Solvent extraction modelling of Ce/Eu/Y from chloride media using D2EHPA

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ABSTRACT

End-of-life fluorescent lamps are becoming essential in the REEs field and suppose a feasible secondary source for getting them, reducing thus their supply risk. Considering the proved viability of the cationic extractants, the present study aims at establishing a solvent extraction model using di-(2-ethylhexyl)phosphoric acid (D2EHPA) not only based on the individual Ce, Eu and Y behaviour in chloride media, but also bearing in mind the competitive extraction of these metals in Ce/Eu/Y mixtures, depending on the media variables. Furthermore, the model allow determinining the optimal REEs separation conditions. The results disclose that Y could be separated from the mixture using 0.1 mol/L di-(2-ethylhexyl)phosphoric acid, acidity above of 3 mol/L of protons and chloride concentrations higher than 4 mol/L.

Keywords

Mathematical modelling; D2EHPA; Solvent extraction; Rare earths; Separation

INTRODUCTION

The rare earths (REEs) group has gained importance in the last years due to the intensive use of these metals in many advanced technological applications. The consumption of these metals has considerably increased because of their continuously growing market. Taking into account the REEs supply risk, their importance in the clean energy markets and the continuous increase in the demand of these metals, neodymium, terbium, dysprosium, yttrium and europium have been considered as critical [1]. The REEs demand is enhanced by the supply risk, that has led to considering new techniques for recovering and recycling these metals.

Because of the traditional incandescent bulb eradication and the efficient use of lighting energy, the manufacture of the fluorescent lamps containing phosphors has increased in the last years [2,3]. Since the high REEs content in the red phosphors (55%, mainly yttrium and europium) [4], our investigation is focused on these phosphors.

To date, solvent extraction (SX) is the most common technique used for the recovery and separation of REEs using a wide range of extractants, mainly the cationic ones such as bis-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272, Cy272), di-(2-ethylhexyl)phosphoric acid and a mixture of phosphinic and phosphonic acids (Cyanex 572, Cy572) have been reached [5–7]. Owing to the acidic character of these extractants (Cy272 < Cy572 < D2EHPA), the pH turns out to be one of the most interesting parameters to study because the protons play a crucial role in the extraction mechanism [8–11]. Innocenzi et al. suggest that the REEs extraction is possible using Cy272, Cy572 and D2EHPA from sulphuric leaching solutions coming from the dissolution of fluorescent powders of lamps. However, the terbium and yttrium separation from other REEs from end-of-life fluorescent lamps only was achieved using D2EHPA [12]. Nie et al. postulate Cy572 as the best extractant, instead

of P507 (2-ethylhexylphosponic acid mono-2-ethylhexyl ester), TBP (tributyl-phosphate) or Cyanex 923 (a mixture of four trialkylphosphine oxides), to recover Sc in chloride media from leaching solutions of a tungsten residue by SX [13]. A mixture of HEHAPP (2-ethylhexyl-3-(2-ethylhexylamino)pentan-3-yl-phosphonic acid) and D2EHPA could be an efficient synergic extraction system for the heavy REEs separation according to Kuang et al. [9].

Finding suitable working conditions to achieve the REEs separation of high purity is essential to take advantage of spent products and thus find a green alternative to recover these metals. Usually, the REEs recovery processes depicted in the literature start off by dissolving synthetic or real materials in acidic media and using SX to recover the REEs. Most of them try to find suitable working conditions to achieve the REEs separation of high purity metals because it is essential to revaluate spent products applying green alternatives to recover them. However, less research has focused on the optimisation of the separation processes for metal extraction developing an extraction model that allows simulating the REEs behaviour in different operating conditions. Determining such conditions experimentally is labourious and time-consuming. For this reason, this paper proposes that to have an extraction model will be useful to minimize the efforts on the optimization process.

Although different REEs modelling are depicted in the literature, only a few are considering the metal speciation and the ionic strength. Furthermore, most of them are taking in consideration just one extraction mechanism, without (1) investigating other mechanisms and (2) finding the optimal working conditions to the REEs separation. Lyon et al. developed a dynamic modelling for the Nd separation from an Nd/Pr mixture using PC88A (P507), just considering one extraction mechanism, $REE^{3+}{}_{aq} + 3(HA)_{2org} \leftrightarrow REE(HA_2)_{3org} + 3H^+{}_{aq}$ [14]. Bearing in mind the

$$REE^{3+}_{aq} + 3(HA)_{2\,org} \leftrightarrow REEA_3(HA)_{3\,org} + 3H^+_{aq}$$ mechanism, Nian-Xin et al. proposed a solvent extraction model for Y(III) and Eu(III) using also the same extractant but any separation conditions for the Y/Eu mixture were suggested [15]. Methyl-tri(octyl/decyl)ammonium oleate ionic liquid was used as extractant to propose the following solvent extraction mechanism for Nd/Tb/Dy mixture, $$MeCl^{2+}_{aq} + 2Cl^-_{aq} + 2R_4N^+A^-_{org} \leftrightarrow (R_4N^+Cl^-)_2 \cdot MeClA_{2\,org},$$ after evaluating the minimum error comparing different described model. Although the extraction mechanism was developed considering the metal speciation and the ionic strength, the REEs separation conditions were not found in the working parameters range studied [16].

In this sense, the current research develops a mathematical solvent extraction model for individual cerium, europium and yttrium ions in chloride media considering the metal speciation and the ionic strength using D2EHPA as the extractant. Several extraction mechanisms have been suggested and the *Matlab R2017b* software was used to solve the proposed mass balances and equilibria equations. Selected model parameters were optimized fitting the calculated to the experimental data. The individual models for each metal have been successfully used to predict the behaviour of these metal ions in a mixture containing these three REEs and also to determine the optimal conditions for the metal separation.

METHODS

Materials

The aqueous solutions were prepared by dissolving $CeCl_3 \cdot 7H_2O$, Eu_2O_3 and Y_2O_3 (Sigma Aldrich Ref. 228931, 289221 and 205168, respectively) in the adequate quantity of hydrochloric acid. In order to adjust the pH and the chloride concentration

in the medium, NaCl, NaOH or HCl were added as needed. D2EHPA, supplied by Sigma-Aldrich (Ref. 237825), was chosen as extractant and kerosene (Ref. 607010) from Sigma-Aldrich was the diluent for the organic solutions, both were used as received. HCl was used as a stripping solution.

Solvent extraction procedure

The cerium, europium and yttrium concentration in the feed solution was 1 g/L of each metal in chloride 2 mol/L. The experiments were carried out in separatory funnels in which 10 mL of aqueous and organic phase were equilibrated at room temperature (20 ± 2 °C) using a horizontal mechanical shaker (SBS Mechanical Shaker) at 140 rpm for 10 min until the equilibrium was achieved. After phases separation, the aqueous phase pH was measured and the concentration of the REEs was determined by atomic emission spectrometry using a 4100 MP AES System (Agilent Technologies) with an analytical error ≤ 5%. The organic phase was kept for the stripping experiments. According to Wu et al., 6 mol/L hydrochloric acid was used as stripping solution to recover the 100% of the loaded metals [17].

The effect of the equilibrium pH, the D2EHPA and the chloride concentrations on the extraction yield of each metal separately (Ce/Eu/Y) were studied and the competitive extraction of a Ce/Eu/Y mixture was also investigated.

