]} \times 100 \tag{4}$$

Where [Solvent] refer to the solvent concentration in organic phase and TOC refer to the amount of organic carbon in the aqueous phase after phase separation.

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The interfacial tension measurements were carried out by the method of the hanging liquid drop using a KRUSS DSA30 tensiometer, 8 mL of the solvent was prior loaded with metal for 30 minutes at room temperature. A 1 ml syringe was allowed to expel through a straight capillary of 1.494 mm diameter a drop of an aqueous phase (20 µL) in the 8mL of loaded solvent. The Drop Shape Analysis DSA1 v1.91 software was used for calculate the interfacial tension IFT (mN.m^{-1}) by the following relation:

$$\mathrm{FT}\ (\mathrm{mN.m^{-1}}) = \frac{(\rho_{aq} - \rho_{org}) g d_e^2}{H} \qquad (5)$$

Where ρ_{aq} and ρ_{org} are the densities (g.cm^{-3}) of aqueous and loaded solvent, d_e is equatorial diameter and H an empirically evaluated form factor. The density measurements were performed with a DSA 5000 thermo-regulated digital densimeter (Anton Paar).

All rheological measurements were performed using an AMVn automated microviscosimeter (Anton Paar). The apparatus measures viscosities using the rolling ball/falling ball principle, which consists in measuring ball rolling time in a diagonally mounted glass capillary filled with the sample.

3. Results

3.1. Hydrodynamic properties of MAcPh

The interfacial tension, solubility, density and viscosity measurements of the 4-MAcPh were carried out according to the protocol described in the Materials and experimental Method part and are presented in Table 2.

Table 2. Physicochemical properties of 4-MAcPh.

Molecular weight (g.mol^{-1})	134.18
Molarity (mol.L^{-1})	7.11
Density at 20°C(g cm^{-3})	0.99997 ± 0.00002
Dynamic Viscosity at 20°C (mPa.s)	1.735 ± 0.003
Solubility in water (w%)	0.197 ± 0.001
Interfacial tension (mN.m^{-1})	21.3 ± 0.4 *

* IFT with an aqueous phase (0.4 mol.L^{-1} of HF, 6 mol.L^{-1} of H_2SO_4 and 6.6 g.L^{-1} of Ta).

The physical and chemical properties determined in this work were in close agreement with literature data when available. The solubility results highlight a low loss in the aqueous phase (0.197%w) which is much less than that of the commonly used MIBK (about 2%w).

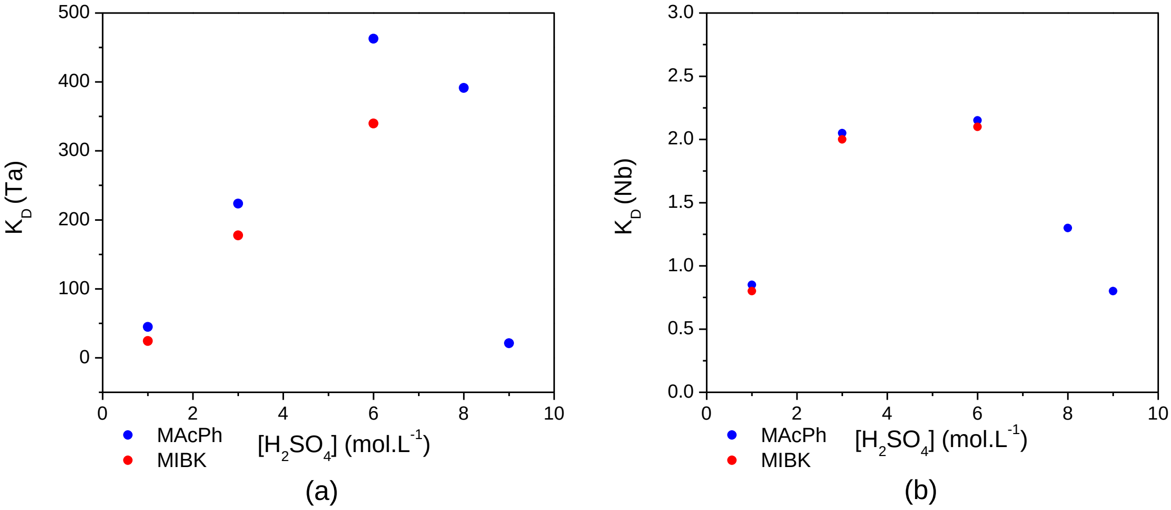
The density of pure 4-MAcPh (0.99997 g.cm^{-3}) did not cause settler difficulties during our tests although it is closer to that of the classical aqueous phases compared to solvents such as TBP 30% in dodecane (0.83 g.cm^{-3}).

