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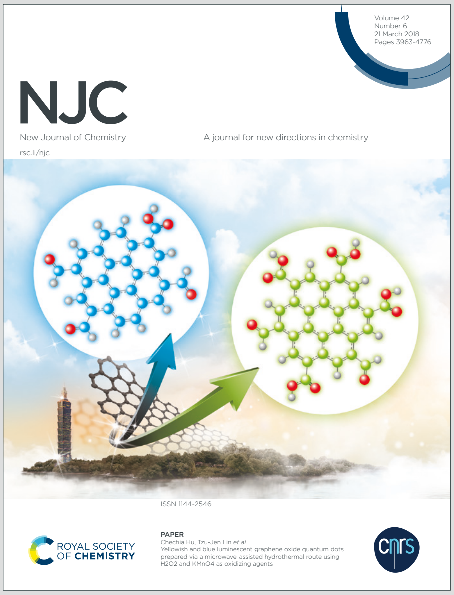

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PAPER

Spectroscopic study of acetohydroxamic acid (AHA) hydrolysis in presence of europium. Implications in the extraction systems studies for lanthanides and actinides separation

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Acetohydroxamic acid (AHA) has been widely used in the development of reprocessing processes for spent nuclear fuel (SNF) due to its ability to form hydrophilic complexes preferentially with tetravalent metals and to contribute to the control of their oxidation states. It is also well known that AHA undergoes hydrolytic degradation at the acidic conditions used during reprocessing. In spite of the wide variety of already published studies concerning the use of AHA, a further analysis of the effect of its hydrolysis on the metal complexing capacity of the extraction system is still needed. In this work we present a spectroscopic study (Raman and fluorescence emission) with the aim of analyzing not only the hydrolysis of AHA in the presence of europium (Eu), but also the effect of its degradation with regard to the global extraction system behavior. Particularly, we have focused on the actinides (An) stripping from lanthanides (Ln) in EURO-GANEX process. To analyze these effects we have first measured the influence in the An/Ln separation factor. Then, the hydrolysis rate constant and Eu(III) fluorescence as a function of the AHA hydrolysis time have been evaluated to explain these effects. Our results show a decrease in $D_{M(III)}$ values that should be considered for all those studies of process development taking more than 24 hours. An increase in the Eu complexation in the aqueous phase as a function of time has also been observed, which is not directly associated with the formation of AHA hydrolysis products. This behavior predicts AHA degradation could have an additional effect on the coordination of some Ln when it is employed for An/Ln separation.

Introduction

Acetohydroxamic acid (AHA) is a bidentate ligand with numerous applications in diverse fields such as biology,[1] medicine[2] and analytic chemistry.[3, 4] As O,O donor ligand, AHA is considered a hard Lewis base able to interact with metals[5] with high charge densities by forming 5-member ring chelates.[6] Moreover, the ability of AHA to strip tetravalent actinides from organic solvents due to its preferential complexes with tetravalent metals over metals with other oxidation states such as tri- and pentavalent oxidation states is well known.[7] For this reason, and given its additional ability as reducing agent,[8-10] during last decades this molecule has become a candidate for its application in reprocessing strategies of spent nuclear fuel (SNF).[11]

Over the latest decades, PUREX process (*Plutonium Uranium Redox Extraction*) has been applied at a commercial scale to recover U and Pu from SNF as a partially closed cycle.[12] As a variation of PUREX, other processes like UREX and an Advanced PUREX have been developed and tested using AHA to separate and control the oxidation states of Pu(IV)/Np(IV) from U(VI).[13, 14] But also, these properties of AHA are being applied to the development of recent concepts for advanced fuel cycles such as the GANEX (*Grouped ActiNide EXtraction*) concept,[15] where all transuranic elements (TRU) are co-separated together from SNF. For the GANEX process, initially developed at CEA in France, a first cycle (GANEX-1)[16] where the uranium (VI) is selectively extracted from the solution before the group separation of transuranic elements (Np, Pu, Am, Cm), which occurs in the second cycle (GANEX-2), has been demonstrated.[12] Particularly, within the EURATOM framework, a spiked and a hot flow-sheet trial have been performed for the second cycle known as EURO-GANEX process, where AHA plays an important role assisting in Pu and Np stripping.[17,18] The EURO-GANEX solvent consists of a synergic combination of a diglycolamide and a malonamide ligand (0.2 mol/L *N*,*N*,*N*′,*N*′-tetraoctyl diglycolamide, TODGA[19] + 0.5 mol/L *N*,*N*′-dimethyl-*N*,*N*′-dioctylhexyloxyethyl malonamide, DMDOHEMA[20]) in odorless kerosene (OK), which first co-extracts lanthanides (Ln) and actinides (An) from the highly acidic raffinate (HAR) obtained from the U recovering step. The TRU elements are extracted from Ln using a mixture of water-soluble An complexants, AHA and a sulphonated bis-triazinyl pyridine (1 mol/L AHA + 0.018 mol/L 2,6-bis(5,6-di(sulphophenyl)-1,2,4-triazin-3-yl)pyridine, SO_3-Ph-BTP,[21] named in this work as BTP, in 0.5 mol/L HNO_3).