To evaluate the results, extraction efficiency (%E) and stripping efficiency (%S) were defined in Eqs. (1) and (2) as:

$$\%E = \frac{\overline{[Me]}}{[Me]_0} \cdot 100 \tag{1}$$

$$\%S = \frac{[Me]_{str}}{\overline{[Me]}} \cdot 100 \tag{2}$$

where *[Me]₀* refers to the initial rare earth concentration in the aqueous phase, *[Me]ₛₜᵣ* is the equilibrium concentration of REE in the stripping phase and $\overline{[Me]}$ is the concentration of REE in the loaded organic phase.

THEORETICAL MODEL

The mass balances and the chemical equilibria involved in the extraction process were considered to develop the mathematical model of the Ce/Eu/Y separation system using D2EHPA in chloride media. The chemical equilibria were derived considering the Ce/Eu/Y speciation and the most appropriate extraction model.

Equilibria equations

Chloro complex formation equilibria in the aqueous phase

The metal speciation considers that several chloride complexes can be formed according to the overall formula $MeCl_m^{3-m}$, where *m* is the chloride ions bonded to the metal ion as is shown in (3).

$$Me^{3+} + m\,Cl^- \overset{\beta_m}{\leftrightarrow} MeCl_m{}^{3-m} \tag{3}$$

According to Agarwall et al., the species are formed with *m* = 1, 2, 3 or 4 ((4) − (7)) [6]. The stepwise stability formation constants, represented by K_1, K_2, K_3 and K_4 in the equilibria Me-Cl complexes, allow us to know the theoretical distribution of metal present in the aqueous phase.

$$Me^{3+} + Cl^- \overset{K_1}{\leftrightarrow} MeCl^{2+} \tag{4}$$

$$MeCl^{2+} + Cl^- \overset{K_2}{\leftrightarrow} MeCl_2{}^+ \tag{5}$$

$$MeCl_2{}^+ + Cl^- \overset{K_3}{\leftrightarrow} MeCl_3 \tag{6}$$

$$MeCl_3 + Cl^- \overset{K_4}{\leftrightarrow} MeCl_4^- \tag{7}$$

The stepwise stability formation constants are expressed in activity terms (a_i) of the species i as follows:

$$K_1 = \frac{a_{MeCl^{2+}}}{a_{Me^{3+}} \cdot a_{Cl^-}} = \frac{[MeCl^{2+}]}{[Me^{3+}] \cdot [Cl^-]} \cdot \frac{\gamma_{MeCl^{2+}}}{\gamma_{Me^{3+}} \cdot \gamma_{Cl^-}} \tag{8}$$

$$K_2 = \frac{a_{MeCl_2^+}}{a_{MeCl^{2+}} \cdot a_{Cl^-}} = \frac{[MeCl_2^+]}{[MeCl^{2+}] \cdot [Cl^-]} \cdot \frac{\gamma_{MeCl_2^+}}{\gamma_{MeCl^{2+}} \cdot \gamma_{Cl^-}} \tag{9}$$

$$K_3 = \frac{a_{MeCl_3}}{a_{MeCl_2^+} \cdot a_{Cl^-}} = \frac{[MeCl_3]}{[MeCl_2^+] \cdot [Cl^-]} \cdot \frac{\gamma_{MeCl_3}}{\gamma_{MeCl_2^+} \cdot \gamma_{Cl^-}} \tag{10}$$

$$K_4 = \frac{a_{MeCl_4^-}}{a_{MeCl_3} \cdot a_{Cl^-}} = \frac{[MeCl_4^-]}{[MeCl_3] \cdot [Cl^-]} \cdot \frac{\gamma_{MeCl_4^-}}{\gamma_{MeCl_3} \cdot \gamma_{Cl^-}} \tag{11}$$

where γ_i represents the activity coefficients of the species i. These values have been considered to be equal to 1 for the aqueous neutral species and all the organic species.

The Davis equation defined in Eq. (12) was used to calculate the activity coefficients in the aqueous phase:

$$log_{10}\gamma_i = -0.5102 \cdot z_i \left(\frac{\sqrt{I_m}}{(1+\sqrt{I_m})} - 0.3 \cdot I_m \right) \tag{12}$$

and the ionic strength (I_m) of the media were calculated according to the Eq. (13), where c_i is the concentration and z_i is the species charge.

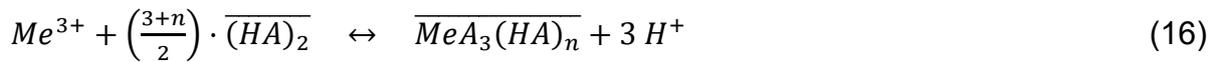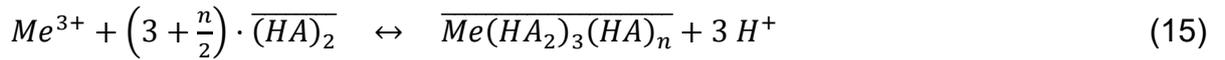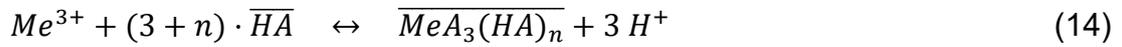$$I_m = 0.5 \sum z_i^2 \cdot c_i \tag{13}$$

Extraction equilibria

The extraction mechanism of rare earths using acidic extractants has been investigated in different researches [10,18,19]. Taking into account these studies and the

speciation depicted in Eqs. (4)-(7), different extraction mechanisms of Ce/Eu/Y from chloride medium were considered.

Although D2EHPA usually is being as a dimeric compound, in this study, it has also been considered without dimerization $\overline{HA}$, as shown in Eqs. (14) and (17) and Eqs. (15), (16), (18) and (19) are the mechanisms assuming the extractant in the dimeric form $\overline{(HA)_2}$.

It is well known that this kind of extractants only extract cationic species. Moreover, the monovalent species, such as $MeCl_2^+$, are usually not extracted. For this reason, in the current investigation, Me^{3+} and $MeCl^{2+}$ are the species investigated in the proposed models. The extraction reactions that could take place on the Ce/Eu/Y separation system by using D2EHPA in chloride media have been described by the following reactions (Eqs. (14)-(19)):
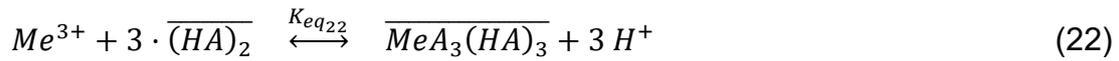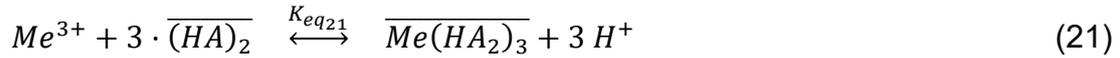
$$Me^{3+} + (3+n) \cdot \overline{HA} \quad \leftrightarrow \quad \overline{MeA_3(HA)_n} + 3\,H^+ \tag{14}$$

$$Me^{3+} + \left(3 + \frac{n}{2}\right) \cdot \overline{(HA)_2} \quad \leftrightarrow \quad \overline{Me(HA_2)_3(HA)_n} + 3\,H^+ \tag{15}$$

$$Me^{3+} + \left(\frac{3+n}{2}\right) \cdot \overline{(HA)_2} \quad \leftrightarrow \quad \overline{MeA_3(HA)_n} + 3\,H^+ \tag{16}$$

$$MeCl^{2+} + (2+n) \cdot \overline{HA} \quad \leftrightarrow \quad \overline{MeClA_2(HA)_n} + 2\,H^+ \tag{17}$$

$$MeCl^{2+} + \left(2 + \frac{n}{2}\right) \cdot \overline{(HA)_2} \quad \leftrightarrow \quad \overline{MeCl(HA_2)_2(HA)_n} + 2\,H^+ \tag{18}$$

$$MeCl^{2+} + \left(1 + \frac{n}{2}\right) \cdot \overline{(HA)_2} \quad \leftrightarrow \quad \overline{MeClA_2(HA)_n} + 2\,H^+ \tag{19}$$

where *n* is the number of *HA* bonded with the *Me* in the organic phase. The species under the bar are in the organic phase.