Pure 4-MAcPh (7.11 mol.L^{-1}) gives an interfacial tension (IFT) of 21.3 ± 0.4 mN.m^{-1} in equilibrium with an aqueous phase composed of 0.4 mol.L^{-1} of HF, 6 mol.L^{-1} of H_2SO_4 and 6.6 g.L^{-1} of Ta. For example, the IFT with TBP 30% in the PUREX process varies between 12-15 mN.m^{-1} for about thirty seconds of phase separation time (PST) [25].

Liquid–liquid extraction is strongly influenced by hydrodynamic parameters such as viscosity. Indeed, the kinetic, the mass transfer and the phase separation time (PST) can be affected by the viscosity. The viscosity of pure 4-MAcPh increases slightly when loaded with Ta from 1.88 mPa.s (without Ta) to 2.96 mPa.s (when loaded with 0.97 g.L^{-1} of Ta) and 4.54 mPa.s (when loaded with 34.78 g.L^{-1} of Ta). This increase has no significant influence on the PST. These values are of the same order of magnitude as those published for TBP and the N,N-dihexyloctanamide (DHOA), precisely, the viscosity of 1.1 mol.L^{-1} of DHOA varies from 2.6 mPa.s (without U) to 3.5 mPa.s (at 30 g.L^{-1} of U) and for 1.1 mol.L^{-1} of TBP, it varies from 1.6 mPa.s (without U) to 2.5 mPa.s (at 30 g.L^{-1} of U) [25]. This variation causes a little increase in the PST between 25 and 110 s.

3.2. Grouped and sequential extraction of Ta and Nb : Comparison between MAcPh and MIBK

Extraction of Ta and Nb by 4-MAcPh and MIBK was evaluated on a synthetic aqueous solution comprising Ta and Nb at 1 g.L^{-1} dissolved in a mixture of 0.06 mol L^{-1} of HF and H_2SO_4 whose concentration varies from 1 to 9 mol.L^{-1}. The organics phases studied were 4-MAcPh (7.11 mol.L^{-1}) and MIBK (7.58 mol.L^{-1}). Figure 3 shows the comparison between the 4-MAcPh and the MIBK with respect to the variation of the Ta and Nb k_D values as a function of the concentration of the H_2SO_4. The table 3 presents the k_D and $SF_{Ta/Nb}$ values for Ta and Nb for both solvents.



(a)

(b)

Figure 3: Effect of H_2SO_4 concentration on the distribution coefficient k_D of (a) Ta and (b) Nb. Extraction condition: O/A = 1; T° = 22°C. Extraction time: 30min. Org. phase: 4-MAcPh (●) or MIBK (●); Aq. phase: [Ta]= [Nb]= 1g.L^{-1}, [H_2SO_4]= 1 - 9 M, [HF] = 0.06 M

Table 3. The k_D and $SF_{Ta/Nb}$ values for Ta and Nb for 4-MAcPh And MIBK.

