The use of Rare Earth Elements (REEs) is continuously growing since they are essential for the development of a wide variety of new technologies such as the manufacture of hybrid cars, wind turbines, mobile phones and televisions, disc drives, and defence technologies (Xie et al., 2014). Although the term “rare” is inappropriate taking into account that they are relatively abundant in the Earth’s crust, the critical status of REEs is related to their heterogeneous geological location, meaning that they cannot be found all over the earth but just in specific areas, their low concentration in the ores, which make them hard to be mined, and the environmental issues related to their mining due to the high volume of concentrated acids needed to lixiviate them from the ores and the large amount of secondary waste generated after the process (European Commission, 2014).

Investigations into the recovery of REEs from aqueous solutions using ionic liquids have been carried out over time (Baba et al., 2011; Radhika et al., 2010; Sun et al., 2011; Zhu et al., 2012). Ionic liquids (ILs) are attracting the scientific community’s interest lately as a result of growing safety and environmental concerns over the use of volatile solvents and due to their special features they have been part of numerous research studies. They have been applied as solvents in organic synthesis (Vekariya, 2017), lubricants and fuel additives (Hernández Battez et al., 2016; Li and Ren, 2017), catalysts and electro catalysts (Megias-Sayago et al., 2016; Zhang and Etzold, 2016), as electrolytes (Simonetti et al., 2017), heat storage (Mehrkesh and Karunanithi, 2016), solid support and chemical separation (Grunauer et al., 2016), nanoparticle formation (Zhang et al., 2016) and metal extraction (Aba et al., 2011).

The present manuscript describes a study on the solvent extraction of Neodymium, Terbium and Dysprosium, which are essential metals in green energy applications and in turn, some of the most critical REEs according to the
US Energy Department reviews (U.S. Department of Energy, 2011). The metals were extracted from chloride media using AliOle, an ionic liquid prepared from Aliquat 336 and Oleic Acid, dissolved in kerosene. AliOle IL was shown to be promising for the extraction of REEs from aqueous solutions.

This paper develops a mathematical model of single Nd(III), Tb(III) and Dy(III) solvent extraction. Matlab R2016a software was used to solve the equilibria equations and mass balances involved to determine the equilibria constants. Several equilibria equations were tested to find out the most suitable model. The proposed extraction model has proven to fit perfectly single metal extraction data and to faithfully predict the simultaneous extraction of neodymium, terbium and dysprosium mixed in the aqueous phase. The validity of the approached equilibria constants was confirmed by comparing the plotted experimental and calculated data.

Similar extraction models can be applied in the future to predict the extraction extension of other REEs with AliOle and establish this information as a background for the metals transport in an SLM system. It could be also helpful to predict the potential separation factor between two rare earth elements at different experimental conditions.

### 2.2 Experimental procedure

#### 2.1.2.1 Reagents

Neodymium(III), terbium(III) and dysprosium(III) chloride solutions were prepared dissolving 99.9% purity Nd₂O₃, Tb₂O₃ and Dy₂O₃ (Sigma Aldrich; Ref. 228656, 590509 and 289264, respectively) by an acid attack with the minimal amount of HCl. NaCl was added when needed up to the required chloride concentration. The initial pH of the solutions was adjusted to 3.5 with NaOH.

As an organic phase, the synthesized IL AliOle, prepared by reacting equimolar amounts of Methyl-tri(octyl/decyl)ammonium Chloride (Aliquat 336) and Oleic Acid following the procedure established in previous studies was used (Coll et al., 2014; Fortuny et al., 2012). Kerosene was used as a diluent.

#### 2.1.2.2 Procedure

Metal extraction experiments were carried out in separatory funnels in which equal volumes of aqueous and organic phases (10 mL) were shaken with an MVH-40 SBS horizontal mechanical shaker (150 rpm) at room temperature (21 ± 2 °C) for 15 minutes. After separation of phases, the aqueous phase was collected and the pH was measured. Then Nd(III), Tb(III) and Dy(III) concentrations in the aqueous phase were determined by Microwave Plasma Atomic Emission Spectroscopy with an MP-AES 4100 spectrophotometer (Agilent Technologies).