In accordance with different studies depicted in the literature, some extraction reactions have been considered. The simplest extraction mechanism has been described by Cytec (Eq. (20)) where monomeric form was considered with n equal 0 [20].

$$Me^{3+} + 3 \cdot \overline{HA} \xrightarrow{K_{eq20}} \overline{MeA_3} + 3\,H^+ \tag{20}$$

Agarwal et al. and N.E. El-Hefny et al. proposed that three dimeric molecules of Cyanex 572 are involved in the extraction mechanism (Eqs. (21) and (22), respectively) [5,6].
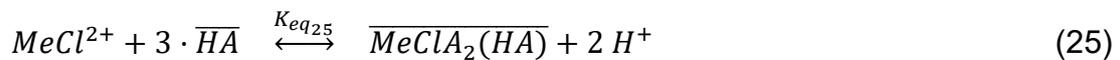
$$Me^{3+} + 3 \cdot \overline{(HA)_2} \xrightarrow{K_{eq21}} \overline{Me(HA_2)_3} + 3\,H^+ \tag{21}$$

$$Me^{3+} + 3 \cdot \overline{(HA)_2} \xrightarrow{K_{eq22}} \overline{MeA_3(HA)_3} + 3\,H^+ \tag{22}$$

MeA$_3$(HA)$_2$ was also considered according to the Chen et al. study. They suggested this extracted species using P507 as extractant [21].

$$Me^{3+} + 2.5 \cdot \overline{(HA)_2} \xrightarrow{K_{eq23}} \overline{MeA_3(HA)_2} + 3\,H^+ \tag{23}$$
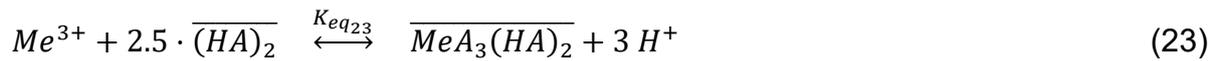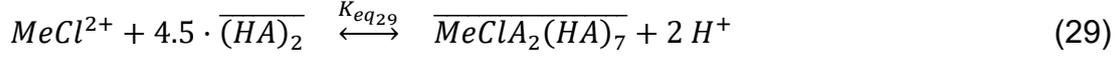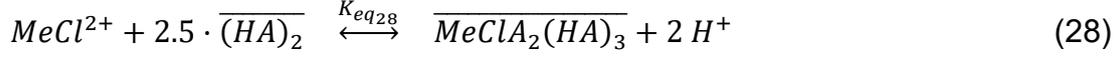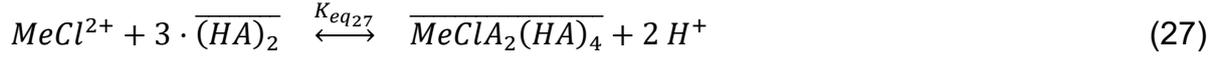
Taking into account that the most frequently observed coordination number for heavy and light rare earths (HREEs and LREEs, respectively) are within the range 6-9 and 7-12, respectively, the mechanism described in Eq. (24) was also considered [22].

$$Me^{3+} + 4.5 \cdot \overline{(HA)_2} \xrightarrow{K_{eq24}} \overline{MeA_3(HA)_6} + 3\,H^+ \tag{24}$$
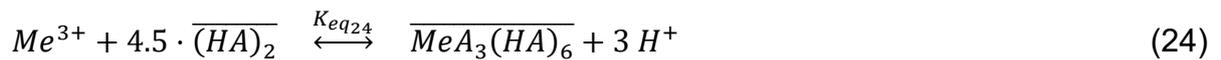
The same stoichiometries were tested when $MeCl^{2+}$ was the extracted species.

$$MeCl^{2+} + 3 \cdot \overline{HA} \xrightarrow{K_{eq25}} \overline{MeClA_2(HA)} + 2\,H^+ \tag{25}$$

$$MeCl^{2+} + 3 \cdot \overline{(HA)_2} \xrightarrow{K_{eq26}} \overline{MeCl(HA_2)_2(HA)_2} + 2\,H^+ \tag{26}$$

$$MeCl^{2+} + 3 \cdot \overline{(HA)_2} \xleftrightarrow{K_{eq27}} \overline{MeClA_2(HA)_4} + 2\,H^+ \tag{27}$$

$$MeCl^{2+} + 2.5 \cdot \overline{(HA)_2} \xleftrightarrow{K_{eq28}} \overline{MeClA_2(HA)_3} + 2\,H^+ \tag{28}$$

$$MeCl^{2+} + 4.5 \cdot \overline{(HA)_2} \xleftrightarrow{K_{eq29}} \overline{MeClA_2(HA)_7} + 2\,H^+ \tag{29}$$

The corresponding equilibrium extraction constants are listed below:

$$K_{eq20} = \frac{a_{\overline{MeA_3}} \cdot a_{H^+}{}^3}{a_{Me^{3+}} \cdot a_{\overline{HA}}{}^3} = \frac{[\overline{MeA_3}] \cdot [H^+]^3}{[Me^{3+}] \cdot [\overline{HA}]^3} \cdot \frac{\gamma_{\overline{MeA_3}} \cdot \gamma_{H^+}{}^3}{\gamma_{Me^{3+}} \cdot \gamma_{\overline{HA}}{}^3} \tag{30}$$

$$K_{eq21} = \frac{a_{\overline{Me(HA_2)_3}} \cdot a_{H^+}{}^3}{a_{Me^{3+}} \cdot a_{\overline{(HA)_2}}{}^3} = \frac{[\overline{Me(HA_2)_3}] \cdot [H^+]^3}{[Me^{3+}] \cdot [\overline{(HA)_2}]^3} \cdot \frac{\gamma_{\overline{Me(HA_2)_3}} \cdot \gamma_{H^+}{}^3}{\gamma_{Me^{3+}} \cdot \gamma_{\overline{(HA)_2}}{}^3} \tag{31}$$