H_2SO_4 (mol L^{-1})	**MAcPh**			**MIBK**		
	k_D (Ta)	**k_D (Nb)**	**$SF_{Ta/Nb}$**	**k_D (Ta)**	**k_D (Nb)**	**$SF_{Ta/Nb}$**
1	44.6	0.8	55.8	24.4	0.8	30.5
3	223.6	2.0	111.8	177.4	2.0	88.7
6	462.7	2.1	220.3	339.7	2.1	161.8
8	391.4	1.3	301.1	N.A *	N.A *	N.A *
9	20.9	0.8	26.1	N.A *	N.A *	N.A *

* N.A: Not Applicable because at concentrations of H_2SO_4 above 6M, MIBK is solubilized

With an increase in Ta and Nb extraction by 4-MAcPh from 1 to 6 mol.L^{-1} of H_2SO_4, the value of k_D increases from 45 to 463 for Ta and from 0.8 to 2 for Nb. Despite the increase of the extraction of Nb, the selectivity of Ta is well pronounced with high separation factor $SF_{Ta/Nb}$ of 56 and more than 220 respectively for 1 and 6 mol.L^{-1} of H_2SO_4.

On the other hand, from 6 until 9 mol.L^{-1} of H_2SO_4, the k_D decreases to 21 for Ta corresponding to a decrease of 4% in the extraction of the metal cation (from 99.8% to 95.5%) and 0.8 for Nb corresponding to a decrease of 22% in the extraction (from 66,7% to 44,4%). This decrease could be due to the carbonyl protonation of the 4-MAcPh providing the enolization of the compound as demonstrated by R. A. Cox et al [26] as well as significant increase in the solubility loss of 4-MAcPh. The total organic carbon (TOC) measurements in the equilibrium aqueous phase supported this hypothesis by reporting an increase in solubility loss of 4-MAcPh from 0.14 to 4% w between 6 and 9 mol.L^{-1} of H_2SO_4. This difference in their extraction performance could be used for the separation of the two metals. Niobium complexes in the solution are stronger Lewis acids than that of tantalum. Therefore, the extraction of niobium with 4-MAcPh requires stronger solution acidity than that of tantalum [9].

Thereby, these results highlight two possible routes to extract Ta and Nb. One possibility is to co-extract Ta and Nb from an aqueous phase of acidity between 3 and 6 mol.L^{-1} of H_2SO_4. Both elements could be then separated from an aqueous phase concentrated to less than 1 mol.L^{-1} of H_2SO_4 since under these conditions the Nb extraction performance is low. The second approach is based on a sequential extraction of the two elements. In this scheme, the Ta is selectively extracted in a first step at 1 mol.L^{-1} of H_2SO_4 followed by the Nb extraction between 3 and 6 mol.L^{-1} of H_2SO_4.

However, the result illustrated in Figure 3, shows a similar extraction tendency of Ta and Nb for the 4-MAcPh and the MIBK. The k_D values of Nb remain nearly similar from 1 to 6 mol.L^{-1} of H_2SO_4 for these solvents. However, those of Ta are higher for the 4-MAcPh precisely by a factor of 1.3 at 6 mol.L^{-1} of H_2SO_4. In addition MIBK is completely solubilized from 6 mol.L^{-1} of H_2SO_4 while only a loss of 0.14 to 4% w is observed with 4-MAcPh between 6 and 9 mol.L^{-1} of H_2SO_4.In terms of stability and efficiency, 4-MAcPh appear to be more suitable for the extraction of Ta and Nb from a solution composed of 0.06 mol.L^{-1} of HF and 1 to 9 mol.L^{-1} of H_2SO_4.

3.3. Extraction Isotherm and McCabe–Thiele Diagram Loading capacity of 4-MAcPh for Ta

The Ta extraction distribution isotherm and the McCabe–Thiele diagram obtained with 4-MacPh are shown in Figure 4. The feed solution containing 7 g.L^{-1} of Ta in acidic aqueous solution (0.4 mol. L^{-1} of HF, 6 mol.L^{-1} of H_2SO_4) was contacted with 4-MAcPh at different A/O phase ratios from 1 to 60 at ambient temperature. No third phase was observed, and the results presented in Figure 4 indicated a loading capacity higher than 150 g.L^{-1} since the saturation seems to be reached.