Consequently, complexation of AHA with all these metals has been studied over years. Among others, Tkac *et. al*[22] reported the complexation of uranium (VI) with AHA by UV-Vis method and Sinkov and Choppin[23] studied the AHA complexes with trivalent f-block metal cations by optical absorbance spectroscopy. In addition, due to fluorescence of metals such as Eu, or Tb, many authors have used the luminescence spectroscopy as a technique to understand the complexation of different An and Ln with AHA.[23-25]

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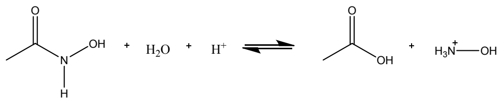
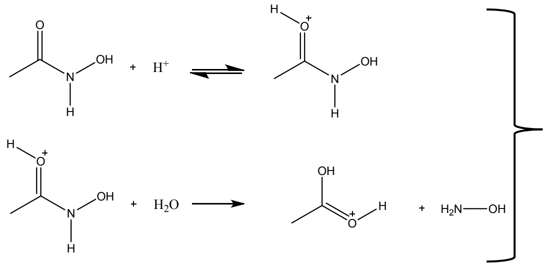
It is also very well known that AHA hydrolysis is catalyzed in acidic media giving place to acetic acid (AcOH) and hydroxylamine (HA)[5, 6, 14, 26-28], being kinetically insignificant in neutral media.[27] Equation 1 shows the accepted summary of acid-basic equilibria and the nucleophilic attack on the carbonyl group of AHA that take place in acidic media, which are described in more detail in Equation 2.



Equation 1



Equation 2

In general, the hydroxamic acids hydrolysis reaction has been considered as 2nd order reaction overall, 1st order with respect to each substrates, following Equation 3.[6,27,29,30] Several studies of AHA hydrolysis at different conditions have been performed. For example, Taylor and May calculated a rate constant k = 0.00205 L·mol^{-1}·min^{-1} at 25ºC for $[AHA]_o$ = 0.1 mol/L and $[HNO_3]_o$ = 0.5 mol/L.[29] On the other hand, Chung *et al.*[27] calculated k´ and k as a pseudo-first order reaction (k´ = k[H$^+$]) by measuring hydrolysis at a different nitric acid concentration (k = 0.0015 L·mol^{-1}·min^{-1} at 25ºC for $[AHA]_o$ = 0.1 mol/L and $[HNO_3]_o$ = 0.267-4 mol/L). More recently, Sampath *et al.*[30] have estimated a rate constant value of 0.0014 L·mol^{-1}·min^{-1} for non-limiting concentration of reactants from experiments varying initial AHA and nitric acid concentration. All these data were calculated by colorimetric method through the measurement of the Fe(III)-AHA complex absorption. In one of our recent works[32] it has been demonstrated that AHA hydrolysis can be studied by using Raman spectroscopy and it has been compared with the data gathered in the literature, concluding that Raman spectroscopy is a good technique to measure the kinetics of AHA hydrolysis, since the result (k = 0.00154 L·mol^{-1}·min^{-1}) is in good agreement with such literature.

$$-\frac{\mathrm{d}\,[\mathrm{AHA}]}{\mathrm{dt}} = \mathrm{k}[\mathrm{AHA}][\mathrm{H}^+] \qquad \text{Equation 3}$$

Despite the fact that hydrolysis reaction is acid catalyzed, *i.e.* protons are not consumed, one of its products (hydroxylamine, HA) acts as a base increasing the pH of the solution as a function of hydrolysis time due to the formation of hydroxyl ammonium (see Equation 4). That is why some published kinetic regression fits are considered valid only at the early stage of the reaction.

$$\mathrm{NH_2OH} + \mathrm{HNO_3} \leftrightarrow \mathrm{NH_3OHNO_3} \qquad \text{Equation 4}$$

Notwithstanding the hydrolysis of AHA in acid conditions, its use in different advanced fuel reprocessing processes is considered advantageous, since the residence times in centrifugal contactors would be very low compared to the half-lives of AHA in nitric acid solutions.[29] However, studies about the effects of its degradation on the performance of the global system would be needed. Accordingly, the goal of this research is to study the implications of AHA hydrolysis in EURO-GANEX extraction systems during TRU/Ln separation step ($[AHA]_o$ = 1.0 mol/L > $[HNO_3]_o$ = 0.5 mol/L); this study is not only for a controlled situation with short times in the centrifugal contactors, but also for non-controlled situations or deliberate longer residence times studies, *e.g.* long term behavior stability studies, etc. In this work, the implications of the AHA degradation in the extraction capacity of the Euro-GANEX system for different metals (Am, Eu, Gd) have been studied, evaluating the distribution ratios (D_M) as a function of AHA hydrolysis time. Secondly, the kinetics of AHA hydrolysis in nitric acid medium and in the presence of a metal has been evaluated by using quantitative Raman spectroscopy (QRS). Finally, the effect of AHA hydrolysis on M-L complexation has been studied by analyzing the Eu fluorescence emission as a function of the media composition.

Results and discussion

Many authors have reported the addition of AHA to the extraction systems with the purpose of facilitating the stripping of metals like Np and Pu previously,[10, 31] but not its effects on $D_{M(III)}$ as a function of time. Therefore, in order to study the effects of AHA hydrolysis on the general behavior of the EURO-GANEX extracting system, the extraction capacity of Ln and An with and without AHA in the media *(i.e.* time 0 of hydrolysis) and as a function of hydrolysis time was first explored.

