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Article

Chemical Degradation of a Mixture of tri-*n*-Octylamine and 1-Tridecanol in the Presence of Chromium(VI) in Acidic Sulfate Media

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Abstract: The chemical degradation of an extraction solvent composed of a mixture of tri-*n*-octylamine (extractant) and 1-tridecanol (phase modifier) in *n*-dodecane in contact with an acidic aqueous sulfate solution containing chromium(VI) has been investigated. The kinetics of degradation and the degradation products have been determined. GC-MS analyses evidenced the formation of 1-tridecanol, di-*n*-octylamine, *N,N,N*-octen-1-yl-dioctylamine, and an unidentified degradation compound, which may have contained a double bond and a carboxylic acid function. The mechanisms of degradation have been discussed on the basis of these identified degradation compounds. The study of the degradation kinetics showed that an increase of tri-*n*-octylamine concentration in the organic phase is responsible for a decrease of the degradation rate, while an increase in sulfuric acid concentration in the aqueous phase leads to a strong increase in the degradation rate.

Keywords: Alamine[®] 336; solvent extraction; chromium(VI); degradation; tri-*n*-octylamine

1. Introduction

Solvent extraction is a well-established technology used in hydrometallurgy to produce high-grade metals such as copper, nickel, cobalt, rare earths, uranium, etc. [1]. The chemistry involved in metal extraction is complex, as redox, hydrolysis, precipitation, acido-basic and complexation equilibria occur both in organic and aqueous phases. Solvent extraction processes are sensitive to the nature of the ores, the redox potential, the pH of the feed solution, etc., and a modification of these parameters can be responsible for a dysfunction of extraction plants, including crud formation, chemical degradation of the extraction solvent, and drops in extraction efficiency and selectivity [2].

Although chemical degradation and crud formation are normal in solvent extraction plants, only few papers have reported these phenomena and thoroughly investigated their origins. Diluents, especially alkanes, are very stable materials, whereas extractants or phase modifiers exhibit a stronger tendency to degrade [3]. For instance, degradation of the organic phases due to the presence of NO_x has been observed in the extraction circuits of hydrometallurgical plants [4]. Since the mid-1970s, there have been a few episodes where the tertiary amine has been quickly and severely degraded under certain conditions. In particular, Feather et al. [5] mentioned the chemical degradation of Alamine[®] 336 (mainly constituted of trioctylamine) in kerosene modified with isodecanol during the recovery of uranium from South African ores containing nitrate from residual amounts of the blasting agent. The leach liquor, which contained nitrate in addition to the uranyl sulfate, was passed

through an ion-exchange column to recover uranium. In this process, both the uranium and nitrate were collected by the ion-exchange column. The column was then stripped with strong sulfuric acid, which removed both the uranium and the nitrate. The uranium was then extracted from the ion-exchange eluate with Alamine[®] 336 in a solvent extraction process. Due to the recycling of the solution, the nitrate concentration built up in the system to a point where an attack on the amine occurred, resulting in the formation of nitrosoamines and other degradation products. More recently, Chagnes et al. [6] showed that tri-*n*-octylamine in *n*-dodecane modified with 1-tridecanol is sensitive to oxidation in the presence of Vanadium (V(V)) initially present in the feed solution. It was shown that the presence of V(V) co-extracted in the extraction solvent, likely as polyvanadates [7], and molecular dioxygen are responsible for the chemical degradation of the extraction solvent via two simultaneous routes: (i) the oxidation of 1-tridecanol by V(V) with formation of radicals that induce, in turn, a series of subsequent degradation reactions, including the degradation of tri-*n*-octylamine into *N,N,N*-octen-1-yl-dioctylamine and di-*n*-octylamine; and (ii) the oxidation of tri-*n*-octylamine by molecular oxygen catalyzed by extracted V(V) [6]. Such chemical degradations of extraction solvents are of great concern in liquid-liquid extraction processes, because they are responsible for an increase of the operating costs due to dramatic solvent consumption and crud formation [8].