$$K_{eq22} = \frac{a_{\overline{MeA_3(HA)_3}} \cdot a_{H^+}{}^3}{a_{Me^{3+}} \cdot a_{\overline{(HA)_2}}{}^3} = \frac{[\overline{MeA_3(HA)_3}] \cdot [H^+]^3}{[Me^{3+}] \cdot [\overline{(HA)_2}]^3} \cdot \frac{\gamma_{\overline{MeA_3(HA)_3}} \cdot \gamma_{H^+}{}^3}{\gamma_{Me^{3+}} \cdot \gamma_{\overline{(HA)_2}}{}^3} \tag{32}$$

$$K_{eq23} = \frac{a_{\overline{MeA_3(HA)_2}} \cdot a_{H^+}{}^3}{a_{Me^{3+}} \cdot a_{\overline{(HA)_2}}{}^{2.5}} = \frac{[\overline{MeA_3(HA)_2}] \cdot [H^+]^3}{[Me^{3+}] \cdot [\overline{(HA)_2}]^{2.5}} \cdot \frac{\gamma_{\overline{MeA_3(HA)_2}} \cdot \gamma_{H^+}{}^3}{\gamma_{Me^{3+}} \cdot \gamma_{\overline{(HA)_2}}{}^{2.5}} \tag{33}$$

$$K_{eq24} = \frac{a_{\overline{MeA_3(HA)_6}} \cdot a_{H^+}{}^3}{a_{Me^{3+}} \cdot a_{\overline{(HA)_2}}{}^{4.5}} = \frac{[\overline{MeA_3(HA)_6}] \cdot [H^+]^3}{[Me^{3+}] \cdot [\overline{(HA)_2}]^{4.5}} \cdot \frac{\gamma_{\overline{MeA_3(HA)_6}} \cdot \gamma_{H^+}{}^3}{\gamma_{Me^{3+}} \cdot \gamma_{\overline{(HA)_2}}{}^{4.5}} \tag{34}$$

$$K_{eq25} = \frac{a_{\overline{MeClA_2(HA)}} \cdot a_{H^+}{}^2}{a_{MeCl^{2+}} \cdot a_{\overline{HA}}{}^3} = \frac{[\overline{MeClA_2(HA)}] \cdot [H^+]^2}{[MeCl^{2+}] \cdot [\overline{HA}]^3} \cdot \frac{\gamma_{\overline{MeClA_2(HA)}} \cdot \gamma_{H^+}{}^2}{\gamma_{MeCl^{2+}} \cdot \gamma_{\overline{HA}}{}^3} \tag{35}$$

$$K_{eq26} = \frac{a_{\overline{MeCl(HA_2)_2(HA)_2}} \cdot a_{H^+}{}^2}{a_{MeCl^{2+}} \cdot a_{\overline{(HA)_2}}{}^3} = \frac{[\overline{MeCl(HA_2)_2(HA)_2}] \cdot [H^+]^2}{[MeCl^{2+}] \cdot [\overline{(HA)_2}]^3} \cdot \frac{\gamma_{\overline{MeCl(HA_2)_2(HA)_2}} \cdot \gamma_{H^+}{}^2}{\gamma_{MeCl^{2+}} \cdot \gamma_{\overline{(HA)_2}}{}^3}$$

$$\tag{36}$$

$$K_{eq27} = \frac{a_{\overline{MeClA_2(HA)_4}} \cdot a_{H^+}{}^2}{a_{MeCl^{2+}} \cdot a_{\overline{(HA)_2}}{}^3} = \frac{[\overline{MeClA_2(HA)_4}] \cdot [H^+]^2}{[MeCl^{2+}] \cdot [\overline{(HA)_2}]^3} \cdot \frac{\gamma_{\overline{MeClA_2(HA)_4}} \cdot \gamma_{H^+}{}^2}{\gamma_{MeCl^{2+}} \cdot \gamma_{\overline{(HA)_2}}{}^3} \tag{37}$$

$$K_{eq28} = \frac{a_{\overline{MeClA_2(HA)_3}} \cdot a_{H^+}{}^2}{a_{MeCl^{2+}} \cdot a_{\overline{(HA)_2}}{}^{2.5}} = \frac{[\overline{MeClA_2(HA)_3}] \cdot [H^+]^2}{[MeCl^{2+}] \cdot [\overline{(HA)_2}]^{2.5}} \cdot \frac{\gamma_{\overline{MeClA_2(HA)_3}} \cdot \gamma_{H^+}{}^2}{\gamma_{MeCl^{2+}} \cdot \gamma_{\overline{(HA)_2}}{}^{2.5}} \tag{38}$$

$$K_{eq29} = \frac{a_{\overline{MeClA_2(HA)_7}} \cdot a_{H^+}{}^2}{a_{MeCl^{2+}} \cdot a_{\overline{(HA)_2}}{}^{4.5}} = \frac{[\overline{MeClA_2(HA)_7}] \cdot [H^+]^2}{[MeCl^{2+}] \cdot [\overline{(HA)_2}]^{4.5}} \cdot \frac{\gamma_{\overline{MeClA_2(HA)_7}} \cdot \gamma_{H^+}{}^2}{\gamma_{MeCl^{2+}} \cdot \gamma_{\overline{(HA)_2}}{}^{4.5}} \tag{39}$$

Mass balance for individual metals

In order to complete the model, the mass balances for each metal (Ce/Eu/Y), chlorides, protons and D2EHPA are required. Since the equal volumes of the aqueous and organic phases have been used in all the experiments and according to the mass balance law, the total concentration of each reagent in the extraction system can be described by the sum of the concentration of species being in both phases in the equilibrium.

Mass balance of cerium, europium and yttrium related to Eqs. (14)-(19):

$$[Me^{3+}]_0 = [Me^{3+}] + [MeCl^{2+}] + [MeCl_2^+] + [MeCl_3] + [MeCl_4^-] + \overline{[Me]} \quad (40)$$

Mass balance of chloride ions depending on the Eqs. (14)-(16) or Eqs. (17)-(19), respectively:

$$[Cl^-]_0 = [Cl^-] + [MeCl^{2+}] + 2 \cdot [MeCl_2^+] + 3 \cdot [MeCl_3] + 4 \cdot [MeCl_4^-] \quad (41)$$

$$[Cl^-]_0 = [Cl^-] + [MeCl^{2+}] + 2 \cdot [MeCl_2^+] + 3 \cdot [MeCl_3] + 4 \cdot [MeCl_4^-] + \overline{[Me]}$$

$$(42)$$

Mass balance of protons depending on the Eqs. (14), Eq. (15), Eqs. (16) and (17), Eq. (18), respectively:

$$[H^+]_0 + \left[\overline{HA}\right]_0 = [H^+] + \left[\overline{HA}\right] + n \cdot \overline{[Me]} \quad (43)$$

$$[H^+]_0 + 2 \cdot \left[\overline{(HA)_2}\right]_0 = [H^+] + 2 \cdot \left[\overline{(HA)_2}\right] + (3+n) \cdot \overline{[Me]} \quad (44)$$

$$[H^+]_0 + 2 \cdot \left[\overline{(HA)_2}\right]_0 = [H^+] + 2 \cdot \left[\overline{(HA)_2}\right] + n \cdot \overline{[Me]} \quad (45)$$

$$[H^+]_0 + 2 \cdot \left[\overline{(HA)_2}\right]_0 = [H^+] + 2 \cdot \left[\overline{(HA)_2}\right] + (2+n) \cdot \overline{[Me]} \quad (46)$$