To perform these experiments, Eu(III) and Am(III) were chosen as representative trivalent Ln and An elements respectively; where Eu(III) would be extracted from the aqueous to the organic phase by complexation with TODGA-DMDOHEMA, while Am(III) would stay in the aqueous phase due to the Am-BTP complexation. Table 1 shows distribution ratios of Am (III), Eu(III) and Gd(III) either when AHA is present or absent in the aqueous phase. A moderate decrease of all of them was observed when AHA was added to the system. These results point out towards an Am and Eu complexation by AHA.

Therefore, for an easier understanding of the system, additional extraction experiments were done in parallel with a simplified solvent with neither DMDOHEMA in the organic phase nor BTP in the aqueous phase. The distribution ratios for this simplified system (TODGA//AHA) are also shown in Table 1. From the comparison between D values obtained by EURO-GANEX and the simplified systems it can be seen that the extraction of both metals by TODGA decreased when AHA was added to the system.

Figure 1 shows the $D_{M(III)}$ values of Eu(III), Gd(III) and Am(III) as a function of time for the EURO-GANEX system conditions. As it was done before, a parallel study with Gd(III) was carried out. In Figure 1, a far from negligible decrease in the distribution ratios is observed for all metals as a function of time: at short times such as four hours, there is a reduction by 30 % for D_{Am}, 36 % for D_{Eu} and 40 % for D_{Gd}, reaching 95 %, 96 % and 95 % respectively for long times.

It is known that $D_{M(III)}$ values are directly linked to the counter ion (nitrate) concentration in the aqueous phase and moreover, in TODGA-based solvents $D_{M(III)}$ increase as function of nitric acid concentration.[19] Since it does not exist a variation of nitrate

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Table 1. Distribution ratios of Ln(III) and An(III) by EURO-GANEX and a simplified TODGA-based solvents from the corresponding aqueous phase with and without AHA (fresh, t = 0). Organics: a) *EURO-GANEX solvent* (0.2 mol/L TODGA and 0.5 mol/L DMDOHEMA in kerosene); b) *Simplified TODGA-based solvent* (0.2 mol/L TODGA in kerosene). Aqueous: a) 0.018 mol/L BTP with and without 1 mol/L AHA in 0.5 mol/L HNO_3; b) 0.5 mol/L HNO_3 with and without 1 mol/L AHA. Metals: 10^{-8} mol/L for ^{241}Am(III), 10^{-10} mol/L for ^{152}Eu(III) and $5.5 \cdot 10^{-5}$ mol/L for ^{158}Gd(III).

Org	EURO-GANEX solvent		Simplified TODGA-based solvent	
Aq	BTP in 0.5 mol/L HNO_3	AHA+BTP in 0.5 mol/L HNO_3	0.5 mol/L HNO_3	AHA in 0.5 mol/L HNO_3
*D_{Am}	0.06	0.02	17	10
*D_{Eu}	23	9	94	62
**D_{Gd}	21	11	-	-

*Distribution coefficient calculated for ^{152}Eu and ^{241}Am by gamma spectrometry.
**Distribution coefficient calculated for ^{158}Gd by ICP-MS, as an individual experiment.

concentration, the reduction of $D_{M(III)}$ values in Figure 1 can be explained by the expected increase of pH due to the reaction between hydroxylamine and HNO_3 forming hydroxylamine nitrate, as described by Equation 4. Therefore, proton concentration was measured by the titration method explained in the experimental section, where a decrease from 0.52 mol/L to 0.07 mol/L after approximately 120 hours was corroborated, explaining the reduction in $D_{M(III)}$ observed in Figure 1.

Although AHA half-life is long enough for being used in centrifugal contactors of nuclear fuel reprocessing,[29] this reduction in the extraction efficiency of the systems could have many other implications, such as a loss of efficiency under longer operation situations or even the way that stability studies should be performed. Thus, the comprehension and control of AHA hydrolysis in the extracting systems under study will help to model and predict unexpected situations for future industrial applications.

On that basis, the kinetic aspects of AHA hydrolysis in more real experimental conditions were also addressed; that is in the presence of a Ln and without adding Fe for the quantitative colorimetric measurements of AHA concentration. For that purpose, solutions of AHA in nitric acid and in the presence of Eu(III) were studied by spectroscopic techniques (Raman and luminescence), using the experimental conditions of the real system. Eu(III) was chosen for these studies since it is present in the real feed of EURO-GANEX systems, forms complexes with AHA,[23] enables working with radioactive and non-radioactive solutions and shows spectroscopic properties that can be followed by spectroscopic techniques. Besides, proton concentration was followed by pH measurements using the experimental procedure explained in the Experimental section.

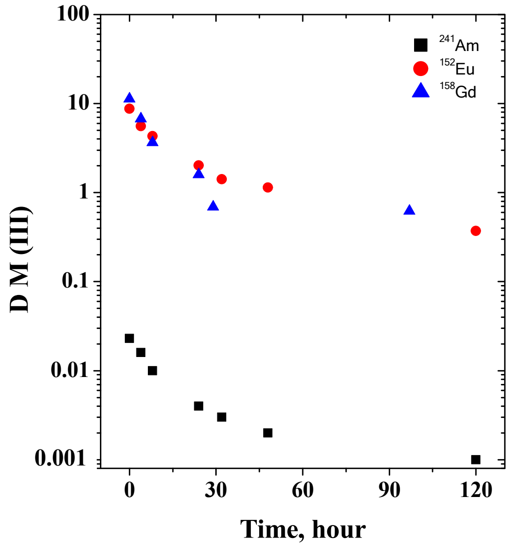

Figure 1. Distribution ratios of M(III) (Am, Eu and Gd) obtained by EURO-GANEX system as a function of time (0-120 h). Organic: 0.2 mol/L TODGA and 0.5 mol/L DMDOHEMA in kerosene. Aqueous: 0.018 mol/L BTP and 1 mol/L AHA in 0.5 mol/L HNO_3. Metals: 10^{-8} mol/L for ^{241}Am(III), 10^{-10} mol/L for ^{152}Eu(III) and $5.5 \cdot 10^{-5}$ mol/L for ^{158}Gd(III).