Cr(VI) is also present in the feed solution treated by the solvent extraction process implemented in the Niger plant for uranium production, and this metal species is also known to be a strong oxidant that can oxidize organic molecules such as alcohols, aldehydes or ketones [9–13]. Therefore, it is also of great interest to investigate the oxidation properties of Cr(VI) towards the extraction solvent used in the Niger plant, namely tri-*n*-octylamine in *n*-dodecane modified with 1-tridecanol. In the present work, the ageing of a mixture of tri-*n*-octylamine (extractant) and 1-tridecanol (phase modifier) in *n*-dodecane has been investigated in the presence of a model aqueous sulfuric acid solution containing Cr(VI) dissolved in sulfuric acid.

2. Materials and Methods

2.1. Reagents

n-Dodecane (purity > 99%, Aldrich, Lyon, France), 1-tridecanol (purity > 98%, Aldrich), tri-*n*-octylamine (purity > 99%, Aldrich), di-*n*-octylamine (purity > 99%, Aldrich), *n*-heptane (analytical grade, Aldrich), and ethyl ethanolate (analytical grade, Aldrich) were used as delivered. Sulfuric acid (purity 98%), chromium(VI) oxide (purity > 99.9%) from Aldrich and water (resistivity > 18 MΩ·cm) purified with a milli-Q Gradient system from Millipore Corporation (Molsheim, France) were used for preparing the aqueous solutions.

The concentrations of the solutes were given in the molality scale (mole of solute per kg of *n*-dodecane for organic phases and mole of solute per kg of water for aqueous phases).

2.2. Methods and Equipments

The chemical degradation of the organic phases in contact with sulfuric acid containing Cr(VI) arises from a redox reaction leading to the appearance of Cr(III) in the aqueous phase. Therefore, the oxidation of the extraction solvent was investigated by following the evolution of Cr(III) concentration in the aqueous phase by UV-visible spectroscopy at 417 and 587 nm [10].

tri-*n*-Octylamine dissolved in *n*-dodecane modified by 1-tridecanol was pre-equilibrated with sulfuric acid at 1 mol·kg⁻¹ before studying the degradation of the solvent (1-tridecanol is a phase modifier used in the formulation of extraction solvent in order to avoid third-phase formation). Each organic phase (5 mL) was mixed with an aqueous phase (5 mL) containing sulfuric acid and Cr(VI). During the degradation tests, the two phases were stirred at 25 °C with a mechanical stirring apparatus (Gherardt Laboshake, Richwiller, France) thermostated with a Gherard Thermoshake. All samples were protected from the light to avoid photo-induced degradation of the organic compounds in the presence of Cr(VI). The degradation occurred over a period ranging from 1 day and 18 days, depending

on the composition of the aqueous phase, and it should be pointed out that the degradation of the organic phases was observed only in the presence of Cr(VI) in the aqueous phases.

Samples of the aqueous phase were periodically removed with an Eppendorf pipette and analyzed by UV-Visible spectroscopy (Agilent Varian, Grenoble, France) before being returned to the experimental flask. At the end of the degradation tests, the aqueous and organic phases were analyzed by GC-MS (Agilent Varian, Grenoble, France).

Before GC-MS analyses, each sample was treated as follows: Aqueous phases were contacted with (i) *n*-heptane after neutralization with sodium hydroxide to extract apolar degradation products, and then with (ii) ethyl ethanoate to extract polar degradation products; and *n*-Heptane and ethyl ethanoate phases were dried with magnesium sulfate before GC-MS analyses. Identification of the degradation compounds was performed based on analyses of the mass spectra with the NIST database.

UV-Visible analyses of the aqueous and organic phases were performed with a Carry 100 Scan UV-Vis spectrometer (Agilent Varian, Grenoble, France).