The organic phase was kept for stripping experiments. Hydrochloric acid 1 mol-L⁻¹ was used to strip the REEs from the organic phase by three contacts.

Extraction experiments were performed using AliOle dissolved in kerosene from 0.005 to 0.1 mol-L⁻¹ as organic phase and aqueous solutions containing 1000 mg/L of Nd(III), Tb(III) and Dy(III).

The effect of the AliOle concentration, the chloride concentration on the aqueous phase and the competitive extraction of the metals were studied.

### 3.3 Mathematical modelling

The mathematical model proposed was developed taking into account the equilibria equations involved in the REEs extraction process with AliOle. Model equations of solvent extraction of Nd(III), Tb(III) and Dy(III) individually incorporate the equilibria and the mass balance equations. Different equilibria (speciation and extraction) were considered regarding the speciation of the metals in chloride medium in order to figure out the most suitable extraction model.

#### 3.1.3.1 Equilibria equations

The extraction mechanism of Nd(III) was superficially investigated in a previous research (Obón et al., 2017). The neodymium extraction with AliOle was found to be in the form NdClₓ⁺ when the chloride concentration in the solution was above 2 mol-L⁻¹, which resembles the chloride concentration usually found in the leachates from end-of-life products (Tunsu et al., 2014). That study was drawn from the premise that there was just a single metal species in the aqueous phase. However, in the current report, the metal speciation is taken into account as several chloride complexes can be formed according to the formula MeClₓ⁻ⁿ, where Me can be Nd(III), Tb(III) or Dy(III) and n = 1, 2 or 3 depending on the number of chlorides bonded with the metal ion. Therefore, the REEs distribution in the aqueous phase can be described as follows:

\[
\text{Me}^{3+} + n\text{Cl}^- \rightarrow \text{MeCl}_n^{3-n}
\]

(R.1)

\[
\text{MeCl}_n^{3-n} + \text{Cl}^- \rightarrow \text{MeCl}_{n+1}^{3-(n+1)}
\]

(R.2)
\[
\text{MeCl}_3^{-} + \text{Cl}^{-} \rightleftharpoons K_1 \text{MeCl}_4^2-
\]

where Me can be Nd(III), Tb(III) or Dy(III) and \(K_1, K_2\) and \(K_3\) represent the stepwise stability constants.

The equilibria expressions of the complex formation constants expressed as a function of the activities of the species (\(a_i\)) are listed below:

\[K_1 = \frac{a_{\text{MeCl}_4^2-}}{a_{\text{MeCl}_3^-}a_{\text{Cl}^-}} = \frac{[\text{MeCl}_4^2-]}{[\text{MeCl}_3^-][\text{Cl}^-]} \frac{\gamma_{\text{MeCl}_4^2-}}{\gamma_{\text{MeCl}_3^-}\gamma_{\text{Cl}^-}}\]  

\[K_2 = \frac{a_{\text{MeCl}_5^3-}}{a_{\text{MeCl}_4^2-}a_{\text{Cl}^-}} = \frac{[\text{MeCl}_5^3-]}{[\text{MeCl}_4^2-][\text{Cl}^-]} \frac{\gamma_{\text{MeCl}_5^3-}}{\gamma_{\text{MeCl}_4^2-}\gamma_{\text{Cl}^-}}\]  

\[K_3 = \frac{a_{\text{MeCl}_6^4-}}{a_{\text{MeCl}_5^3-}a_{\text{Cl}^-}} = \frac{[\text{MeCl}_6^4-]}{[\text{MeCl}_5^3-][\text{Cl}^-]} \frac{\gamma_{\text{MeCl}_6^4-}}{\gamma_{\text{MeCl}_5^3-}\gamma_{\text{Cl}^-}}\]

Here \(\gamma_i\) represents the activity coefficient of the species \(i\) and the stepwise formation constants can be converted easily into their cumulative form taking into account that they are described as the product of the simple ones: \(\beta_1 = K_1; \beta_2 = K_1 \cdot K_2; \beta_3 = K_1 \cdot K_2 \cdot K_3\).

