GENIORS

Research and Innovation Action (RIA)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 755171.

Start date : 2017-06-01 Duration : 48 Months
http://geniors.eu/

Status of flowsheet calculations made for WP22 process testing

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GENIORS - Contract Number: 755171

Project officer: Roger Garbil

Document title	Status of flowsheet calculations made for WP22 process testing
Author(s)	Dr. Robin TAYLOR, D Woodhead (NNL) K Wallace (NNL) R Taylor (NNL)
Number of pages	98
Document type	Deliverable
Work Package	WP5
Document number	D5.5
Issued by	NNL
Date of completion	2021-06-18 11:10:34
Dissemination level	Public

Summary

Previous work in GENIORS has considered the modelling of acid extraction in TODGA based solvents with a specific focus on the i-SANEX system (where the solvent phase comprises 0.2M TODGA in 5% octanol/diluent) as this is the reference process for minor actinide separations (see D. Woodhead et al., Solv. Extr. Ion Exch. 37, 173-190 (2019)). To be useful, models must obviously consider more than just acid. Building on initial developments made under the SACSESS project, this report now seeks to consider in greater detail the extraction of metals, focussing on those for which the most comprehensive sets of experimentally measured distribution data are available to parameterise and validate the models.

Approval

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GENIORS

GEN IV integrated oxide fuels recycling strategies

Deliverable 5.5 - Status of Flowsheet Calculations made for WP22 Process Testing

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PD02 Deliverable 5.5 – NNL 15596

Version 1 issued on 31/03/2021

Version 2 issued on 24/05/2021

EXEC SUMMARY

Previous work in GENIORS has considered the modelling of acid extraction in TODGA based solvents with a specific focus on the i-SANEX system (where the solvent phase comprises 0.2M TODGA in 5% octanol/diluent) as this is the reference process for minor actinide separations (see D. Woodhead et al., Solv. Extr. Ion Exch. 37, 173-190 (2019)). To be useful, models must obviously consider more than just acid. Building on initial developments made under the SACSESS project, this report now seeks to consider in greater detail the extraction of metals, focussing on those for which the most comprehensive sets of experimentally measured distribution data are available to parameterise and validate the models.

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1. INTRODUCTION

It is known from previous work that trivalent actinides and lanthanides typically extract into TODGA in complexes that include 3 TODGA ligands. This is, however, not the complete story. There is evidence from the work of KIT undertaken as part of the SACSESS and GENIORS projects [1] that under high loading conditions complexes with 2 TODGA ligands may be significant. This is because it is possible to extract neodymium, at least, to give solvent phase metal concentrations that are in excess of one third of the TODGA concentration. It is also clear from previous work that coextraction with nitric acid occurs to a significant extent, with americium extraction showing a dependence on nitrate concentration which is far stronger than that which would be implied by the formation of $Am(NO_3)_3.nTODGA$ complexes. In the case of neodymium (an exemplar mid-range lanthanide and often used as a surrogate for americium), measurements of solvent phase acidity resulted in the finding that as much acid could be extracted in the presence of high Nd loading as in its absence, a result that would be inconsistent with a model in which metal extraction resulted in the displacement of acid from the solvent.

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2. GENERAL APPROACH TO MODELLING

The modelling of equilibrium distribution reflects the complexes that are expected to form in the solvent phase. Initial review of the data suggests the likely form of these complexes and model fitting allows for the existence of all complexes that could plausibly exist For example, in the case of neodymium described in section 4 experimental work at low metal concentrations with variable TODGA concentrations suggests complexes with three TODGA ligands, while loading data (high metal concentrations) indicates that complexes with less than three TODGA ligands must also exist. Data obtained over a range of different acidities indicate that the dependence of the Nd distribution value on nitrate concentration is stronger than would be expected if the complex only contained the three nitrate ions necessary to give a neutral solvent phase complex suggesting that co-extraction with acid may be significant. Direct measurement of acid in a solvent phase heavily loaded with Nd supports this suggestion. The initial modelling therefore allowed for complexes of the form $Nd(NO_3)_3.nHNO_3.mTODGA$ for n in range 0 to 4 and m in range 1 to 4, the ranges of n and m being chosen to allow any complex considered credible. Many of the hypothesised complexes (values of n and/or m) will be discounted in the course of fitting as their inclusion in the model does not allow a statistically significant improvement in the fit of the model to the data.

Calculation of the equilibrium constants for the complexes requires the inclusion of expressions for the activity coefficients of the species involved in the formation of complexes, including where appropriate the metal being extracted, the acid, the nitrate and the extractant (TODGA). The approach adopted for modelling here has been to assume that the activity coefficient for a particular species can be represented by a parameterised correlation that can produce curves with the same qualitative shape as curves corresponding to literature data for activity coefficients. The parameters for this correlation are fitted as part of the model fitting procedure.

Typically, fitting proceeds iteratively with the activity coefficient expression for an extractable species being fitted alternately with the values of the stability constants for the complexes. Attempts to fit all parameters simultaneously tend to cause numerical problems, with local minima some distance from the global optimum tending to be found. Fitting of the correlations for activity coefficients was typically constrained so as to ensure that the fitted curve is at least physically plausible, despite being ultimately an empirical fit. Requirements here include that the activity coefficient is never negative and that when plotted against nitrate concentration there is at most one turning point.

In all cases it is assumed that solvent phase activity coefficients are unity. The empirical fitting of the aqueous phase activity coefficients will have the effect of mitigating at least some of the consequences of this assumption. Acid and nitrate activity correlations[1] were derived when fitting the acid extraction algorithm and have not been modified to take account of the effect of the presence of other aqueous species.