Figure 2 shows the typical Raman spectra obtained on fresh AHA, AcOH, and HA dissolved in HNO_3 and containing $Eu(NO_3)_3$. In this figure, the assignment of the main bands, based on one of our previous studies,[32] is indicated and it is described in the appendix A of the supplementary information. The two most intense bands correspond to the NO_3^- and water molecules, *i.e.* the narrow and intense peak at ~ 1037 cm^{-1} is due to the symmetric stretching vibration of NO_3^- and the broad band at around 2800-3400 cm^{-1} is assigned to the OH stretch region (Figure 2.a). AHA molecule is characterized by two bands at 950 and 985 cm^{-1} corresponding to the C-C and N-O stretching vibrations, respectively, [ν_s(C-C) and ν_s(N-O)], whereas the band corresponding to the ν_s(C-C) in the AcOH appears at ~ 881 cm^{-1} and the band of the hydroxylamine at ~ 997 cm^{-1} is assigned to the N-O stretching ν_s(N-O) (Figure 2.b).

Once all Raman peaks related to the aqueous solution were assigned, this aqueous solution of 1 mol/L AHA and 0.5 mol/L $Eu(NO_3)_3 \cdot 6H_2O$ in 0.5 mol/L HNO_3 was measured immediately after the pure components were dissolved, and as a function of time (Figure 3.a). As it can be appreciated, the intensity of those bands corresponding to AHA (ν_s(C-C) ~950 and ν_s(N-O) ~985 cm^{-1}) decreases as a function of time, whereas the intensity of the bands corresponding to acetic acid (ν_s(C-C) ~881 cm^{-1}) and hydroxylamine (ν_s(N-O) ~997 cm^{-1}) increase.

Since these peaks do not completely overlap, it is possible to study the kinetics of the reaction by measuring, not only the decrease in concentration of the AHA but also the increase in concentration of AcOH and HA by using quantitative Raman spectroscopy (QRS), i.e. the Raman analysis of the relative

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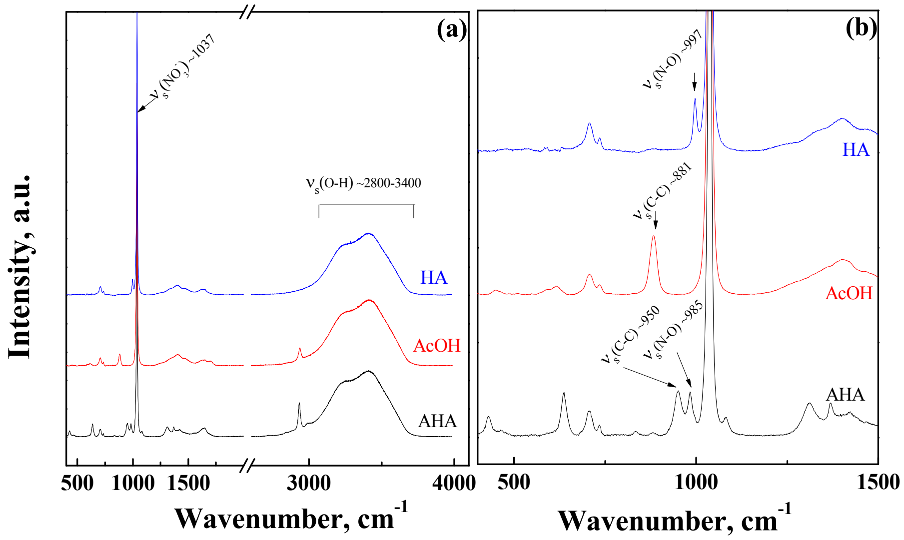

Figure 2. Raman spectra of 1 mol/L AHA, 0.5 mol/L acetic acid (AcOH) and 0.5 mol/L hydroxylamine (HA) dissolved in 0.5 mol/L HNO_3 containing 0.5 mol/L $Eu(NO_3)_3$: (a) from 450 to 4000 cm^{-1} and (b) from 450 to 1500 cm^{-1}.

integrated intensities of the mentioned bands give us a measure of the relative concentration.[32] The experimental Raman spectra, fitted curves and calibration curves are shown in the appendix B of the supplementary information. Results of the quantitative Raman analysis are shown in Figure 3.b., as well as the proton concentration.

Two different stages can be observed: a first variation until ~72 hours followed by a steady stage. In the case of AHA, its concentration decreases from 1 mol/L to ~0.41 mol/L, while AcOH and HA concentrations increase with time from 0 mol/L to ~0.5 mol/L. Proton concentration decreases inasmuch as HA is formed following equation 4, from 0.52 to 0.08 mol/L in 48 hours, reaching the minimum at 0.06 mol/L after approximately 100 hours. Therefore, this leads to an increase from the initial pH ~0.28 to pH ~1.21, explaining the changes observed in the extraction experiments results and shown in Figure 1.