The ionic strength of the metals was calculated from the equation:

\[I_a = 0.5 \sum z_i^2 c_i\]

where \(c_i\) is the concentration and \(z_i\) is the charge of the species \(i\).

The Davies equation was used to calculate the activity coefficients of the species in the aqueous phase when \(I_a = 0\):

\[\log_{10} \gamma_i = -0.5102 \cdot \left( \frac{\sqrt{I_a}}{(1 + \sqrt{I_a})} - 0.3 \cdot I_a \right)\]

According to the speciation described, several extraction mechanisms of REEs from chloride medium were considered. A distinction was made between extraction of REEs by ionic exchange (Rout and Binnemans, 2015) and by solvation (Aba et al., 2011; Rout et al., 2013; Vander Hoogerstraete et al., 2013; Kubota et al., 2011), since both mechanisms have been depicted in the literature. The proposed equilibria equations assume that there can be just one Me-organic species in the organic phase, meaning that extraction of several metal species simultaneously does not occur. The model takes also into account the competitive extraction of HCl. As a result, the extraction reactions that could take place in this separation system of a single metal with the AliOle IL are listed below:

\[
\begin{align*}
3 \text{R}_n^+\text{A}^- + \text{Me}^{3+} + 3 \text{Cl}^- & \rightleftharpoons 3 \text{R}_n^+\text{Cl}^- + \text{MeA}_3 \\
2 \text{R}_n^+\text{A}^- + \text{MeCl}^{2+} + 2 \text{Cl}^- & \rightleftharpoons 2 \text{R}_n^+\text{Cl}^- + \text{MeClA}_2 \\
2 \text{R}_n^+\text{A}^- + \text{MeCl}^{2+} + 2 \text{Cl}^- & \rightleftharpoons 2 \text{R}_n^+\text{Cl}^- + \text{MeClA}_2
\end{align*}
\]
With the corresponding equilibria equations written as follows:
The bar above the species denotes that they are in the organic phase.

In the equilibria equations, the activity coefficients ($\gamma$) of the organic and the aqueous neutral species are considered equal to 1.

### 3.2 Mass balances

The mass balances are based on the stoichiometry of the equilibria equations. Taking into account the equal volumes of the aqueous and the organic phases, the total concentration of the reagents involved in the reaction can be calculated as the sum of the species present in the system. Generalized mass balances for the equilibria of single extraction reactions (R.4–R.13) can be written as follows:

**REEs mass balance**

\[
[M_{\text{tot}}] = [M^{3+}] + [\text{MeCl}^{+}] + [\text{MeCl}_2^{+}] + [\text{MeCl}_3] + [\text{Me}]_{\text{org}}
\]  

**Chloride mass balance**

\[
[C^{-}]_{\text{aq}} = [\text{MeCl}^{+}] + 2 [\text{MeCl}_2^{+}] + 3 [\text{MeCl}_3] + 3 [\text{Me}]_{\text{org}} + \Lambda [H^+]
\]  

**AliOle mass balance**

\[
\left[\text{E}^{-}\right]_{\text{tot}} = \left[\text{E}^{-}\right]_{\text{org}} + m [\text{E}]_{\text{org}} + \Lambda [H^+]
\]

where the subscript t means the total concentration of the species, which in turn is the initial concentration, org represents the concentration of the species in the organic phase, $E^{-}_{\text{tot}}$ is the extractant concentration available after HCl and metal extraction, $\Lambda[H^+]$ is equal to the concentration of HCl in the organic phase and m can be 1, 2 or 3 depending on the stoichiometry of the equilibria reaction considered.