It is recognised that there are other methods available for the calculation of activity coefficients which have a sounder theoretical underpinning. The two notable schemes are Specific Ion Interaction Theory (SIT) [2] and Pitzer equations [3]. The present semi-empirical approach has been adopted in preference to either of these approaches for the below reasons.

- Both SIT and Pitzer (particularly the latter) require a large number of interaction terms to be specified in the model. It is not clear that all the required terms would be available from the literature or easily acquired experimentally.

[1] These will be the same due to the use of mean stoichiometric activity coefficients in the acid extraction model

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- SIT has a limited range of applicability, typically quoted as up to ~ 3M. It is desired that the models operate at acid concentrations substantially in excess of this range. It is probable that at higher concentrations empirical fixes to an SIT model would be needed. Pitzer has a better range of applicability but is significantly more complex.
- SIT and Pitzer both have the potential to describe the aqueous phase, but a calculation of distribution values also requires knowledge of the solvent phase activities. A method would be required to deal with activity in the solvent phase. The empirical approach avoids this issue by including solvent phase activity effects in the fitting of the aqueous phase activities.
- Consideration would need to be given as to how partially dissociated species (notably HNO_3) would be handled in a SIT or Pitzer based implementation. This is likely to add significant complexity. The empirical approach includes effects attributable to partial dissociation in the fitting of the aqueous phase activities.

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3. ACID EXTRACTION MODELS

Modelling of the extraction of Nd in TODGA based systems sits on top of a model of acid extraction in the same system and models fitted to the metal extraction data will differ depending on the details of the acid distribution models they operate in conjunction with. The linkage occurs due to acid and metals competing for the free extractant. Two distinct acid extraction models have been developed previously as summarised below.

Acid model A:

This model was fitted using Excel solver. Weights were applied to data with a certain amount of engineering judgement applied as to the reliability of data in question and importance of getting an accurate fit in the region the data relates to.

Acid Model B:

This model was fitted using gPROMS parameter estimation. All data were treated equally with regard to fitting. This approach has advantages in terms of provision of statistics relating to the quality of the fit and the confidence intervals associated with the fitted parameters. Disadvantages of this approach are a tendency to be thrown by outliers and a focus of fitting in regions where the greatest amount of data are available. This model was developed in light of reviewer's comments when looking to publish the modelling work. It is described in [4].

Attempts were made to develop neodymium extraction models to work in conjunction with both of these acid extraction models. It was found that it was possible to develop better models to work with acid model A and in light of this acid model A was used as the base when developing metal extraction models described in this memo. This model is described in detail in [5] and summarised below.

The acid extraction model calculates the concentration of the acid-containing solvent phase complexes based on an estimate of the activity of acid in the aqueous phase and fitted stability constants for the solvent phase species. The mean stoichiometric activity coefficient for nitric acid is calculated as below:

$$\gamma_s = \left[\frac{0.37613}{(0.90969 + [HNO_3])^2} + 0.462 + 0.18585[HNO_3] - 0.011869[HNO_3]^2 \right]$$

Stability constants for a number of solvent phase complexes are used as in Table 1 below with constant β_{xyz} corresponding to the complex $xHNO_3.yTODGA.z$ octanol

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Table 1: Stability Constants in the acid extraction model [5].

Complex	Stability Constant	Value
HNO_3.octanol	β_{101}	0.006003
HNO_3.2octanol	β_{102}	0.001995
HNO_3.3octanol	β_{103}	0.000269
HNO_3.2TODGA	β_{120}	1.68184
HNO_3.TODGA	β_{110}	0.498468
$2HNO_3$.TODGA	β_{210}	0.028287
$4HNO_3$.TODGA	β_{410}	1.84E-06
TODGA.octanol	β_{011}	0.416717
$2HNO_3$.TODGA.octanol	β_{211}	0.017875
$3HNO_3$.TODGA.octanol	β_{311}	0.001989

Temperature dependence is determined by a temperature correction factor following a standard Arrhenius relationship, set up to take a value of 1 when evaluated at 293.15 K.

$$CorrectionFactor = 2.08691 \times 10^{-4} e^{\left(\frac{20656}{RT}\right)}$$

The metal extraction models fitted to work with this acid model are constructed in a broadly similar manner with an expression for the activity coefficient, fitted stability constants for the complexes being extracted and a term to deal with temperature dependence. The fitting of these models is described in subsequent sections.

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4. NEODYMIUM

4.1. AVAILABLE NEODYMIUM EXTRACTION DATA

Existing data on the distribution of Nd into TODGA / octanol mixtures have been collated in order to construct preliminary models of the distribution of Nd into such mixtures. Five data series were used in the fitting of these models as summarised briefly below. All distribution experiments used an initial solvent/aqueous ratio of 1.

Series 1

A series of 6 data points giving distribution values for trace concentrations (20 mg/l initial aqueous concentration) of various actinides and lanthanides including Nd into 0.2 M TODGA / 5% 1-octanol in TPH at 20 °C. Data reported were initial HNO_3, Nd and D_{Nd}. Acidity range 0.15 to 1.0 M.

Series 2

A series of 34 data points giving distribution values for trace concentrations (10 mg/l initial aqueous concentration) of various actinides and lanthanides including Nd into 0.1 or 0.2 M TODGA / 5% octanol at 10, 20, 30, 40, 50 °C and initial HNO_3 (aqueous) concentrations of 0.11, 0.3, 0.98, 2.9M. Some permutations that would give very high distribution values were omitted.