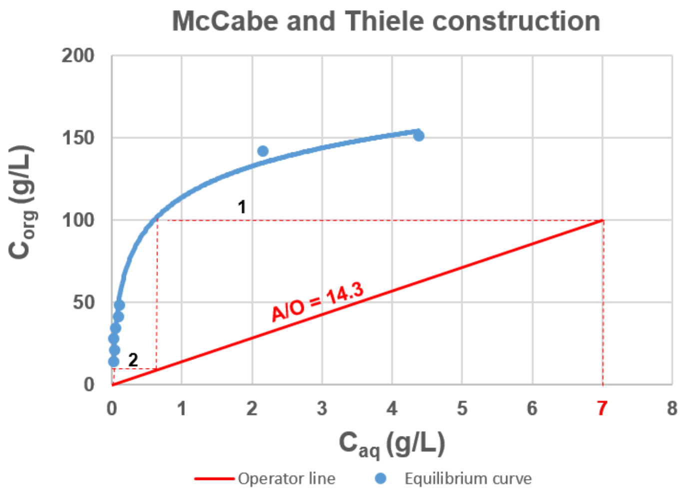


Figure 4: McCabe and Thiele diagram for the 4-MAcPh-Tantalum system. Extraction condition: O/A = 1 to 60; T° = 22°C. Extraction time: 30min. Org. phase: 4-MAcPh, Aq. phase: [Ta] = 7g.L^{-1}, [H_2SO_4] = 6 M, HF = 0.4 M.

The McCabe–Thiele diagram for Ta extraction highlight that for a flux composed of a feed containing 7 g L^{-1} of Ta and an organic phase leaving the process with 100 g L^{-1} of Ta, a flow ratio of 14.3 and 2 stages are required for have a process yield of 99.9% *i.e* a raffinate composed of 0.01 g.L^{-1} of Ta.

The Operator line equation is defined by the relation: $y = \frac{A}{O}x + (y_s - \frac{A}{O}x_e)$ (6)

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with the slope $\frac{A}{O}=\frac{y_s}{x_e - x_s}$; y_s = 100 g.L^{-1} *i.e* Ta concentration in the solvent at the outlet of the process ; x_e = 7 g.L^{-1} *i.e* Ta concentration in the feed ; x_s= 0.01 g.L^{-1} *i.e* Ta concentration in the raffinate.

The table 4 shows the tantalum concentration in aqueous and organic phases and the distribution coefficient at equilibrium as function of various phase ratios (A/O) from 1 to 60.

Table 4: Tantalum concentration in aqueous and organic phases and the distribution coefficient at equilibrium as function of various phase ratios (A/O).

A/O	$[Ta]_{aqueous}$ (g.L^{-1})	$[Ta]_{organic}$ (g.L^{-1})	k_D
1	0.02	13.98	570.45
3	0.04	20.93	572.58
4	0.03	27.93	950.89
5	0.06	34.79	627.61
6	0.09	41.52	445.57
7	0.11	48.31	436.93
30	2.16	142.27	65.99
60	4.38	151.37	34.60

The figure 5 proposed a flow sheet for the recovery of Ta by 4-MAcPh from aqueous solution composed by 0.4 mol.L^{-1} of HF, 6 mol.L^{-1} of H_2SO_4 and 7 g.L^{-1} of Ta. The phase ratios (A/O) are of 14.3 for extraction 1 and 2.

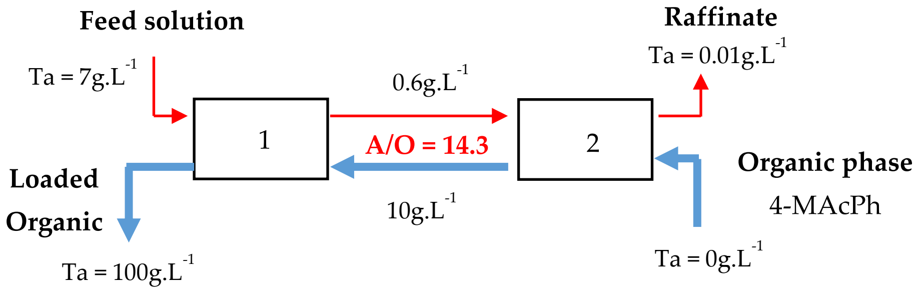

Figure 5: Flow sheet for Ta recovery by 4-MAcPh with two stages at A/O=14.3.