GC-MS analyses were performed with a Varian 3300 gas chromatograph coupled with a Ribermag R1010 C (Nermag S.A., Rueil Malmaison, France) mass spectrometer. A fused silica capillary column (30 m × 0.2 mm × 0.2 μm) with cross-linked octadecanyl silicone of CP Sil 5 CB Low Bleed type (Chrompack, Agilent Varian, Grenoble, France) was used in gas chromatography. For gas chromatography experiments, the detector temperature was equal to 250 °C, the injection was of 1 μL in splitless mode, the carrier gas was helium, and the ionizing energy was equal to 70 eV.

3. Results

3.1. Identification of Degradation Products

The extraction solvent composed of tri-*n*-octylamine, 1-tridecanol and *n*-dodecane was loaded with Cr(VI) at 25 °C by contacting it with an acidic sulfate solution containing Cr(VI). Both phases were kept in contact under shaking for 15 h at 25 °C. During the degradation tests, gas chromatography-mass spectrometry (GS-MS) showed the presence of a series of degradation compounds, namely 1-tridecanal, di-*n*-octylamine, *n*-dodecane tridecanoate and *N,N,N*-octen-1-yl-dioctylamine, in addition to the starting compounds of the extraction solvent (1-tridecanol, tri-*n*-octylamine and *n*-dodecane). The retention times of these compounds are gathered in Table 1.

Table 1. Retention time of the products identified by GC-MS analyses in the extraction solvent after its degradation.

Products	Retention Time/min
<i>n</i> -dodecane	6.20
1-tridecanal	9.10
1-tridecanol	9.60
Unidentified compound	10.40
<i>n</i> -dodecane tridecanoate	11.30
tri- <i>n</i> -Octylamine	20.00
di- <i>n</i> -Octylamine	20.60
<i>N,N,N</i> -octen-1-yl-dioctylamine	29.50

An unidentified degradation compound that may contain a double bond and a carboxylic acid function was also identified, but it is difficult to draw conclusions about its exact nature. The details of the mass spectra have been reported elsewhere [6].

3.2. Degradation Mechanisms

The diagram of speciation of Cr(VI) was calculated using the free software Medusa with the thermodynamic constants reported in Table 2 [14], and shows that, below pH 6, Cr(VI) exists mainly as HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$, which are well-known oxidant species (Figure 1) [12].

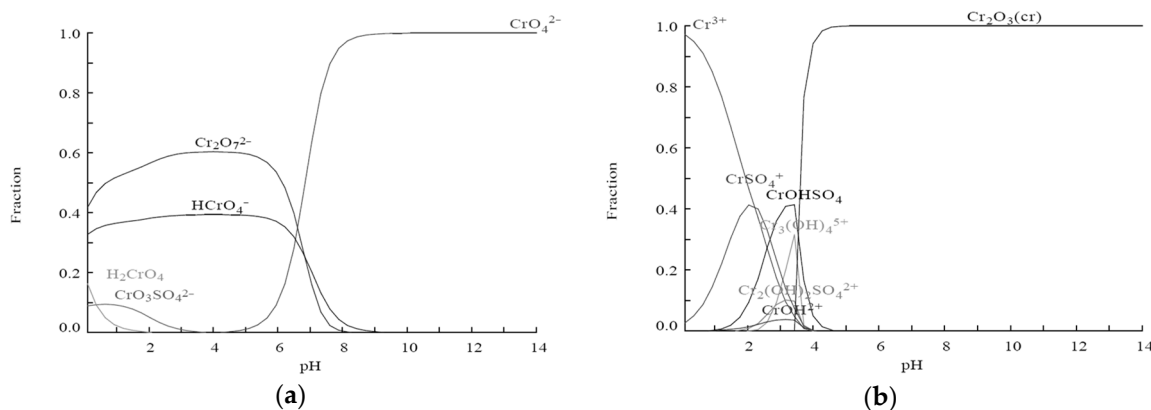


Figure 1. Speciation diagrams of (a) Cr(VI) and (b) Cr(III). $[\text{Cr}] = 0.05 \text{ mol}\cdot\text{L}^{-1}$, ionic strength = $0.1 \text{ mol}\cdot\text{L}^{-1}$, $T = 25 \text{ }^\circ\text{C}$. Calculation performed with Medusa by using the thermodynamic data reported in Table 2.