The steady state is reached when AHA, AcOH, HA are ~0.5 mol/L (similar to the initial HNO_3 concentration) and [H$^+$] is reduced to 0.06 mol/L. Therefore, this indicates that the reaction reaches a steady state when nitric acid is neutralized, in this case after ~72 hours (see Figure 3.b).

The obtained concentration of AHA and protons as a function of time was used to estimate the rate constant (k) of AHA hydrolysis in the presence of Eu(III). The experimental conditions chosen for EURO-GANEX system ($[AHA]_o$ = 1 mol/L and $[HNO_3]_o$ = 0.5 mol/L) do not fit with the typically described hydrolysis kinetics performed until now as a pseudo first order reaction (where [AHA] < [HNO_3]). However, from experiments varying initial AHA and nitric acid concentration, Sampath *et al.*[30] obtained curves fitting with a first order reaction with respect to both components even when [AHA] > [HNO_3]. Hence, following the previously described methodology,[5, 30] a k value of 0.00156 ± 0.00005 L·mol^{-1}·min^{-1} was obtained at 25 ºC

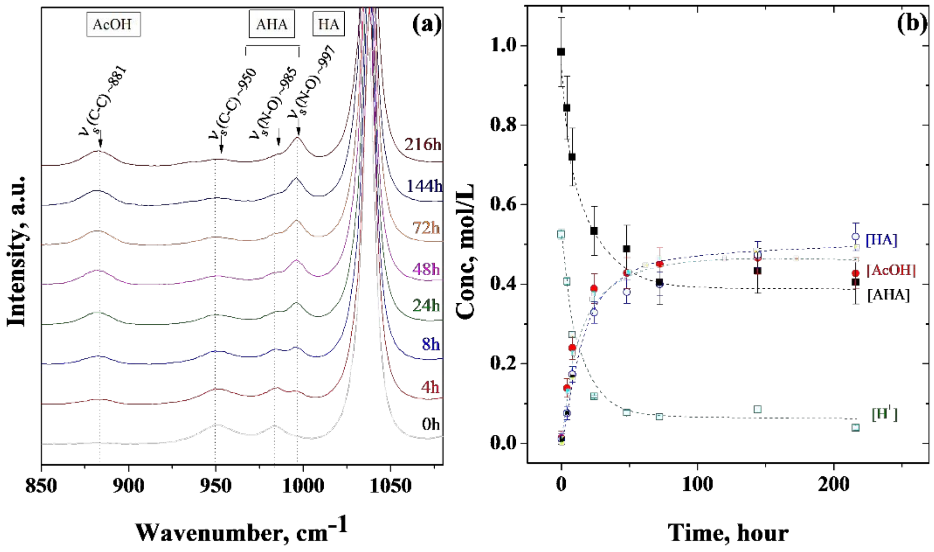

Figure 3. (a) Raman spectra of Eu-AHA hydrolysis as a function of time (from 0 to 216 hours) and (b) Concentrations obtained of AHA, Acetic acid (AcOH), Hydroxylamine (HA) and protons (H$^+$) for AHA hydrolysis.

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under Euro-GANEX experimental conditions. This result is lower than that obtained by *Taylor and May* (k= 0.00205 L·mol^{-1}·min^{-1}, for $[H^+]_o$ = 1 mol/L and $[AHA]_o$ = 0.05 mol/L),[29] probably because of the lower concentration of nitric acid in the media; but it is consistent with the values obtained by Chung *et al.*[27] and Sampath *et al.*[30] Since for *in situ* Raman spectroscopy it is not necessary to add Fe to quantify AHA concentration as function of time, and Eu(III) was added to simulate more real conditions, it can be stated that a more realistic methodology to measure AHA hydrolysis during extraction experiments has been developed.

Conversely, as long as Eu is also in the medium and able to form complex with AHA, its presence might affect the kinetics of hydrolytic reaction. In that sense, for a better understanding of the system, a similar kinetic study of AHA hydrolysis was carried out by fluorescence emission spectroscopy. Figure 4.a shows the typical Eu^{3+} emission spectrum obtained from a solution of 0.5 mol/L $Eu(NO_3)_3$ in 0.5 mol/L HNO_3, in which the characteristic transitions of europium fluorescence can be observed. It is well known that a luminescence spectrum of Eu^{+3} ions presents characteristic peaks at 579 nm ($^5D_0 \rightarrow {}^7F_0$ transition, only observed in C_n, C_{nv} and C_s symmetry, electric dipole), 592 nm ($^5D_0 \rightarrow {}^7F_1$ transition, intensity largely independent of environment, magnetic dipole), 617 nm ($^5D_0 \rightarrow {}^7F_2$ hypersensitive transition, intensity very strongly dependent on environment, electric dipole), 650 nm ($^5D_0 \rightarrow {}^7F_3$ forbidden transition, electric dipole), and 695 nm ($^5D_0 \rightarrow {}^7F_4$ transition, intensity dependent on Eu^{3+} environment, electric dipole).[25, 33] Figure 4.b shows the behavior of the emission fluorescence spectra with time of 0.5 mol/L $Eu(NO_3)_3$ in the presence of 1 mol/L AHA in 0.5 mol/L HNO_3. In Figure 4.c the intensity of $^5D_0 \rightarrow {}^7F_1$ transition is represented, and it can be appreciated that the intensity of the bands also decreases with time.