Series 3

A series of 11 data points dealing with extraction of Nd at various concentrations (0.01 – 1.0 M initial aqueous Nd) from 1 M HNO_3 into 0.1 M TODGA / 5% 1-octanol in TPH at 20 °C. One point is the average of duplicates and one is the average of triplicates, other points are single measurements. Data reported were initial aqueous, equilibrium aqueous and equilibrium organic Nd concentrations.

Series 4

A series of 12 data points dealing with extraction of 0.009 – 0.18 M Nd from 3 and 4 M initial aqueous HNO_3 into 0.1M TODGA / 5% octanol at 20 °C. Data reported are initial aqueous acidity, initial aqueous Nd and equilibrium organic Nd.

Series 5

A series of 9 data points for extraction of acid into Nd loaded solvent. Contains data for extraction of acid into 0.1 M TODGA in / 5% 1-octanol in TPH from 0 – 300 mM Nd(III) in 3 M HNO_3 at 20 °C. Only initial Nd, initial aqueous acidity and equilibrium organic acidity reported.

In summary there are data for distribution of trace Nd into 0.1 and 0.2 M TODGA at a range of temperatures, loading data for extraction of Nd into 0.1M TODGA at 20 °C for aqueous acidity in the range 0 – 1 M and separately for 3 and 4 M. There are also data for extraction of acid into 0.1 M TODGA from 3 M acid with various Nd loadings. Temperature data are only available for trace levels of Nd.

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4.2. FITTED NEODYMIUM EXTRACTION MODEL

A model was fitted using gPROMS parameter estimation to work with the acid extraction model A [5] described in section 3.

Various attempts at fitting were undertaken and the models suggested as optimal were found to be rather dependent on the way in which the data from the experiments are treated when used in the parameter estimation. In the system finally adopted distribution data were resolved into aqueous and organic concentrations so that distribution values themselves are never treated as measured variables from the experiments. This reflects the reality that distribution values are not measured directly. The derivation of distribution values has the consequence that the error profiles of distribution values do not map well onto the variance models supported by gPROMS[2].

In cases where there were initial aqueous concentrations as well as equilibrium concentrations recorded in both phases, the initial concentrations were ignored and a perfect mass balance assumed. The model suggested by parameter estimation is also sensitive to the assumptions made about variance of the measured variables. The final model was derived with the assumption that all neodymium concentrations in both phases and across all experiments were subject to the same variance model, which was fitted by gPROMS assuming a heteroscedastic model. Organic acidity measurements were also assumed to have a separate heteroscedastic variance model. Heteroscedastic variance has the form $\sigma = \omega |x|^{\gamma}$ where σ is the variance, ω and γ are fitted parameters and x is the value of the measurement. The fitted values are summarised in Table 2 below.

Table 2: Variance model parameters for previously performed Nd distribution experiments, as estimated by gPROMS.

Measured Quantity	Units[3]	ω	γ
Neodymium concentration	mg/L	0.124436	0.885924
	mol/L	0.03209353	0.885924
Organic acidity	mol/L	0.00454669	1

[2] The essential issue here is that distribution measurements calculated as the ratio of concentrations in the two phases will tend to have high relative errors when the value is either very high or very low. This is because in such cases the measured concentration in one of the phases will be very low and thus subject to high relative errors which propagate through to high relative errors in the calculated distribution values. The lowest relative errors in distribution values can therefore be expected when distribution values are around one. The main variance models in gPROMS are all variants of the heteroscedastic variance model where $\gamma = 0$ gives constant absolute variance and relative variance monotonically reducing with increasing measurement value and $\gamma = 1$ gives constant relative variance across the range. Neither extreme nor any intermediate value of γ can capture a system in which the relative variance is least at an intermediate value rather than an extreme.

[3] To convert the variance expression from units A to units B multiply ω by $k^{(1-\gamma)}$ where k is the conversion factor to convert from units A to B. For conversion of mgNd/L to mol/L, k = 6.933E-6 and hence ω is multiplied by 0.257912.

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The fitting of the Nd distribution model itself included: fitting of an activity coefficient expression to use for Nd, the fitting of stability constants of the various solvent phase complexes, and the fitting of the free energy associated with formation of the complexes. The same free energy was assumed to apply to formation of all the complexes. This assumption is probably incorrect, but there are insufficient data to have a reasonable chance of accurately identifying free energies associated with the individual complexes. The use of the assumption can be justified by the fact that it allows the construction of a model that gives a good fit to the available data. The fitted activity coefficient expression is as below. Note that this is a function of the total nitrate concentration and is independent of the Nd concentration which will typically be much less than the nitrate concentration[4].

$$\gamma_{Nd} = \left[\frac{0.0516285}{(0.1 + [NO_3^-])^{1.30046}} + 0.430128 + 0.229603[NO_3^-] - 0.022094[NO_3^-]^2 + 0.00405736[NO_3^-]^3\right]$$

Figure 1 below shows the relationship between the Nd activity coefficient and nitrate concentration given by this equation.