### 3.3 Competitive extraction prediction

The models that better fitted the extraction extension of each REE individually as well as the optimized extraction and formation constants calculated in each case were used to forecast the behaviour of the multicomponent extraction process.

In this regard, the mass balances of chloride (Eq. (18)) and AliOle (Eq. (19)) needed to be modified to embrace all the metallic species involved in the extraction system. The modified mass balances can be defined as follows:

**Nd(III) mass balance**

\[
[Nd_{\text{tot}}] = [Nd^{3+}] + [NdCl^{+}] + [NdCl_2^{+}] + [NdCl_3] + [Nd]_{\text{org}}
\]  

**Tb(III) mass balance**

\[
[Tb_{\text{tot}}] = [Tb^{3+}] + [TbCl^{+}] + [TbCl_2^{+}] + [TbCl_3] + [Tb]_{\text{org}}
\]  

**Dy(III) mass balance**

\[
[Dy_{\text{tot}}] = [Dy^{3+}] + [DyCl^{+}] + [DyCl_2^{+}] + [DyCl_3] + [Dy]_{\text{org}}
\]  

**Chloride mass balance**
\[
[\text{Cl}^-] = [\text{NdCl}_2^+] + 2\cdot[\text{TbCl}_2^+] + 3\cdot[\text{DyCl}_3^+] + 2\cdot[\text{NdCl}_3] + 3\cdot[\text{TbCl}_3] + 3\cdot[\text{DyCl}_4^+] + 2\cdot[\text{TbCl}_4^+] + 3\cdot[\text{DyCl}_5^+] + 3\cdot[\text{Dy}]_\text{org} + \Delta [\text{H}^+] 
\]

AliOle mass balance
\[
[E]_{\text{org}} = [E]_{\text{aq}} + m\cdot[\text{Nd}]_{\text{org}} + n\cdot[\text{Tb}]_{\text{org}} + p\cdot[\text{Dy}]_{\text{org}} + \Delta [\text{H}^+] \tag{24}
\]

where \( n \) and \( p \) can be 1, 2 or 3 depending on the stoichiometry of the equilibria reaction considered.

For the competitive extraction prediction Eq. (23) is used instead of Eq. (18) and Eq. (24) is used instead of Eq. (19).

### 4.4 Model resolution

The calculations of the modelling of REEs extraction were performed using the mathematical software Matlab R2016a. The formation (Eq. (1)–(3)) and extraction constants (Eq. (6)–(16)) were used as the optimization parameters in order to find the values that make experimental and calculated data match with the minimum error. The resolution method applied is shown in Figure 1.
According to the flowchart in Figure 1, the resolution of the system starts with a matrix of the experimental data. In the present study, three different matrices have been used to compile the experimental data of Nd(III), Tb(III) and Dy(III) separately (90 experimental points). The experimental matrices contain, in columns, the initial concentrations of the metals and the chloride anion in the aqueous phase, the initial concentration of AlOle, the concentration of protons in the aqueous phase before and after the extraction and the extraction percentages obtained experimentally. Next, the equilibria equations in the aqueous and the organic phase as well as the mass balances involved were introduced. Nine extraction models have been tested, one for each of the equilibria equations described in Eqs. (6–15). The initial concentrations guesses for all the metal species in the system (X₀) were entered. The nonlinear system of equations was solved with the Matlab function *fsolve*. Once calculated the concentration of the metals in the organic phase from the equations system, the expression used to obtain the calculated percentage of metal extraction is given as:

\[
\%E_{\text{calc}} = \left( \frac{[\text{Me}]_{\text{org}}}{[\text{Me}]_{\text{int}}} \right) \times 100
\]

The calculated extraction percentage is a key parameter of the model resolution since the optimization of the stability and equilibria constants depends on the sum of the square of the differences between the calculated and the experimental percentages of extraction.

Finally, the function \(F(x)\), defined as:

\[
F(x) = \sum \left[ \left( \%E_{\text{calc}} - \%E_{\text{exp}} \right) \right]^2
\]

was minimized using the Matlab function *fmincon*, which finds the minimum constrained of a nonlinear multivariable function. Formation constants based on the literature (Table 1) and guessed equilibria constants were used to initialize the program (K₀).