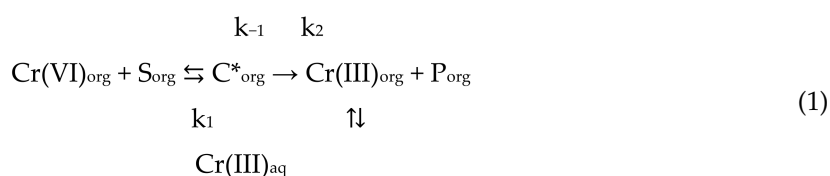
Table 2. Thermodynamic constants ($25 \text{ }^\circ\text{C}$) for the calculation of the speciation diagram of Cr(VI) [14].

Equilibria	Thermodynamic Constants at $25 \text{ }^\circ\text{C}$
$\text{CrO}_4^{2-} + \text{H}^+ = \text{HCrO}_4^-$	3.5×10^6
$\text{CrO}_4^{2-} + 2\text{H}^+ = \text{H}_2\text{CrO}_4$	2.2×10^6
$2\text{CrO}_4^{2-} + 2\text{H}^+ = \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$	4.9×10^{14}
$\text{CrO}_4^{2-} + 2\text{H}^+ + \text{SO}_4^{2-} = \text{CrO}_3\text{SO}_4^{2-} + \text{H}_2\text{O}$	9.9×10^8
$\text{Cr}^{3+} + \text{SO}_4^{2-} = \text{CrSO}_4^+$	2.2×10^1
$\text{Cr}^{3+} + \text{SO}_4^{2-} + \text{H}_2\text{O} = \text{H}^+ + \text{CrOHHSO}_4$	4.5×10^{-2}
$3\text{Cr}^{3+} + 4\text{H}_2\text{O} = 4\text{H}^+ + \text{Cr}_3(\text{OH})_4^{5+}$	7.1×10^{-9}
$2\text{Cr}^{3+} + 2\text{H}_2\text{O} + \text{SO}_4^{2-} = 2\text{H}^+ + \text{Cr}_2(\text{OH})_2\text{SO}_4^{2+}$	8.3×10^{-4}
$\text{Cr}^{3+} + \text{H}_2\text{O} = \text{CrOH}^{2+} + \text{H}^+$	2.7×10^{-4}

Thus, the degradation mechanisms of tri-*n*-octylamine diluted in *n*-dodecane modified with 1-tridecanol could be explained mainly in consideration of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ as the oxidant species.

The UV-Visible spectra of the organic and aqueous phases were recorded throughout the degradation test (Figure 2). Figure 2a shows a peak located at 417 nm in the spectrum of the organic phase attributed to Cr(VI) extracted by tri-*n*-octylamine [10]. The intensity of this peak decreased over time. Figure 2b shows a peak located at 587 nm in the spectrum of the aqueous phase corresponding to Cr(III) [10]. The intensity of this peak increased over time. The decrease of Cr(VI) concentration in the organic phase and the increase of Cr(III) concentration in the aqueous phase can be attributed to the Cr(VI) being stripped from the organic phase into the aqueous phase due to redox reactions responsible for the reduction of Cr(VI) into Cr(III). Cr(III) was spontaneously stripped from the organic phase into the aqueous phase likely due to its having a weak affinity with the extraction solvent because of the electrostatic repulsion between Cr(III) and protonated tri-*n*-octylamine (see speciation diagram of Cr(III) in Figure 1b, which shows that Cr(III) exists as a cation species).

The reduction of Cr(VI) into Cr(III) can be described by the following mechanisms [15]:



where C^* is a transition complex, S is the organic compound that undergoes oxidation, P is the oxidation product and the subscripts “aq” and “org” denote the aqueous and organic phases, respectively.