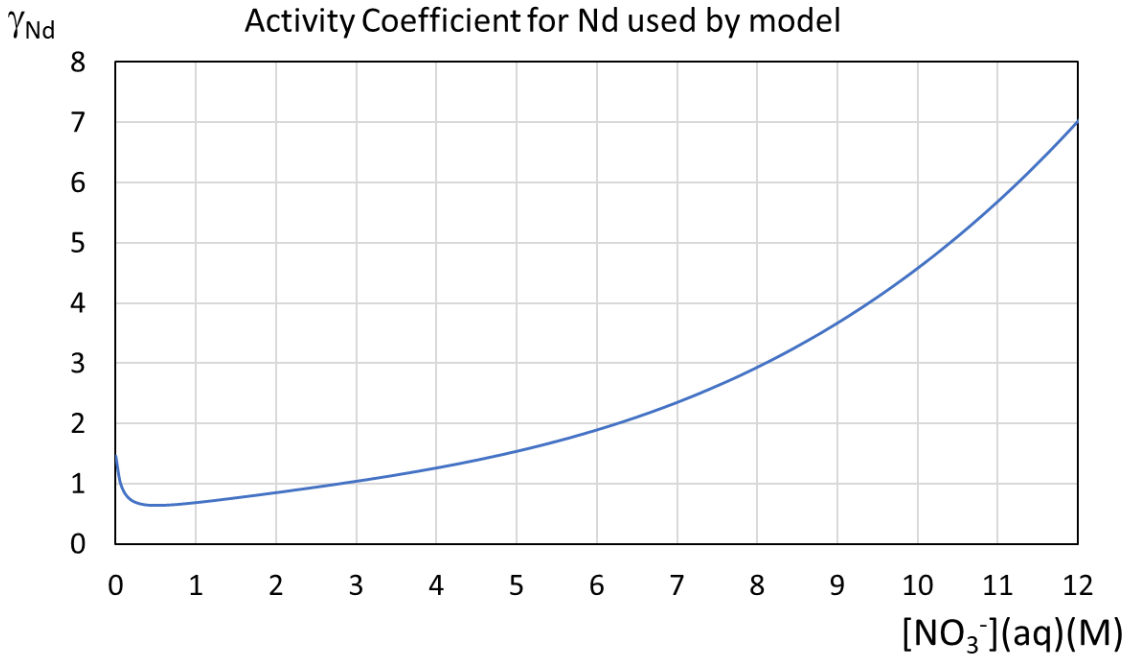

Figure 1: Plot of the Nd activity coefficient as fitted in gPROMS.

Strictly the activity coefficient calculated above is the mean activity coefficient defined by the below equation.

$$\gamma_{Nd}^4 = \gamma_{Nd^{(3+)}}\gamma_{NO_3^-}^3$$

The organic Nd concentration is then calculated as the sum of extracted complexes of form $Nd(NO_3)_3.iHNO_3.jTODGA$ by the below equation.

[4] All the data used to fit the model has been for the nitric acid system. The model has not been tested with, and cannot be considered valid for, systems in which anions other than nitrate are present in significant concentrations.

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$$[Nd]_{org} = Ae^{\frac{-\Delta G}{RT}} \sum_{i,j} \gamma_{Nd}^{4} \gamma_{H}^{2i} \beta_{ij} [Nd^{3+}][NO_3^-]^{2i+3}[TODGA]^j$$

In this equation γ_H is the mean stoichiometric activity coefficient for nitric acid as given in section 3.

Fitted stability constants used in the model were as in Table 3 below. Note that the model allows for the presence of a range of complexes for which the stability constants were fitted by gPROMS[5] as zero.

[5] Stability constants were all given a low bound of zero when fitting, as negative stability constants are physically meaningless. The majority of stability constants were then estimated to lie on this low bound.

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Table 3: Fitted Stability constants for the Nd Distribution Model.

Complex	Constant	Value
$Nd(NO_3)_3$.TODGA	β_{Nd01}	0
$Nd(NO_3)_3$.2TODGA	β_{Nd02}	1590.92
$Nd(NO_3)_3$.3TODGA	β_{Nd03}	990308
$Nd(NO_3)_3$.4TODGA	β_{Nd04}	0
$Nd(NO_3)_3.HNO_3$.TODGA	β_{Nd11}	0
$Nd(NO_3)_3.HNO_3$.2TODGA	β_{Nd12}	0
$Nd(NO_3)_3.HNO_3$.3TODGA	β_{Nd13}	0
$Nd(NO_3)_3.HNO_3$.4TODGA	β_{Nd14}	0
$Nd(NO_3)_3.2HNO_3$.TODGA	β_{Nd21}	0
$Nd(NO_3)_3.2HNO_3$.2TODGA	β_{Nd31}	0
$Nd(NO_3)_3.2HNO_3$.3TODGA	β_{Nd23}	80545.2
$Nd(NO_3)_3.2HNO_3$.4TODGA	β_{Nd24}	0
$Nd(NO_3)_3.3HNO_3$.TODGA	β_{Nd31}	0
$Nd(NO_3)_3.3HNO_3$.2TODGA	β_{Nd32}	0
$Nd(NO_3)_3.3HNO_3$.3TODGA	β_{Nd33}	21808.9
$Nd(NO_3)_3.3HNO_3$.4TODGA	β_{Nd34}	0
$Nd(NO_3)_3.4HNO_3$.TODGA	β_{Nd41}	0
$Nd(NO_3)_3.4HNO_3$.2TODGA	β_{Nd42}	0
$Nd(NO_3)_3.4HNO_3$.3TODGA	β_{Nd43}	714.986
$Nd(NO_3)_3.4HNO_3$.4TODGA	β_{Nd44}	0

Temperature dependence was determined by an Arrhenius equation in the same way as for acid with an estimated value of ΔG = -90761.3 and the pre-exponential term set such that the temperature correction factor evaluates to 1 at 20 °C.[6]

[6] The terminology ΔG has been used in in this report as it plays a role analogous to that of the Gibbs free energy (ΔG^0). However, ΔG as used here is not the same as ΔG^0 since the actual solvent phase adducts are likely to include water extraction of which has not been considered in the model.