The reduction of the intensity in the system Eu-AHA in acidic medium has been previously reported by Sinkov *et al.*,[24] who attributed the intensity drop to a quenching due to the Eu-AHA complex formation. In order to know if our system, 0.5 mol/L $Eu(NO_3)_3$ dissolved in 0.5 mol/L HNO_3, follows the same trend, we carried out a study of the variation of the fluorescence intensity of $^5D_0 \rightarrow {}^7F_1$ transition with the AHA concentration from 0.25 mol/L to

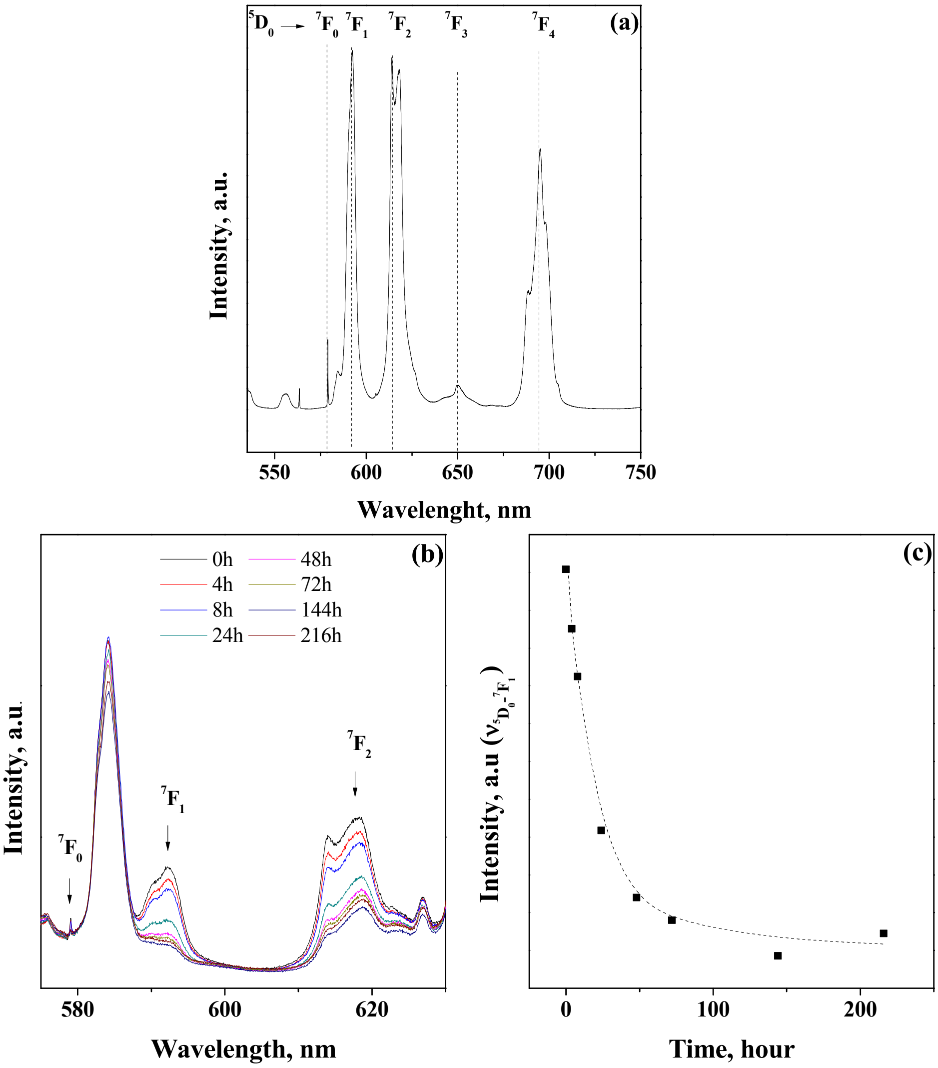

Figure 4. (a) Typical Eu^{3+} emission spectrum, obtained from a solution of 0.5 mol/L $Eu(NO_3)_3$ in 0.5 mol/L HNO_3; (b) Fluorescence emission spectra of $Eu(NO_3)_3$ in the presence of 1 mol/L AHA in HNO_3 as a function of time (from 0 to 216 hours) and (c) Variation of intensity of $^5D_0 \rightarrow {}^7F_1$ transition of Eu - AHA as a function of time.

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1 mol/L AHA in 0.5 mol/L HNO_3. These results are compared in Figure 5 with the ones obtained by Pathak.

As can be seen in Figure 5, both results are concordant; thereupon, it can be assumed that the decrease of intensity obtained as a function of time, is due to a complexation phenomenon, (Figure 4.b), *i.e.* it can be interpreted as an increase in the concentration of complexed Eu(III) with time.

Unlike Pathak's study, the increase in the complexed Eu(III) cannot be a result of the increase in AHA concentration, since in our case AHA concentration decreased as a function of time (see Figure 3.b). Thus, this unexpected behavior could only be related to an effect the products of AHA hydrolysis and/or a pH effect.

Figure 6 shows the fluorescence emission spectra of $Eu(NO_3)_3$ in the presence of increasing concentrations of AcOH and HA in nitric acid, simulating what is happening in the medium as a function of time. As it was mentioned before, HA in nitric acid gives rise to an increase in pH as well, due to the formation of hydroxylamonium nitrate. Therefore, the possible effects on fluorescence as a function of pH should also be measured. However, no decrease in the emission intensity as a function of the concentration of AcOH or HA was detected with europium in the fluorescence study (Figure 6). This indicates that the complexation of the hydrolysis products with the metals is weak due to the acidity of the aqueous solution was still high enough to prevent effective complexation of AcOH and HA with metals. Thus, the Eu^{3+} complexation on time should be related to the presence of both AHA and AcOH and/or HA, but not to the AcOH and HA individually, since no decrease in intensity of europium fluorescence was separately detected.