3.4. Stripping of Ta from loaded 4-MacPh

After the successful extraction of Ta from the feed aqueous solution (1 g.L^{-1} of Ta, 0.06 mol.L^{-1} of HF and 6 mol.L^{-1} of H_2SO_4 with a phase ratio A/O = 1) by 4-MAcPh, another set of experiments were then carried out in order to recover the extracted targeted Ta from the organic phase. The 4-MAcPh already loaded with the extracted Ta was stripped then with ammonium oxalate (0.2 or 0.3 mol.L^{-1}) in A/O ratio of 1 allowing a quantitative recovery of Ta in the stripping phase without any precipitation phenomenon.

3.5. Selective recovery of Ta from a model solution of capacitor waste containing Fe, Mn and Ni as impurities

Recycling has the advantage of reducing the dependency on minerals. Actually around 95% of electronic boards are recycled in copper smelters where Ta is dispersed in slags and cannot be recovered. Except the recycling of manufacturing chips, there is currently no technology which allows tantalum recycle.

Therefore, considering the Ta extraction performances by 4-MAcPh, we studied the efficiency and the selectivity of this system toward Ta contained in a simulated leaching solution of capacitor waste including Fe, Mn and Ni as impurities.

To be as representative as possible to the conditions encountered during the dissolution of capacitors of Ta, we studied the extraction performances from a synthetic aqueous solution containing 0.1 g.L^{-1} of Ta, Fe, Mn and Ni. The whole is dissolved in a mixture of 0.06 mol.L^{-1} of HF and H_2SO_4 whose concentration varies from 1 to 9 mol.L^{-1}. Figure 6 reports the k_D value for all elements as function of H_2SO_4 concentration. The Table 5 also presents the k_D value for all elements as function of H_2SO_4 concentration.

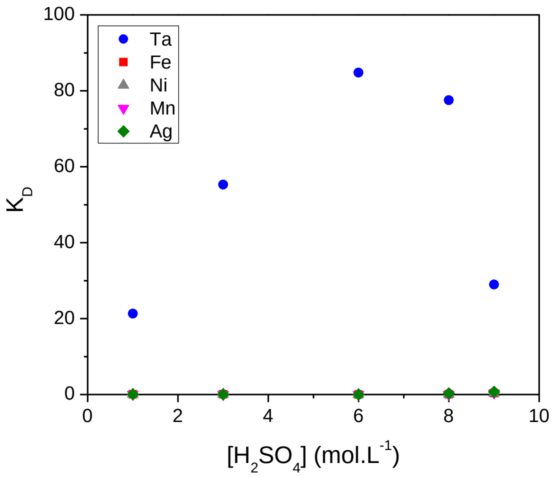

Figure 10: Effect of H_2SO_4 concentration on the distribution coefficient k_D of Ta, Fe, Ni and Mn. Extraction condition: O/A = 1; T° = 22°C. Extraction time: 30min. Org. phase: 4-MAcPh; Aq. phase: [Ta]= [Fe]=[Ni]=[Mn]= 0.1 g.L^{-1}, [H_2SO_4]= 1-9 M, [HF]= 0.06 M.