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4.3. NEODYMIUM EXTRACTION MODEL PERFORMANCE

The model was run against the available data with results as shown in Figure 2 through Figure 11 below.

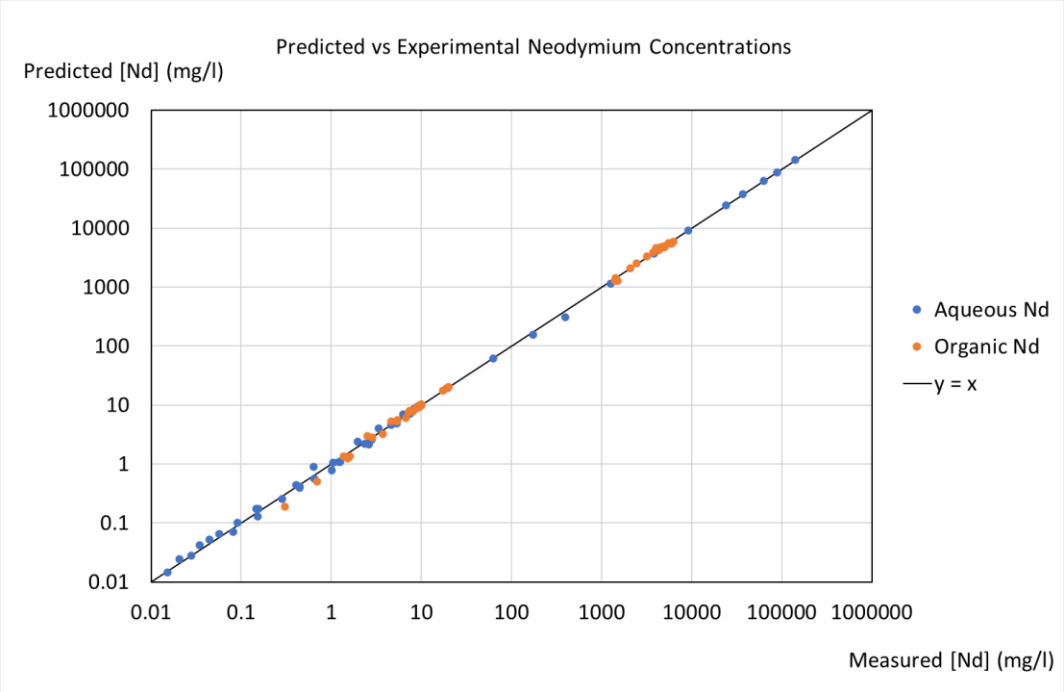

Figure 2: Modelled vs experimental Nd Concentrations.

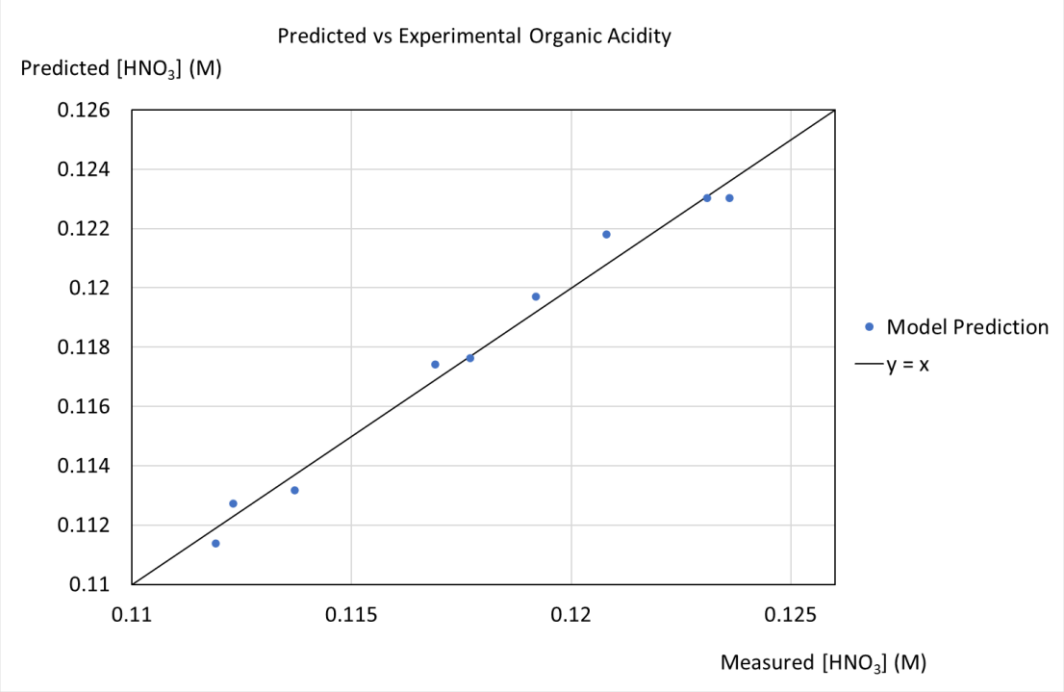

Figure 3: Modelled vs Organic Acid Concentrations.

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In Figure 4 through Figure 11 below, (which show model predictions vs experimental data for the data used to fit the model) the error bars are the model-predicted variance of the measurement at the point in question. Measurement time shown on the x-axis of these and subsequent similar plots is the internal gPROMS model time used when stepping between the experimental data. In the context of these plots it has no significance other than as a means of separating the data points.