These new results point out that the increase in pH might not be the only reason responsible for the decrease of distribution ratios observed in Figure 1, since complexation of Eu(III) in the aqueous phase also changes as a function of time. According to that, further studies are needed to clarify and control the role and behavior of AHA hydrolysis in the complexation taking place along an extraction process for Ln/An separation.

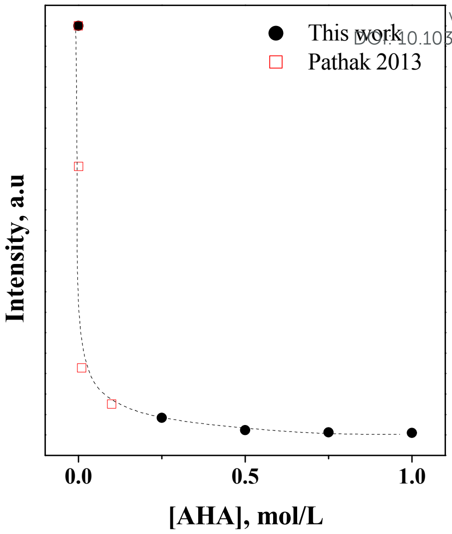

Figure 5. Variation of the fluorescence intensity of ${}^5D_0 \rightarrow {}^7F_1$ transition of Eu-AHA as a function of [AHA] at t = 0 min. Comparison with the results obtained in this work and those obtained by Pathak.[25]

Conclusions

The implications of AHA degradation during the stripping step of TRU from Ln in the EURO-GANEX process have been considered by evaluating the extraction capacity of the system (D_M) for different metals (Am, Eu, Gd), both when AHA is added to the system and as a function of its AHA hydrolysis time. The results indicate a slightly decrease of Ln and An $D_{M(III)}$ due to the presence of AHA, but also a far from negligible decrease as a function of AHA hydrolysis time. This reduction of $D_{M(III)}$ values is related mainly to the increase of pH due to the reaction between hydroxylamine and HNO_3 forming hydroxylamine nitrate. The reaction reaches a steady state when nitric acid is neutralized. Consequently, the ratio between nitric acid AHA concentrations might also be adjusted as a function of resident time and Pu concentration expected in the high active feed.

In situ Raman spectroscopy has been employed to investigate the AHA hydrolysis in the presence of Eu(III) in an acidic medium, which is a more realistic methodology than the colorimetric method

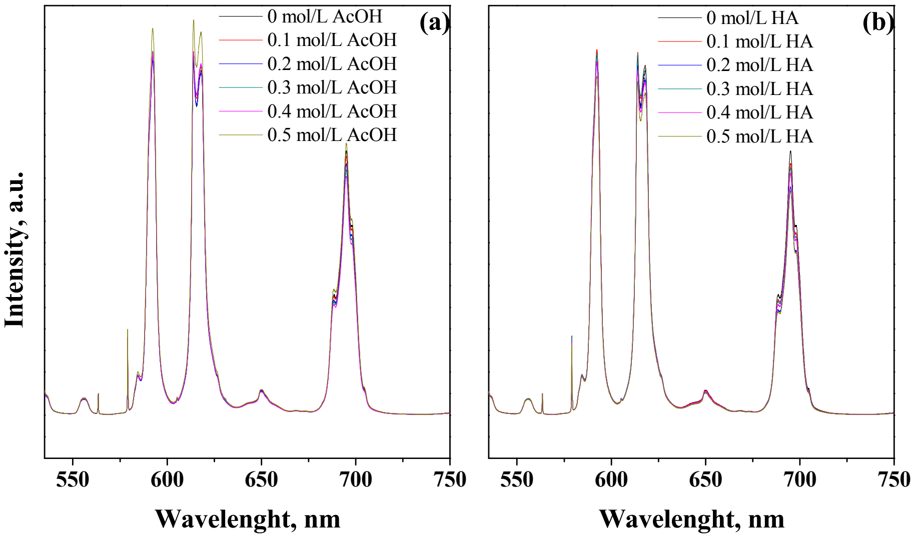

Figure 6. Fluorescence emission spectra of 0.5 mol/L $Eu(NO_3)_3$ in presence of different concentrations of a) AcOH and b) HA, in 0.5 mol/L HNO_3.

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used so far. The results show a rate constant k = 0.00156 ± 0.00005 $L·mol^{-1}·min^{-1}$ at 25 ºC for 1 mol/L AHA and 0.5 mol/L HNO_3.

The effect of AHA hydrolysis in M-L complexation was studied by analyzing the Eu fluorescence emission as a function of the media composition. The results obtained show an intensity decrease in the case of AHA addition, related to the complex formation, but this effect is not observed in the case of hydrolysis products isolated. Further work should be done in a representative concentration of Ln in this respect because the Eu complex was formed as a function of hydrolysis time. Therefore, this effect must be related to the presence of both AHA and hydrolysis products, but not to the isolated AHA, since AHA concentration decreases with time.