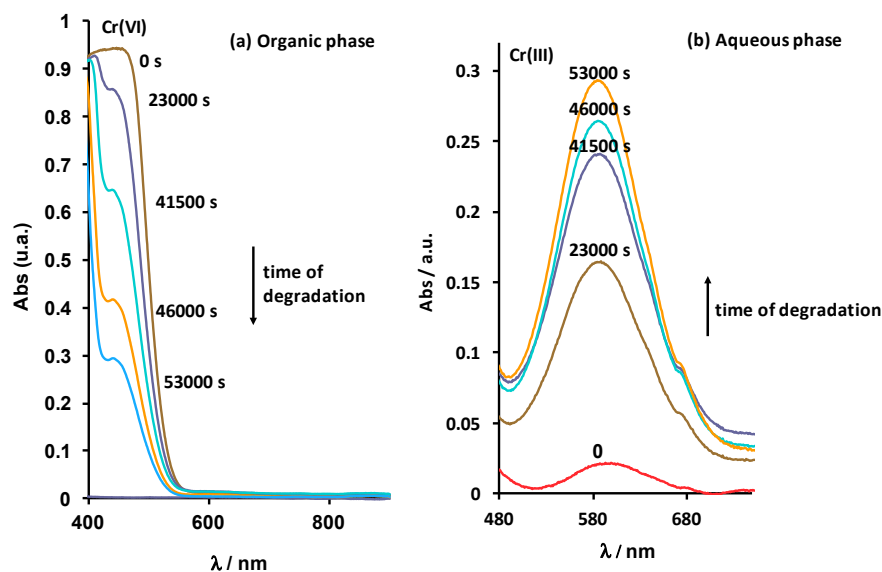


Figure 2. (a) UV-Visible spectra of the organic phase throughout the degradation (organic phase contained initially $0.2 \text{ mol}\cdot\text{kg}^{-1}$ tri-*n*-octylamine diluted in *n*-dodecane modified with 5 wt % 1-tridecanol + $0.05 \text{ mol}\cdot\text{kg}^{-1}$ Cr(VI); (b) UV-Visible spectra of the aqueous phase in contact with the organic phase throughout the chemical degradation of the organic phase. Temperature = $25 \text{ }^\circ\text{C}$.

The net $3e^-$ reduction of Cr(VI) to Cr(III) may proceed in different ways through the formation of various intermediates like Cr(V) and Cr(IV). The mechanism path of the reduction depends on the nature of the reductant and the reaction conditions [16,17]. Watanabe and Westheimer [18] proposed the following mechanism for the reduction of Cr(VI) to Cr(III) by the substrate S (e.g., alcohol, aldehyde, ketones, etc.) as the two-equivalent reductant:

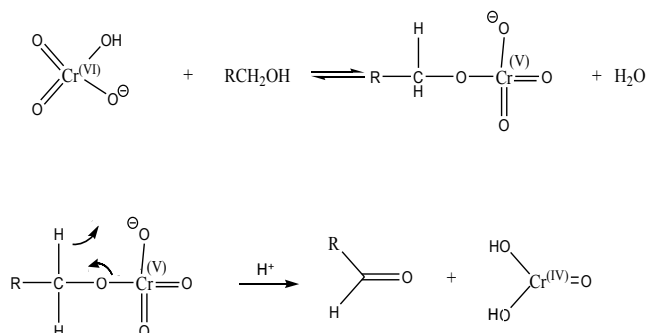


The following oxidation mechanism can also occur via the formation of radical species, as suggested by Rocek [19]:



The chemical degradation of tri-*n*-octylamine and 1-tridecanol in *n*-dodecane in the presence of Cr(VI) dissolved in sulfuric acid likely occurs via the mechanism reported in Equations (2a)–(2d), since no free radicals were observed in the acrylonitrile test (the absence of free radicals is evidenced by no polymerization having occurred after adding a few drops of acrylonitrile to the media) and only Cr(III) species was evidenced in the organic and aqueous phases by UV-visible spectroscopy. The absence of the Cr(V) signature at 510 nm in the UV-visible spectra during chemical degradation may be due to the fast and full reduction of Cr(V) to Cr(III), as reported in Equation (2d) [20].