**Table 1** Stability constants in the literature

<table>
<thead>
<tr>
<th></th>
<th>Nd(III)</th>
<th>Tb(III)</th>
<th>Dy(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( K_1 )</td>
<td>( K_2 )</td>
<td>( K_3 )</td>
</tr>
<tr>
<td>a</td>
<td>2.09</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>8.32 ( \times 10^{-3} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>1.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- b. (Hogfeldt, 1982).
- c. (Lee et al., 2005).
- d. (Sastri, 2003).

The optimization led to the determination of the stability and equilibria constants, whose values allow the experimental extraction extension of the metals to be reproduced with the minimum error.

**5.5 Results and discussion**

The simulation models created were applied to the extraction of Nd(III), Tb(III) and Dy(III) individually. The stability factors from the literature (Table 1) were taken into account although there was not much information because of the recent surge in REEs interest. The reported formation constants were tested out for initialization of the models (K₀) but unfortunately, they were not able to reproduce the experimental extraction values of the metals for any of the proposed models. In this regard, it became necessary to find new constants beyond the literature, from scratch, in order to adjust the models to the experimental data of REEs solvent extraction.
The error, calculated as the sum of the absolute value of the differences between the calculated and the experimental extraction percentages of the metals for each point studied (Eq. [26]), as well as comparative plots between the experimental and the modelled results were used to discern which model, within the nine proposed, is the most appropriate for the reproduction of REEs experimental extraction data. Optimized stability and equilibria constants were determined in each case. Table 2 shows the optimized stability and extraction constants and the error value calculated for each model tested.

<table>
<thead>
<tr>
<th>Table 2 Optimization parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd(III)</td>
</tr>
<tr>
<td>K_{eq1}</td>
</tr>
<tr>
<td>Eq. (26)(a)</td>
</tr>
<tr>
<td>Eq. (27)(b)</td>
</tr>
<tr>
<td>Eq. (28)(c)</td>
</tr>
<tr>
<td>Eq. (29)(d)</td>
</tr>
<tr>
<td>Eq. (30)(e)</td>
</tr>
<tr>
<td>Eq. (31)(f)</td>
</tr>
<tr>
<td>Eq. (32)(g)</td>
</tr>
<tr>
<td>Eq. (33)(h)</td>
</tr>
<tr>
<td>Eq. (34)(i)</td>
</tr>
<tr>
<td>Eq. (35)(j)</td>
</tr>
</tbody>
</table>

The results show that the best fitted model to the experimental data for Nd(III), Tb(III) and Dy(III) is the one corresponding to the reaction 9 which means that the metals are extracted by solvation and the stoichiometry metal–IL is 1:2:

\[
2 \text{R}_nA^– + \text{MeCl}^3 + 2 \text{CT} \rightarrow ([\text{R}_nA^–\text{CT}^–])_2\text{MeCl}_2 \\
2 \text{R}_nA^– + \text{MeCl}^3 + 2 \text{CT} \rightarrow ([\text{R}_nA^–\text{CT}^–])_2\text{MeCl}_2
\]  
(R.9)

This finding is in agreement with the results obtained in previous studies regarding the extraction of Nd(III) in chloride media using AliOle (Osbón et al., 2017). The comparative plots of Nd(III), Tb(III) and Dy(III) extraction from chloride media 2 and 4 mol L⁻¹ concentrated with AliOle show that it is possible to accurately recreate the experimental extraction extension of the metals. Figure 2 shows a comparison between the simulation results of the model obtained by using the optimized parameters calculated with Matlab software and the experimental extraction percentages.
As can be seen, the selected model is able to reproduce the experimental extraction yield of Nd(III), Tb(III) and Dy(III) using the optimized equilibrium parameters listed in Table 2. The effect of the AliOle, the chloride
anion and the REEs concentrations over the extraction process are taken as a reference and as can be observed, the model fits the experimental data with the minimum error.