Mass balance of D2EHPA depending on the Eqs. (14)-(19):

$$[\overline{HA}]_0 = [\overline{HA}] + (3 + n) \cdot [\overline{Me}] \tag{47}$$

$$[\overline{(HA)_2}]_0 = [\overline{(HA)_2}] + \left(3 + \frac{n}{2}\right) \cdot [\overline{Me}] \tag{48}$$

$$[\overline{(HA)_2}]_0 = [\overline{(HA)_2}] + \left(\frac{3+n}{2}\right) \cdot [\overline{Me}] \tag{49}$$

$$[\overline{HA}]_0 = [\overline{HA}] + (2 + n) \cdot [\overline{Me}] \tag{50}$$

$$[\overline{(HA)_2}]_0 = [\overline{(HA)_2}] + \left(2 + \frac{n}{2}\right) \cdot [\overline{Me}] \tag{51}$$

$$[\overline{(HA)_2}]_0 = [\overline{(HA)_2}] + \left(1 + \frac{n}{2}\right) \cdot [\overline{Me}] \tag{52}$$

where the $[Me^{3+}]$, $[Cl^-]$, $[H^+]$ and $\overline{(HA)_n}$ represent the concentration of the free reagent in the system and the values of m and n depend on the stoichiometry of the equilibria reaction considered.

Separation prediction

According to the Ce/Eu/Y separation aim, the model that better fitted the extraction of the single metals was applied to a mixture containing these three REEs at different aqueous conditions. The mass balances depicted previously needed to be modified to include all the species.

Model solving

To obtain the optimized values of the aqueous equilibria and extraction constants, the mathematic model defined in the previous equations was used. The purpose is to find the parameter values of the constants (K_{eq}, K_1, K_2, K_3 and K_4) that fit the calculated

with the experimental data minimizing the error. To carry it out, the *Matlab R2017b* software was used.

Fig. 1 shows the applied algorithm for the resolution of the model in which *fmincon* and *fsolve* Matlab functions were used to minimize the constrained nonlinear multivariable function and to solve the system of nonlinear equations, respectively.
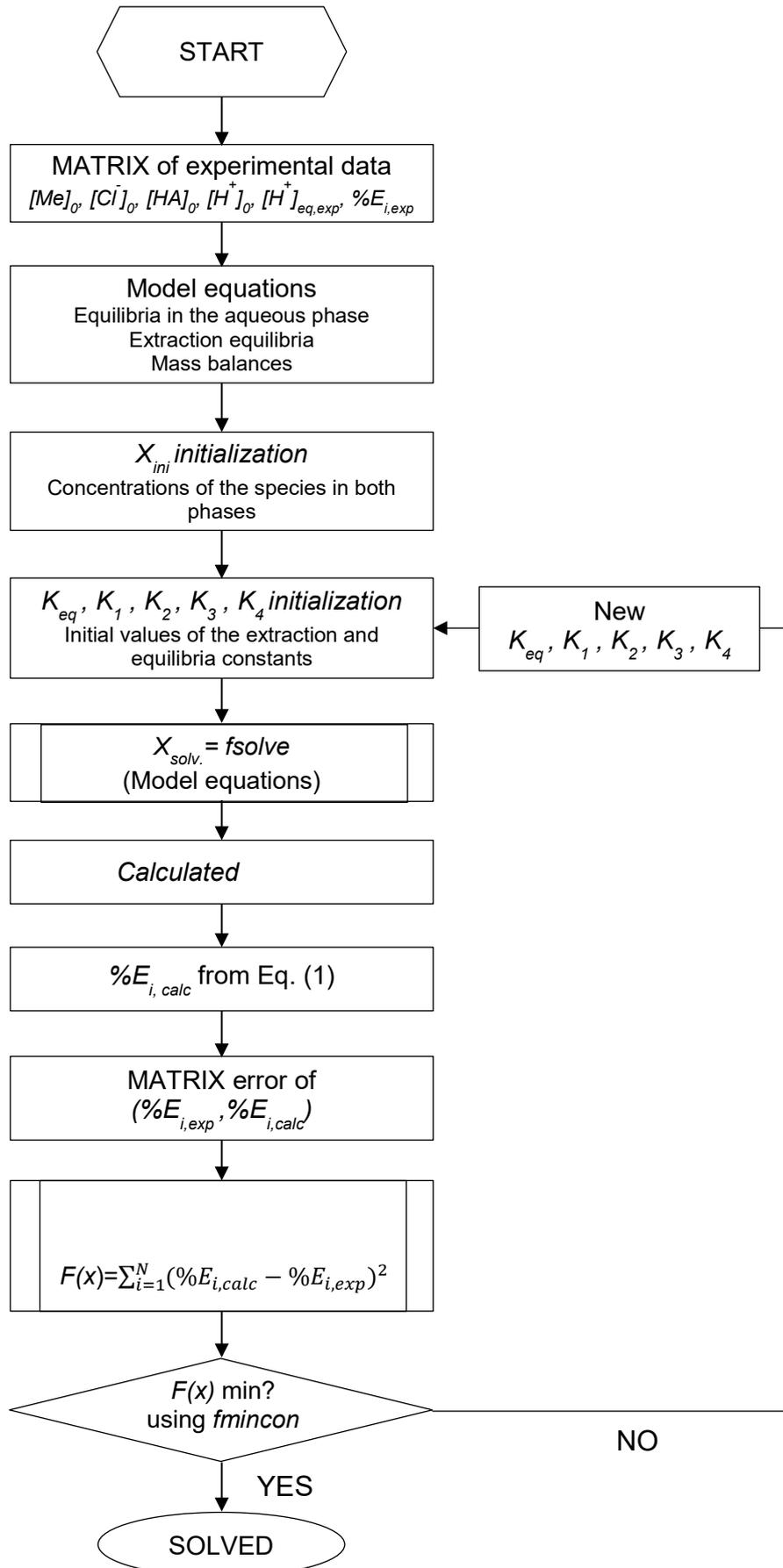
Fig. 1. Flow-sheet of the resolution algorithm of REEs solvent extraction.

The resolution of the system starts introducing the experimental data (96 experiments) in the form of a matrix, whose rows are the initial conditions of the aqueous (Me_0, Cl^-_0, pH_0) and organic solutions (HA_0) and the experimental extraction percentages obtained ($\%E_{i,exp}$ and pH_{eq}). Three different matrices were utilized separately due to the three different metals studied, cerium, europium and yttrium.

Then, the equilibria equations for both phases and the mass balances were introduced. The initial guesses for all the species concentrations were introduced using the X_{ini} vector and the initialization values of the formation constants were the found in the literature (Table 1).

Table 1. Related constants in the literature.

	Ce(III)		Eu(III)				Y(III)	
	K_1	K_2	K_1	K_2	K_3	K_4	K_1	K_2
a [23]	2.04	1.00	1.91	0.47	0.21		0.50	-
b [24]			0.01	0.38				
c [6]			2.06	0.97	0.40	0.17		

The nonlinear system of equations was solved using the *fsolve* function. When the concentration of Ce(III), Eu(III) and Y(III) in the organic phase were computed, the calculated percentage of metal extraction, using the Eq. (1), was obtained. The calculated equilibrium proton concentrations were also obtained to compare these values to the experimental data.