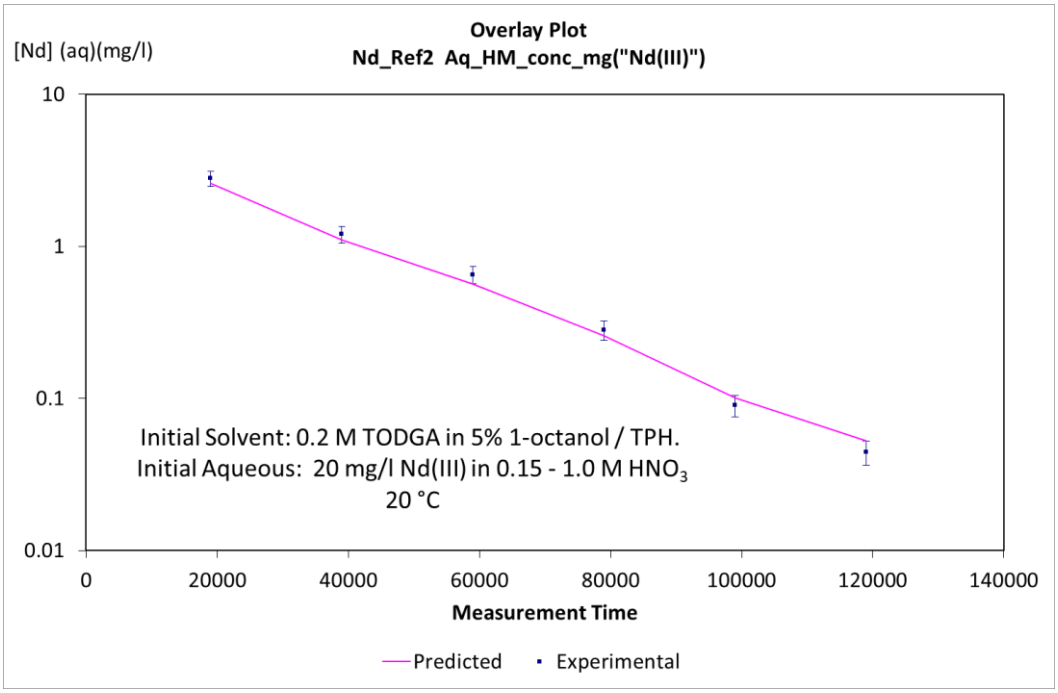

Figure 4: Fit of model to experimental data (Aq Nd data series 1).

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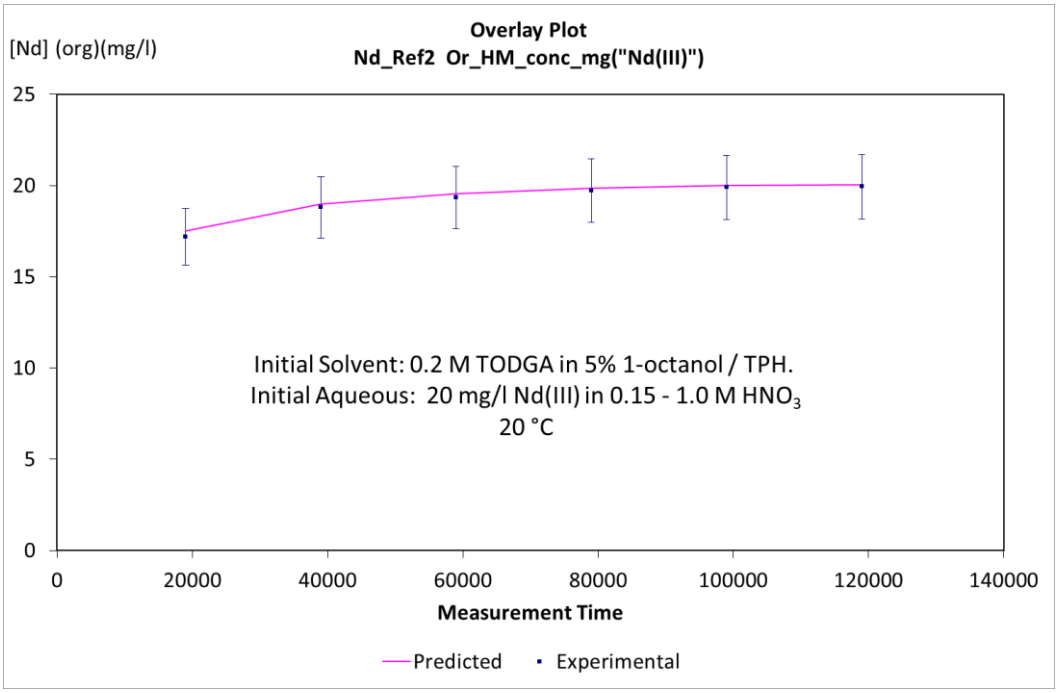

Figure 5: Fit of model to experimental data (Or Nd data series 1).