Therefore, all these effects of AHA hydrolysis should be taken into account for the design of laboratory experiments related to the development of Ln/An separation processes, such as EURO-GANEX. Thus, in order to properly compare data of experiments in which AHA is used, it should be important to take into account the elapsed time from AHA solution preparation to the performed studies (stability, extraction capacity, extraction efficiency, etc) or to consider those mal-operation situations where AHA residence time could be longer than expected for centrifugal contactors. Hence, either in a hot test or in the industrial scale up, if the elapsed time is large enough a decrease in the separation efficiency of radioactive metals might occur.

Experimental

Materials

Acetohydroxamic acid (AHA), acetic acid (AcOH), hydroxylamine (HA) and $Eu(NO_3)_3·6H_2O$, purchased from Acros (Belgium), Probus (Spain), Merck (Germany) and Alfa Aesar (Germany), respectively, were used without further purification. Nitric acid, HNO_3, purchased from VWR Chemical (used as diluent) was purified by Quartz sub-boiling distillation system (MLS- Milestone).

The reagents used in the extraction experiments were: *N*,*N*,*N'*,*N'*-Tetraoctyl diglycolamide (TODGA), which was synthesized at CIEMAT, and *N*,*N'*-dimethyl-*N*,*N'*-dioctylhexylethoxymalonamide (DMDOHEMA) purchased from Technocomm Ltd. in organic phase; water soluble hydro-BTP (2,6-bis(5,6-di-(sulfophenyl)-1,2,4-triazin-3-yl)-pyridine) supplied by Technocomm Ltd. and AHA in aqueous phase. The diluents used in the organic and aqueous phases were odourless kerosene (OK) purchased from Alfa Aesar (Germany) and HNO_3, respectively.

The gadolinium (^{158}Gd) used was Gd_2O_3 in HNO_3 2-3% supplied by Merck. The radioactive tracer solutions of $^{241}Am(III)$ and $^{152}Eu(III)$, were obtained as MCl_3, in HCl 1 mol/L, by Isotope Products Laboratories, California (USA).

Spectroscopic measurements

Raman spectra and fluorescence emission spectra were both acquired by using a Horiba LabRam HR evolution spectrometer (Jobin Yvon Technology). The laser beam was focused onto the sample through the 50x objective of an Olympus BX41 microscope. The scattered radiation was then collected in backscattering geometry, dispersed using a 600 grooves/mm holographic grating and recorded by a CCD detector (256 x 1024 pixels), obtaining a resolution of ~1 cm^{-1}/ pixel.

The kinetics of AHA hydrolysis in the presence of $Eu(NO_3)_3$ in nitric acid medium was evaluated by the Raman technique using a red laser of HeNe with a wavelength of 632.81 nm and an operation power of 20 mW. Moreover, the effect of AHA hydrolysis on the Eu florescence emission has been studied by emission fluorescence using a green laser of HeNe with a wavelength of 532 nm an operation power of 50 mW.

Raman spectra were acquired from 200 to 4000 cm^{-1} with a typical exposition time of 200 s, whereas fluorescence emission spectra were obtained with 2 s of exposition time within the range from 532 to 750 nm. All acquired spectra were daily recalibrated using the Ne emission light.

In the AHA hydrolysis the proton concentration in the medium has also been evaluated. For this purpose, aqueous solutions were potentiometrically titrated with KOH using an automatic titrator Metrohm 798 MPT titrino. The electrode was calibrated employing buffer solutions of pH 4.00 and 7.00 supplied by MetrOhm.

Extraction procedure

The extraction tests are based in liquid–liquid extractions where two phases (organic and aqueous phases) are in contact. Two extraction systems were assessed. The first of them is the so-called EURO-GANEX system and it contains 0.2 mol/L TODGA and 0.5 mol/L DMDOHEMA in kerosene in the organic phase, and 0.018 mol/L BTP and 1 mol/L AHA in 0.5 mol/L HNO_3 in the aqueous phase. The second system, named TODGA//AHA system, is a simplification of the first one keeping TODGA in the organic phase and AHA in the aqueous phase (organic: 0.2 mol/L TODGA in kerosene; aqueous: 1 mol/L AHA in 0.5 mol/L HNO_3).

The extraction experiments were performed by mixing for 30 min at room temperature (22 ± 2 ºC), 500 µL of both, aqueous and organic solutions spiked with ^{241}Am (1000 Bq/mL) and ^{152}Eu (1000 Bq/mL) and using a concentration of ^{158}Gd of $5.5·10^{-5}$ mol/L. After centrifugation (at 5000 rpm), the phases were separated and aliquots of each phase (300 mL) were taken for analysis.

Canberra HP–Ge detector was used for high energy gamma spectrometry measurements, using Genie-2000 as gamma analysis software from Canberra. The gamma characteristic photopeaks at 59.5 keV and 121.8 keV were analyzed for ^{241}Am and ^{152}Eu, respectively. Non-radioactive ^{158}Gd element was analyzed with a Sector Field Inductively Coupled Plasma Mass Spectrometer (Thermo Scientific^{TM} iCAP^{TM} Q ICP-MS, Collision Cell Technology (CCT) mode). The aqueous and organic phases were measured directly after adequate dilution. The results are reported as distribution ratios D ($D_M = [M^{3+}]org./[M^{3+}]aq.$).

Proton concentration in the medium after extraction experiments were potentiometrically titrated with KOH as it has been described in the spectroscopic measurements section.

Conflicts of interest

There are no conflicts to declare.

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