To evaluate the difference between the calculated and experimental extraction percentages for every experimental data, the objective function F(x) was defined as the sum of the quadratic differences between these extraction percentages as can be seen in Eq. (53):

$$F(x) = \sum_{i=1}^{N}(\%E_{i,calc} - \%E_{i,exp})^2 \tag{53}$$

where $\%E_{i,calc}$ is the percentage of extraction calculated by the model, $\%E_{i,exp}$ is the percentage of the extraction determined experimentally and N is the number of experimental points. This function was undergoing to minimization using the *fmincon* subroutine. In order to choose the best REEs extraction mechanism, the standard deviation value (σ) was evaluated following the Eq. (54):

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N}(\%E_{i,calc} - \%E_{i,exp})^2}{N-1}} \tag{54}$$

RESULTS

The extraction of cerium, europium and yttrium were individually simulated following the different models depicted in *Equilibria equations* section. Table 2 shows the optimized stability and the extraction equilibria constants and the standard deviation values calculated for the tested models.

Table 2. Optimization parameters.

	Ce						Eu						Y					
	K_{eq}	K_1	K_2	K_3	K_4	σ	K_{eq}	K_1	K_2	K_3	K_4	σ	$K_{eq}\cdot10^3$	K_1	K_2	K_3	K_4	σ
Eq. 20	2.6	0.73	0.02	0.80	0.64	**1.60**	117	1.86	$3\cdot10^{-6}$	0.01	$2\cdot10^{-3}$	**3.97**	3.1	0.25	0.04	$2\cdot10^{-6}$	0.07	**4.11**
Eq. 21	20	0.69	0.09	0.19	0.86	**1.51**	1083	1.56	$4\cdot10^{-5}$	0.08	0.17	**4.96**	33	0.27	0.02	$2\cdot10^{-3}$	0.02	**4.93**
Eq. 22	20	0.69	0.09	0.19	0.86	**1.51**	1083	1.56	$4\cdot10^{-5}$	0.08	0.17	**4.96**	33	0.27	0.02	$2\cdot10^{-3}$	0.02	**4.93**
Eq. 23	6.8	0.28	0.32	$4\cdot10^{-4}$	$2\cdot10^{-6}$	**1.43**	354	1.50	0.12	$6\cdot10^{-5}$	$5\cdot10^{-3}$	**5.94**	8	0.18	0.15	$1\cdot10^{-3}$	$1\cdot10^{-5}$	**6.61**
Eq. 24	250	1.55	0.07	0.12	$9\cdot10^{-6}$	**2.87**	28948	2.48	0.03	0.04	$6\cdot10^{-4}$	**7.31**	850	0.50	0.02	7.43	0.63	**18.79**
Eq. 25	8.6	0.29	0.18	0.15	$2\cdot10^{-3}$	**7.91**	166	0.87	0.41	0.04	0.02	**13.38**	6	0.50	0.02	2.77	$4\cdot10^{-5}$	**18.67**
Eq. 26	19	0.63	0.12	0.23	$5\cdot10^{-3}$	**1.68**	812	1.27	0.05	0.09	0.02	**5.96**	390	10	$1\cdot10^{-3}$	0.02	$7\cdot10^{-4}$	**14.32**
Eq. 27	19	0.63	0.12	0.23	$5\cdot10^{-3}$	**1.68**	812	1.27	0.05	0.09	0.02	**5.96**	390	10	$1\cdot10^{-3}$	0.02	$7\cdot10^{-4}$	**14.32**
Eq. 28	6.9	0.31	0.19	0.10	0.02	**1.38**	272	1.02	0.08	0.13	0.04	**5.58**	5	0.08	0.03	0.63	0.04	**11.70**
Eq. 29	250	1.36	0.16	1.90	0.01	**2.22**	6804	0.08	0.93	$2\cdot10^{-3}$	0.05	**11.15**	638	0.04	0.02	0.09	0.01	**15.66**

As can been seen in Table 2, there are two pairs of proposed models, Eqs. (21)-(22) and Eqs. (26)-(27) with the same optimization parameters values and standard

deviations. The model equations are identical since the only difference between both models is the molecular structure of the formed species. While for the model depicted in Eq. (21), the formed species contains only anionic ligands, the model in Eq. (22) has two different ligands (anionic and neutral). Furthermore, the coordination numbers are 3 and 6, respectively. Although the models described in Eqs. (26) and (27) contain anionic and neutral ligands in the formed species, the former has HA_2^- and the second one contains A^- as anionic ligands and both of them have the same HA specie as a neutral ligand. Also, their respective coordination numbers are 4 and 6. As a result, using the algorithm proposed in this investigation, it cannot be assured in what way the metal ion and the D2EHPA$_2$ are bound in the extracted species.

Due to the low Ce(III) extraction percentages, only the percentages of extraction of the Y(III) and the Eu(III) have been taken into account for the choice of the best-fitted model to the experimental data. It corresponds to the reactions described in Eqs. (20), (21) and (22) because in these three proposed models, the lowest individual standard deviations were obtained. This means that three molecules of extractant are involved in the Me^{3+} solvent extraction of one molecule of the REEs. However, in the Eq. (20) the D2EHPA extractant is considered as a monomer while in Eqs. (21)-(22) it is as dimeric form.