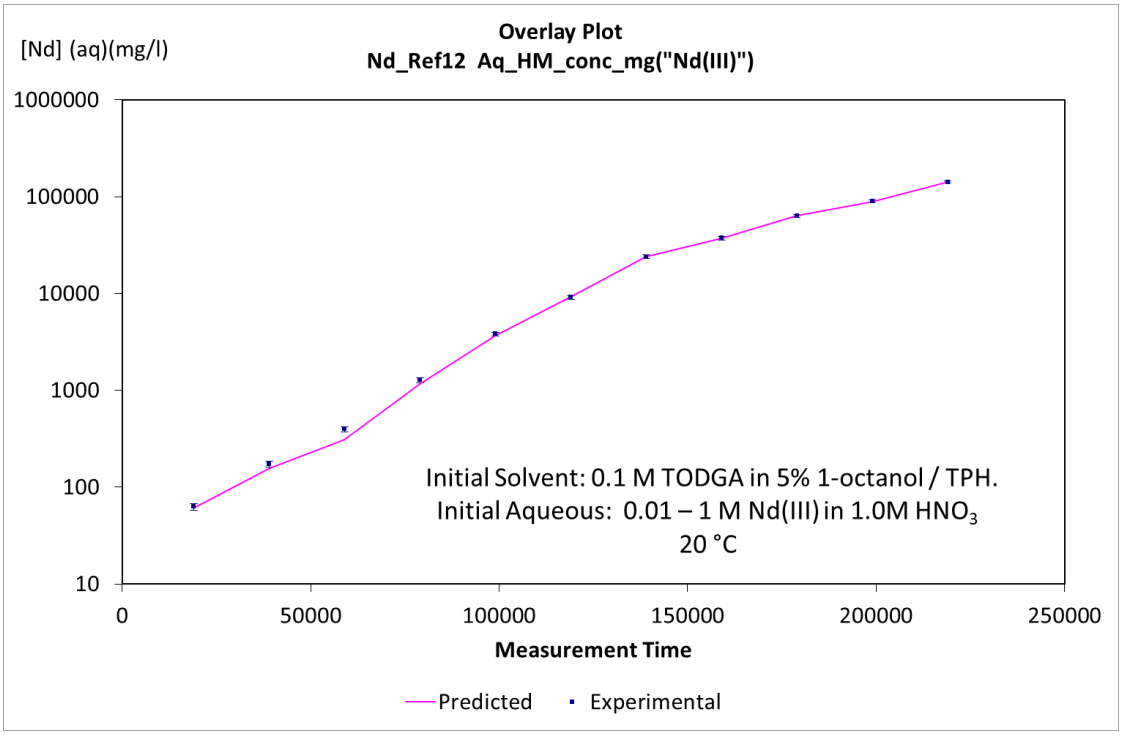

Figure 6: Fit of model to experimental data (Aq Nd data series 2).

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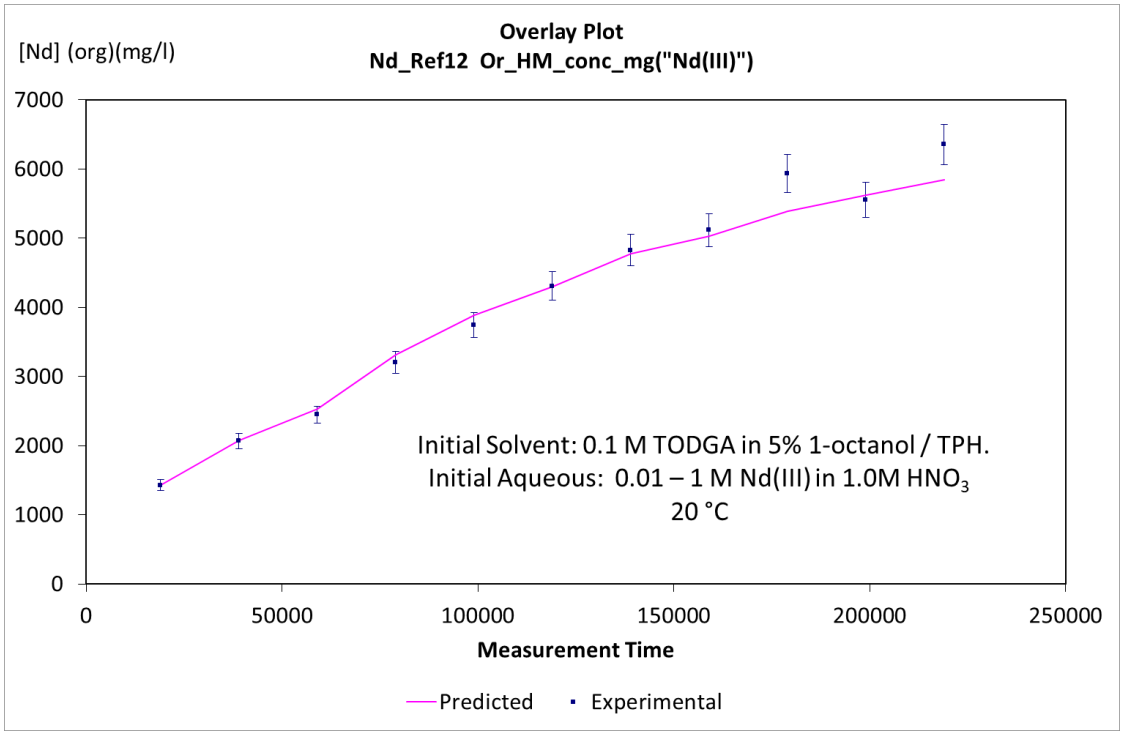

Figure 7: Fit of model to experimental data (Or Nd data series 2).