Table 5: k_D values for Ta, Ni, Mn, Fe and Ag as function of H_2SO_4 concentration

[H_2SO_4] mol.L^{-1}	k_D (Ta)	k_D (Fe)	k_D (Ni)	k_D (Mn)	k_D (Ag)
1	21.28	0.07	0.05	0.05	0.06
3	55.26	0.04	0.04	0.02	0.04
6	84.78	0.02	0.01	0.00	0.01
8	77.54	0.07	0.08	0.08	0.30
9	28.98	0.35	0.37	0.39	0.70

As already observed. there is an increase of k_D values of Ta from 21 to 85 between 1 and 6 mol .L^{-1} of H_2SO_4.The decrease in the k_D values until 29 between 6 and 9 mol.L^{-1} could be due to the competitive protonation of the 4-MAcPh accompanied by a loss per solubility from 0.14 to 4% was already mentioned. The k_D values for impurities (Fe. Mn. Ni) remain less than 0.7 between 1 and 9 mol.L^{-1} of H_2SO_4 (table 5).

The present results demonstrate the potential of 4-MAcPh toward the selective extraction of Ta with respect to competitive ions such as Fe. Ni Mn with selectivity factor $SF_{Ta/M}$ of about 120 at 6 mol .L^{-1} of H_2SO_4.

As indicated previously the recovery of the Ta can then be considered thank to a stripping solution such as ammonium oxalate.

4. Discussion - Conclusion

The interest in 4-MAcPh for the extraction of Ta and Nb has been established. The following conclusions were highlighted:

- The 4-MAcPh presents adapted intrinsic physicochemical properties for its use in liquid-liquid extraction process. Indeed, its solubility highlight a low loss in the aqueous phase (0.2% w) which is much less than that of the commonly used MIBK (about 2%w). The density of pure 4-MAcPh (0.99997 g.cm^{-3}) did not cause settler difficulties during our tests. Pure 4-MAcPh (7.11 mol L^{-1}) gives an interfacial tension (IFT) of 21.3 ± 0.4 mN.m^{-1} in equilibrium with an aqueous phase composed of 0.4 mol L^{-1} of HF. 6 mol L^{-1} of H_2SO_4 and 6.6 g.L^{-1} of Ta. With these 21.3 mN.m^{-1} we need more stirring energy than that for TBP 30% for create emulsion. The viscosity of pure 4-MAcPh is of the same order of magnitude as those published for TBP and the DHOA [25]. It increases slightly when loaded with Ta. This increase has no significant influence on the PST.

- From the results of comparison between MIBK and MAcPh with respect to Ta and Nb extraction, it was concluded that there is a similar extraction tendency for both Ta and Nb. The k_D values of Nb remain nearly similar from 1 to 6 mol.L^{-1} of H_2SO_4 but those of Ta are higher for the 4-MAcPh at 6 mol.L^{-1} of H_2SO_4. In addition MIBK is completely solubilized from 6 mol.L^{-1} of H_2SO_4 while only a loss of 0.14 to 4% w is observed with 4-MAcPh between 6 and 9 mol.L^{-1} of H_2SO_4.In terms of stability and efficiency. 4-MAcPh appear to be more suitable for the extraction of Ta and Nb from a solution composed of 0.06 mol.L^{-1} of HF and 1 to 9 mol.L^{-1} of H_2SO_4. The decrease of k_D value of Ta between 6 and 9 mol.L^{-1} of H_2SO_4 in the case of MAcPh could be due to the carbonyl protonation providing the enolization of the compound as demonstrated by R. A. Cox *etal* [26].

- From the results of the McCabe–Thiele diagram for Ta extraction, it concluded that for a flux composed of a feed containing 7 g.L^{-1} of Ta and an organic phase leaving the process with 100 g. L^{-1} of Ta, a flow ratio of 14.3 and 2 stages are required for have a process yield of 99.9% i.e a raffinate composed of 0.01 g.L^{-1} of Ta.

- From the results of the Ta stripping, it concluded that the ammonium oxalate (0.2 or 0.3 mol.L^{-1}) is adapted for quantitatively recover Ta from loaded 4-MAcPh.

- From the results of the selective extraction of Ta from simulated leaching solution of capacitor waste, it was concluded that the MAcPh is adapted with a separation factor of 120 for Ta with respect to Fe. Ni and Mn.

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