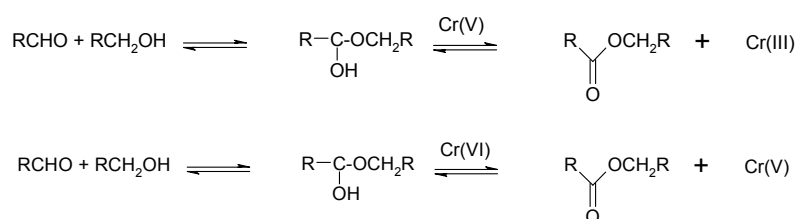
The oxidation of 1-tridecanol by Cr(VI) can lead to the formation of 1-tridecanal and Cr(IV), as reported in Scheme 1 [12]. In this scheme, the oxidation of 1-tridecanol (RCH₂OH) by HCrO₄[−] is represented, and the same mechanism could be considered with Cr₂O₇^{2−}.



Scheme 1. Alcohol oxidation mechanism.

Afterwards, Cr(IV) reacts with Cr(VI) to form Cr(V) (Equation (2c)), which can be reduced into Cr(III) during the oxidation of 1-tridecanol into 1-tridecanal (Equation (2d)). As Cr(III) has no affinity with tri-*n*-octylamine, Cr(III) is stripped from the organic phase into the aqueous phase.

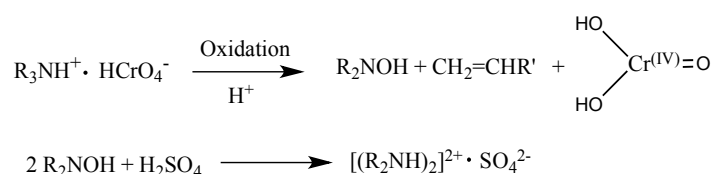
Likewise, *n*-dodecane tridecanoate can be formed by the reaction between 1-tridecanol and 1-tridecanal in the presence of Cr(V) or Cr(VI) as depicted in Scheme 2 [21–24]:



Scheme 2. Aldehyde oxidation mechanisms (R = tridecyl).

A possible mechanistic scenario to account the formation of secondary amines as degradation products is presented in Scheme 3, where R₃NH⁺ is the protonated form of TOA (org and aq denote the organic phase and the aqueous phase, respectively) [25]:

- TOA protonation: (R₃N)_{org} + (H₂SO₄)_{aq} → [(R₃NH)⁺]₂·SO₄^{2−}_{org}
- Anion exchange between SO₄^{2−} and HCrO₄[−] (HCrO₄[−] extraction) [26]:
- [(R₃NH)⁺]₂·SO₄^{2−}_{org} + 2(HCrO₄[−])_{aq} → 2[(R₃NH)⁺·(HCrO₄[−])₂]_{org} + (SO₄^{2−})_{aq}
- Oxidation reactions (in the organic phase) [25]:



Scheme 3. Oxidative mechanism of di-*n*-octylamine formation.

This scheme involves an initial oxidation of tri-*n*-octylamine into tri-*n*-octylamine oxide by Cr(VI). Subsequent degradation of the amine oxide via a 5-membered intermediate generates the protonated dialkylhydroxyamine, which can subsequently undergo N-O bond cleavage via nucleophilic attack at the hydroxyl function [25].

3.3. Kinetics of Degradation

The following empirical equation can be used to describe the kinetics of degradation of trioctylamine-tridecanol in *n*-dodecane by Cr(VI):

$$\ln\left(\frac{A_{\infty}^{Cr(III)} - A^{Cr(III)}}{A_{\infty}^{Cr(III)}}\right) = -k_{obs}t \quad (4)$$

where $A_{\infty}^{Cr(III)}$ is the absorbance of Cr(III) in the aqueous phase at infinite time (at the end of the oxidation, when the absorbance remains constant), $A^{Cr(III)}$ is the absorbance of Cr(III) in the aqueous phase at the time t and k_{obs} is an empirical kinetic parameter.