Fig. 2 shows the effect of the different parameters studied on the REEs extraction for these three models. Furthermore, the loaded metals in all the experiments depicted in Figs. 2.a, 2.b and 2.c were completely stripped using 6 mol/L of HCl.
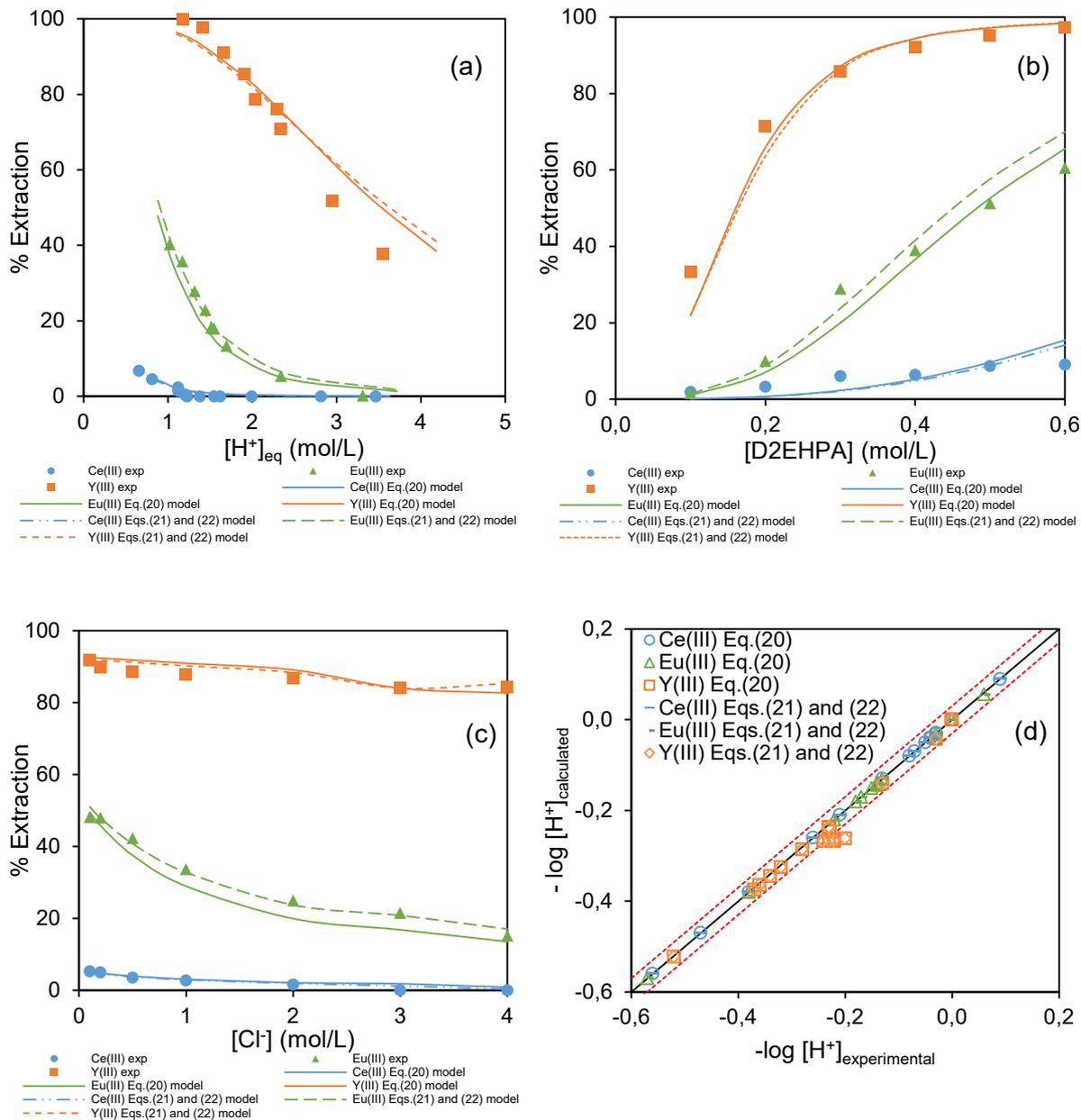
Fig. 2. (a) Effect of proton equilibrium concentration in 2 mol/L Cl⁻ using 0.30 mol/L of D2EHPA. (b) Effect of D2EHPA concentration in 2 mol/L Cl⁻. in an acidic medium ($[H^+]$ = 1.75 mol/L) (c) Effect of the concentration of chloride ions in an acidic medium ($[H^+]$ = 1.75 mol/L) using 0.30 mol/L of D2EHPA. (d) Plot of $pH_{calculated}$ vs. $pH_{experimental}$ for the Ce(III), Eu(III) and Y(III) experiments individually with an error ±5%.

As was expected, the extraction process using D2EHPA is negatively influenced by the proton concentration according to the extraction mechanism using cationic

extractants [10,25]. Accordingly, the REE individual extraction percentages decrease when the proton concentration increases. The effect of the extractant concentration in REEs extraction is depicted in Fig. 2.b. When the D2EHPA concentration increases, the individual extraction percentages of Ce/Eu/Y increase. However, the rise in the extracted Ce(III) was less than for the Eu(III) and Y(III) due to the atomic number, which can be explained by considering the ionic radii and charge densities of these metals. The ionic radii of HREEs are smaller than that of LREEs because of the lanthanide contraction. Hence, the Y(III) charge density is higher than that of Eu(III) and Ce(III) [26–28]. In Fig. 2.c the effect of chloride concentration on the REE extraction is shown. There is an inversely proportional relationship between the REEs extraction percentage and the Cl^- concentration. Since the hypothesis that the Me^{3+} is the extracted species for the three proposed models, the more $MeCl^{2+}$, $MeCl_2^+$, $MeCl_3$ and $MeCl_4^-$ species are produced (Eq. (3)), the less Me^{3+} species is available and therefore, the extraction decreases. Cerium was the most influenced metal by this effect compared to the other two REEs because of the highest cumulative formation constants (β_n) values for the chloride complexes formation. The plot of $pH_{calculated}$ vs. $pH_{experimental}$ (Fig. 2.d) allow us seing that the experimental pHs match with the pHs calculated using the models proposed in Eqs. (20), (21) and (22).

To determine if these models for the single REE extraction are also useful to reproduce their competitive extraction, the models depicted in Eqs. (20), (21) and (22) were tested for a mixture of these three metals (Ce/Eu/Y). The modified mass balances, where i represent the different REE (Ce, Eu and Y), can be written for these models as follows in Eqs. (55)-(60):

Me(III) mass balance:

$$[Me^{3+}]_{i,0} = [Me^{3+}]_i + [MeCl^{2+}]_i + [MeCl_2^+]_i + [MeCl_3]_i + [MeCl_4^-]_i + \overline{[Me]}_i$$

$$i = 1,2,3 \tag{55}$$

Chloride mass balance:

$$[Cl^-]_0 = [Cl^-] + \sum_{i=1}^{3}[MeCl^{2+}]_i + 2 \cdot \sum_{i=1}^{3}[MeCl_2^+]_i + 3 \cdot \sum_{i=1}^{3}[MeCl_3]_i + 4 \cdot \sum_{i=1}^{3}[MeCl_4^-]_i$$

$$\tag{56}$$

Proton mass balance depending on Eq. (20) and Eqs. (21)-(22), respectively:

$$[H^+]_0 + \overline{[(HA)]}_0 = [H^+] + \overline{[(HA)]} \tag{57}$$

$$[H^+]_0 + 2 \cdot \overline{[(HA)_2]}_0 = [H^+] + 2 \cdot \overline{[(HA)_2]} + 3 \cdot \sum_{i=1}^{3}\overline{[Me]}_i$$

$$\tag{58}$$

D2EHPA mass balance depending on Eq. (20) and Eqs. (21)-(22), respectively:

$$\overline{[(HA)]}_0 = \overline{[(HA)]} + 3 \cdot \sum_{i=1}^{3}\overline{[Me]}_i$$

$$\tag{59}$$

$$\overline{[(HA)_2]}_0 = \overline{[(HA)_2]} + 3 \cdot \sum_{i=1}^{3}\overline{[Me]}_i$$