The optimized stability and equilibrium constants calculated on this model were tested on an extraction system of neodymium, terbium and dysprosium contained as a mixture in the aqueous phase in order to determine if the model established for single extraction of the metals was also useful to reproduce their competitive extraction. The effect of the AliOle and chloride concentrations in aqueous phase over the simultaneous extraction of Nd(III), Tb(III) and Dy(III) was studied. Figure 3 shows the comparative graphs between the simulation results of the model and the extraction percentages obtained experimentally.

![Fig. 3 Comparative graphs between simulated extraction results and experimental extraction extension. a) aqueous phase: 1000 mg L⁻¹ of Nd(III), Tb(III) and Dy(III), 4 mol L⁻¹ chloride; b) aqueous phase: 1000 mg L⁻¹ of Nd(III), Tb(III) and Dy(III), 2 mol L⁻¹ chloride.](alt-text: Fig. 3)

As shown, the equilibrium parameters calculated for the extraction of each metal separately allowed us to recreate feasibly the simultaneous extraction of Nd(III), Tb(III) and Dy(III) in the aqueous phase.

The proposed model, which involves solvating extraction of the metals by 1:2 stoichiometry, has proven to be a very handy tool to predict the extraction extension of REEs with AliOle in chloride media. This could also be very useful either to set the parameters on a new experimental study about any other REEs solvent extraction with AliOle, or to model their transport through SLM. It also could be successfully exploited for extraction prediction of REEs from end of life products (urban mining), requiring only minor adjustments of the equilibria equations and mass balances.

### 6.6 Conclusions

This paper reports on the extraction of neodymium, terbium and dysprosium from chloride media with AliOle IL (Methyl-tri(octyl/decyl)ammonium oleate) prepared at the laboratory. The effect of the AliOle, the chloride anion and the REEs concentrations over the extraction yield was studied. Several mathematical models were computed with Matlab software. The models were derived from the chemical equilibria and the mass balances involved in the extraction system of single Nd(III), Tb(III) and Dy(III). The stability and equilibrium parameters of all the proposed models were determined using the fmincon function. The model that better fitted the experimental data was found to be in agreement with preliminary studies. The calculated formation constants of the aqueous Nd-Cl, Tb-Cl and Dy-Cl complexes formed in the aqueous phase were: $K_{1\text{Nd}} = 37.14$; $K_{2\text{Nd}} = 0.15$; $K_{3\text{Nd}} = 9.50 \times 10^{-2}$; $K_{1\text{Tb}} = 252.97$; $K_{2\text{Tb}} = 0.03$; $K_{3\text{Tb}} = 0.30$; $K_{1\text{Dy}} = 98.39$; $K_{2\text{Dy}} = 0.02$; $K_{3\text{Dy}} = 1.00$. The equilibrium constants were calculated as: $K_{eq\text{Nd}} = 4223.02$; $K_{eq\text{Tb}} = 5573.10$; $K_{eq\text{Dy}} = 7239.50$. The reliability of the method was proven by comparative graphs between the simulated model and the experimental extraction extension.
This work provides the basis for the study of the recovery of REEs from chloride media using AliOle as extractant and appears to be very promising for the recycling of these metals from urban mining by solvent extraction and by SLM.

Acknowledgements

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References


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**Highlights**

- The mathematical model proposed is able to accurately reproduce the experimental data of Nd(III), Tb(III) and Dy(III) single extraction.
- Speciation of Nd(III), Tb(III) and Dy(III) in chloride media and competitive extraction of HCl are taken into account.
- The mathematical model proposed is able to predict the simultaneous extraction of Nd(III), Tb(III) and Dy(III).

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**Queries and Answers**

**Query:**

“Table 1” has been changed to “Table 2”. Please check if correct and amend as necessary.

**Answer:** It is correct
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Please provide an update for reference “Obón et al., unpublished results”.

**Answer:** Still not published