The kinetic parameter (k_{obs}) has been deduced by using Equation (4) and the absorbance data of the aqueous phase recorded at 587 nm vs. the time of degradation of the extraction solvent in the presence of Cr(VI). The influence of 1-tridecanol and tri-*n*-octylamine concentrations in the organic phase, and sulfuric acid and chromium (VI) concentrations in the aqueous phase on the kinetics of degradation of the extraction solvent has been reported in Figure 3.

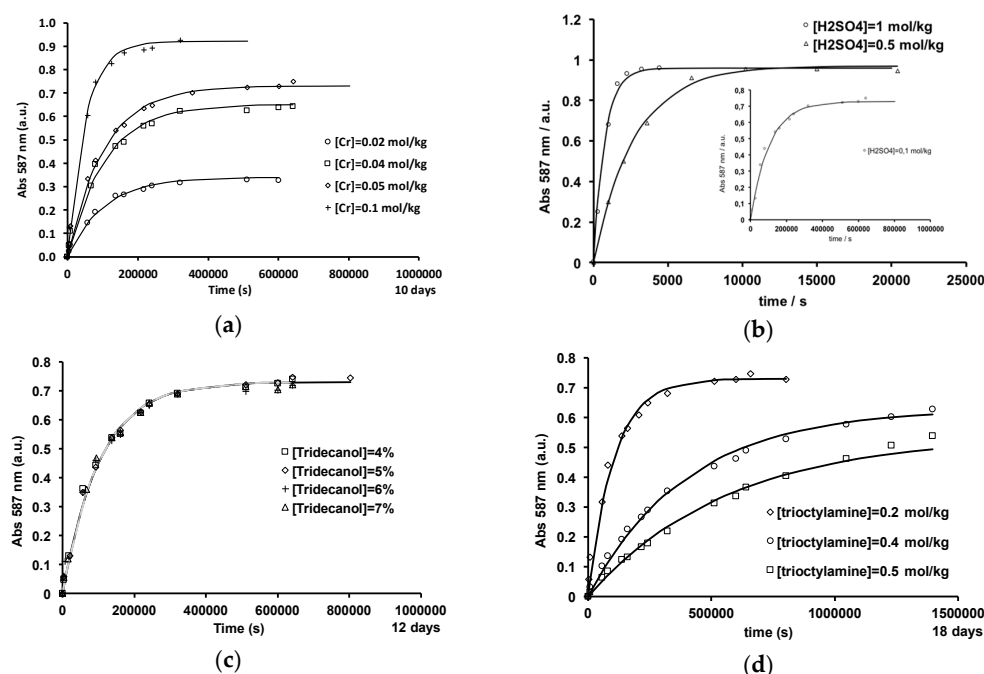


Figure 3. Variation of the absorbance at 587 nm of the aqueous phase during the chemical degradation of $0.2 \text{ mol}\cdot\text{kg}^{-1}$ tri-*n*-octylamine in *n*-dodecane modified by 1-tridecanol. (a) aqueous phase = $0.1 \text{ mol}\cdot\text{kg}^{-1}$ H_2SO_4 + Cr(VI) at different concentrations; organic phase: $0.2 \text{ mol}\cdot\text{kg}^{-1}$ tri-*n*-octylamine + 5 wt % 1-tridecanol; (b) aqueous phase = different concentrations of H_2SO_4 + $0.05 \text{ mol}\cdot\text{kg}^{-1}$ Cr(VI); organic phase: $0.2 \text{ mol}\cdot\text{kg}^{-1}$ tri-*n*-octylamine + 5 wt % 1-tridecanol; (c) aqueous phase = $0.1 \text{ mol}\cdot\text{kg}^{-1}$ H_2SO_4 + $0.05 \text{ mol}\cdot\text{kg}^{-1}$ Cr(VI); organic phase: $0.2 \text{ mol}\cdot\text{kg}^{-1}$ tri-*n*-octylamine + different concentrations of 1-tridecanol, (d): aqueous phase = $0.1 \text{ mol}\cdot\text{kg}^{-1}$ H_2SO_4 + $0.05 \text{ mol}\cdot\text{kg}^{-1}$ Cr(VI); organic phase: different concentrations of tri-*n*-octylamine + 5 wt % 1-tridecanol. Temperature = 25°C . Data were fitted with Equation (4).