$$\tag{60}$$

The extraction yield results of Ce/Eu/Y for the mixture are presented in Fig. 3. The aqueous phase containing 1 g/L for each REE in 2 mol/L Cl⁻ medium were used in this part of the study to investigate the effect of the same parameters (D2EHPA concentration, initial proton concentration and Cl⁻ concentration). The loaded metals were also completely stripped using 6 mol/L of HCl.
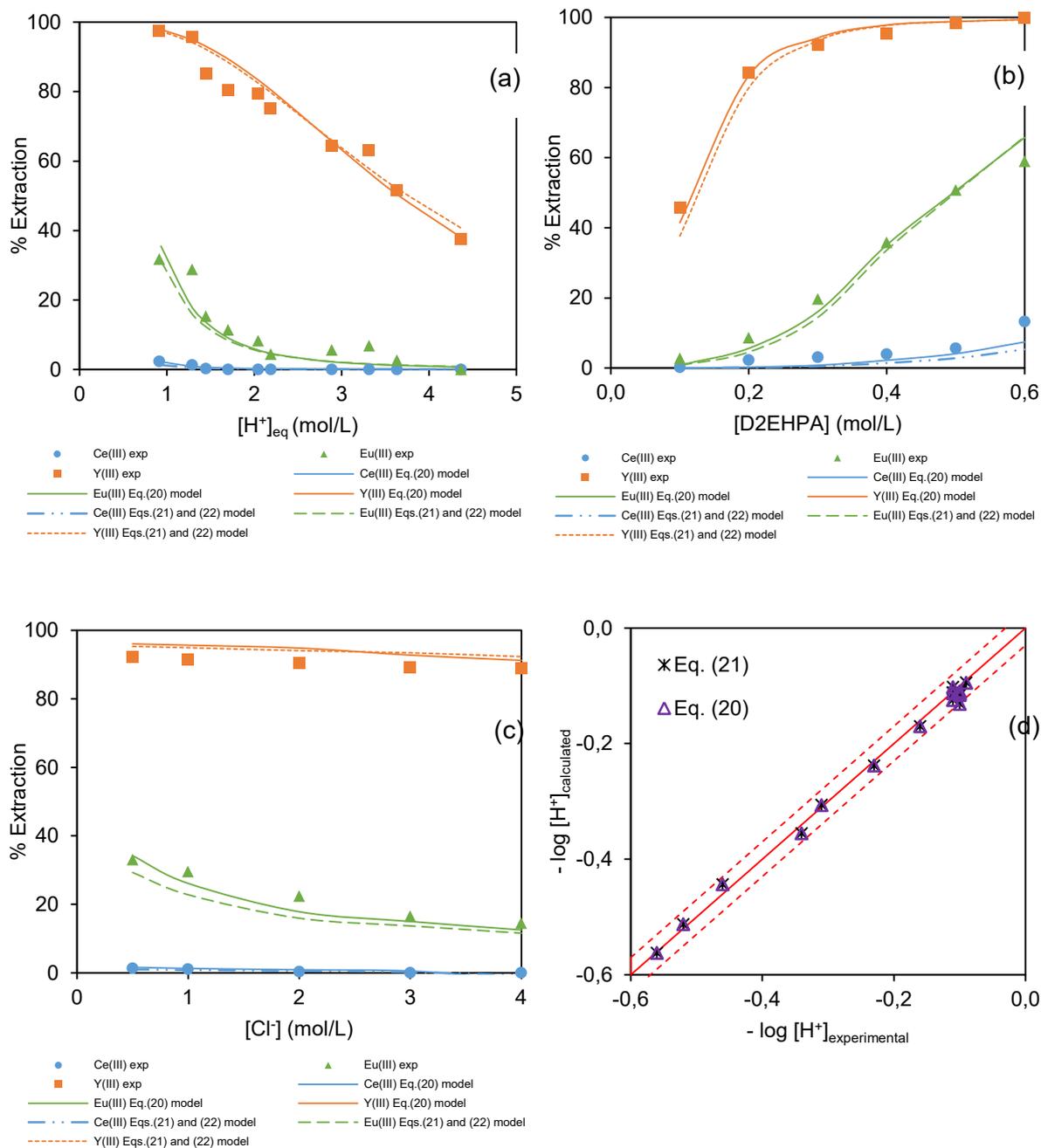
Fig. 3. (a) Effect of proton equilibrium concentration in 2 mol/L Cl⁻ using 0.30 mol/L of D2EHPA in an acidic medium ([H⁺] = 1.25 mol/L). (b) Effect of D2EHPA concentration in 2 mol/L Cl⁻. (c) Effect of the concentration of chloride ions in an acidic medium ([H⁺] = 1.25 mol/L) using 0.30 mol/L of D2EHPA. (d) Plot of pH$_{calculated}$ vs. pH$_{experimental}$ for the Ce/Eu/Y experiments in the mixture with an error ±5%.

As is shown in Fig. 3, all of these three models are able to predict the competitive extraction of Ce/Eu/Y. The standard deviation for the models depicted in Eq. (20) and Eqs. (21)-(22) was 5.8 and 6.7, respectively and it means that the model accuracies are similar in the whole range of the three studied parameters. Since numerous studies in the literature suggested that the cationic extractants like D2EHPA are considered in dimeric form [9,11,29] and its high dimerization constant value ($4 \cdot 10^4$) [30,31], the models described in Eqs. (21)-(22) seem to be the more suitable ones, due to the monomeric consideration of the extractant in the Eq. (20).

According to the most frequently used coordination numbers for REEs [32] and recent publications [6,9,33], the model in Eq. (22) is the one chosen to describe the extraction mechanism for Ce(III), Eu(III) and Y(III) using D2EHPA as extractant. Although the formation constants values found in the literature were used to initialize the program, they were not able to match the experimental extraction results for the REEs.

This investigation also allows foreseeing the optimal conditions to selectively separate Y(III) from the mixture (Ce/Eu/Y). The results are coincident with the Swain and Otu and Wu et al. ones who suggested that the extraction order is heavy rare earths and then, light rare earths [11,34]. The proposed model provides the optimal conditions for the Y(III) separation: high Cl⁻ and proton concentrations and 0.1 mol/L of D2EHPA as can be inferred from Fig. 3.

CONCLUSIONS

The extraction of Ce(III), Eu(III) and Y(III) in chloride media using D2EHPA diluted in kerosene has been investigated. Different extraction models were proposed evaluating which one can predict the Ce/Eu/Y extraction behaviour depending on the proton, chloride and extractant concentrations. The models were derived from the

mass balances and equilibria equations involved in the proposed extraction processes.

The selected extraction mechanism for Ce/Eu/Y mixture was:

$$Me^{3+} + 3 \cdot \overline{(HA)_2} \overset{K_{C_1}}{\longleftrightarrow} \overline{MeA_3(HA)_3} + 3\,H^+$$
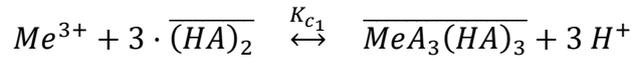
The obtained stepwise stability formation constants for the Ce-Cl, Eu-Cl and Y-Cl species formed in the aqueous phase in equilibrium were $K_{1_{Ce}} = 0.69$, $K_{2_{Ce}} = 0.09$, $K_{3_{Ce}} = 0.19$, $K_{4_{Ce}} = 0.86$, $K_{1_{Eu}} = 1.56$, $K_{2_{Eu}} = 4 \cdot 10^{-5}$, $K_{3_{Eu}} = 0.08$, $K_{4_{Eu}} = 1.17$, $K_{1_Y} = 0.27$ $K_{2_Y} = 0.02$, $K_{3_Y} = 2 \cdot 10^{-3}$, $K_{4_Y} = 0.02$, respectively. The metal extraction equilibrium constant values were calculated as $K_{eq,Ce} = 20$, $K_{eq,Eu} = 1083$, $K_{eq,Y} = 33000$.

The competitive extraction study suggested that yttrium could be separated from the Ce/Eu/Y mixture using D2EHPA as the extractant and a chloride concentration in the aqueous phase higher than 4 mol/L maintaining the proton concentration above of 3 mol/L. The equilibrium determined parameters will be used in the future research to verify the yttrium separation possibility from the mixture using supported liquid membranes.

Acknowledgements

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