There is good agreement between experimental absorbance at 587 nm and the absorbance calculated with Equation (4), as the correlation coefficients reported in Table 3 range from 0.972 to 0.955. The same results are obtained with the absorbance at 417 nm. The fitting parameters (k_{obs}) calculated from Equation (4) are gathered in Table 3.

Table 3. Kinetic rates of degradation (k_{obs}) at 25 °C for different compositions of the extraction solvent and different concentrations in sulfuric acid and Cr(VI). In parentheses: correlation coefficient.

[H ₂ SO ₄] mol·kg ⁻¹	[Cr(VI)] mol·kg ⁻¹	[1-Tridecanol] wt %	[tri- <i>n</i> -Octylamine] mol·kg ⁻¹	k_{obs} s ⁻¹
0.1	0.02	5	0.2	9.7×10^{-6} (0.989)
0.1	0.04	5	0.2	9.5×10^{-6} (0.977)
0.1	0.05	5	0.2	9.6×10^{-6} (0.972)
0.1	1	5	0.2	2.0×10^{-5} (0.985)
1	0.02	5	0.2	1.1×10^{-3} (0.995)
1	0.04	5	0.2	1.1×10^{-3} (0.993)
1	0.05	5	0.2	1.0×10^{-3} (0.994)
1	1	5	0.2	1.0×10^{-3} (0.978)
0.1	0.02	4	0.2	9.6×10^{-6} (0.975)
0.1	0.04	5	0.2	9.6×10^{-6} (0.972)
0.1	0.05	6	0.2	9.6×10^{-6} (0.965)
0.1	1	7	0.2	9.6×10^{-6} (0.961)
0.1	0.05	5	0.2	9.6×10^{-6} (0.972)
0.1	0.05	5	0.4	2.5×10^{-6} (0.992)
0.1	0.05	5	0.5	1.8×10^{-6} (0.993)

Examination of Table 3 shows that the kinetics of degradation is slower when tri-*n*-octylamine concentration increases, as $k_{\text{obs}} = 9.6 \times 10^{-6} \text{ s}^{-1}$ at 0.2 mol kg⁻¹ whereas $k_{\text{obs}} = 1.8 \times 10^{-6} \text{ s}^{-1}$ at 0.5 mol·kg⁻¹ of tri-*n*-octylamine (Table 3). At 0.1 mol·kg⁻¹ H₂SO₄, the kinetic constant remains constant when Cr(VI) concentration is lower than 0.05 mol·kg⁻¹ and then increases at higher concentrations. On the other hand, no influence of Cr(VI) concentration in the aqueous phase is observed when H₂SO₄ concentration is equal to 1 mol·kg⁻¹ (Table 3).

4. Conclusions

Cr(VI) can degrade tri-*n*-octylamine diluted in *n*-dodecane modified with 1-tridecanol. The degradation of this extraction solvent by Cr(VI) led mainly to the formation of 1-tridecanol, *n*-dodecane tridecanoate and di-*n*-octylamine. The degradation of the extraction solvent occurred via the oxidation of 1-tridecanol into 1-tridecanal and the degradation of tri-*n*-octylamine into dialkylhydroxyamine leading to the formation of di-*n*-octylamine in the presence of Cr(VI).

tri-*n*-Octylamine concentration, Cr(VI) concentration and sulfuric acid concentration significantly affected the kinetics of degradation. In particular, an increase of the acidity of the aqueous phase and Cr(VI) concentration were responsible for a dramatic increase of degradation kinetics. It is, therefore, important to decrease the acidity of the aqueous solution and to limit the presence of chromium(VI) by playing on the redox of the leaching solution in the hydrometallurgical process.

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Author Contributions: Alexandre Chagnes wrote the paper and make experiments. Gerard Cote was involved in the discussions.

Conflicts of Interest: The authors declare no conflict of interest.

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