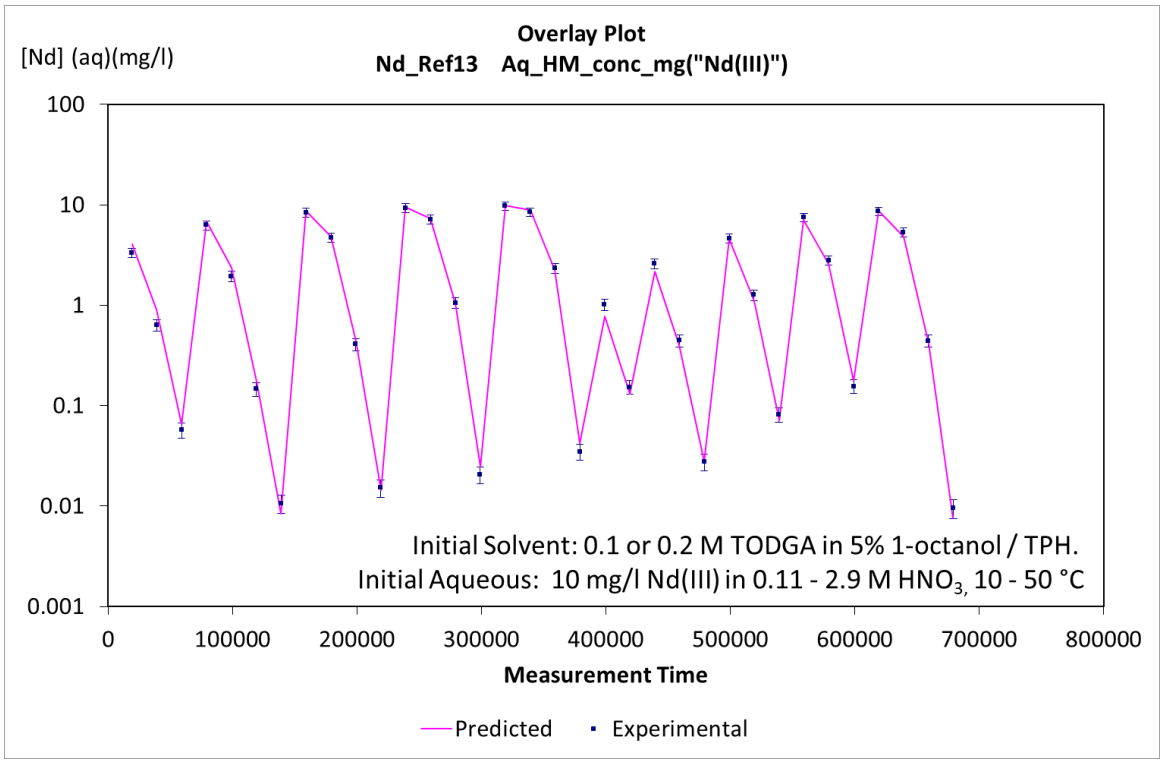

Figure 8: Fit of model to experimental data (Aq Nd data series 3).

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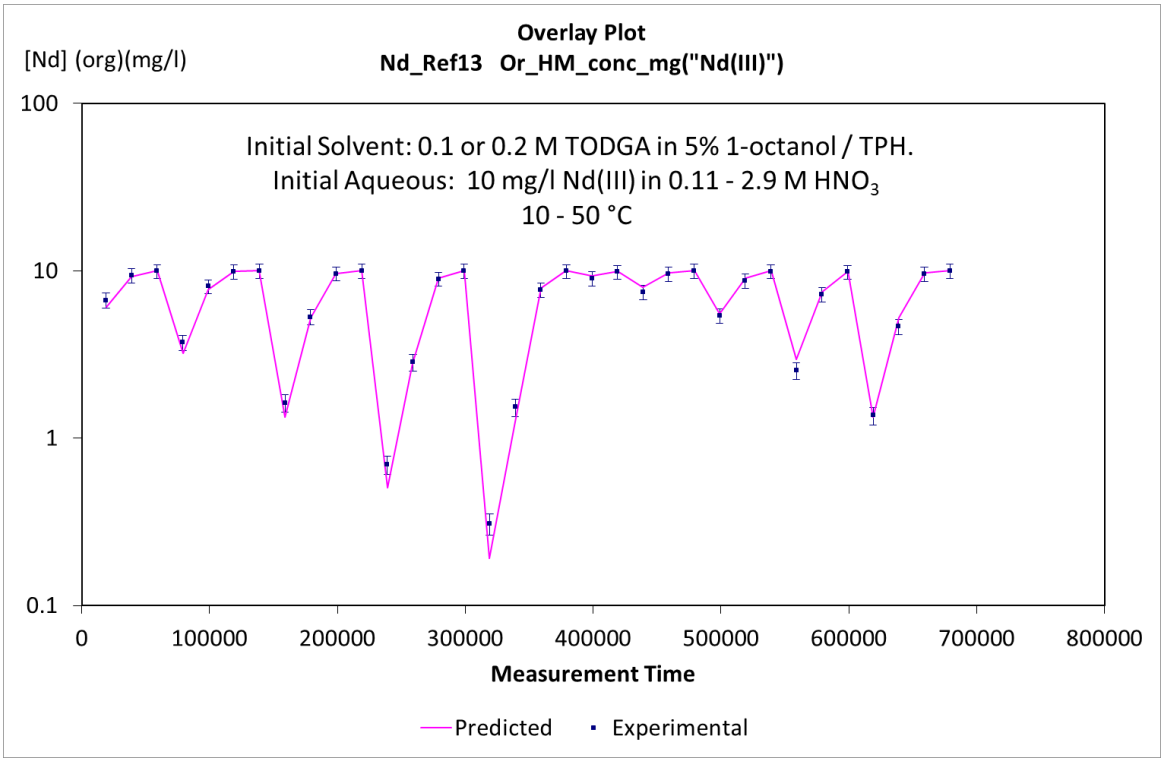

Figure 9: Fit of model to experimental data (Or Nd data series 3).

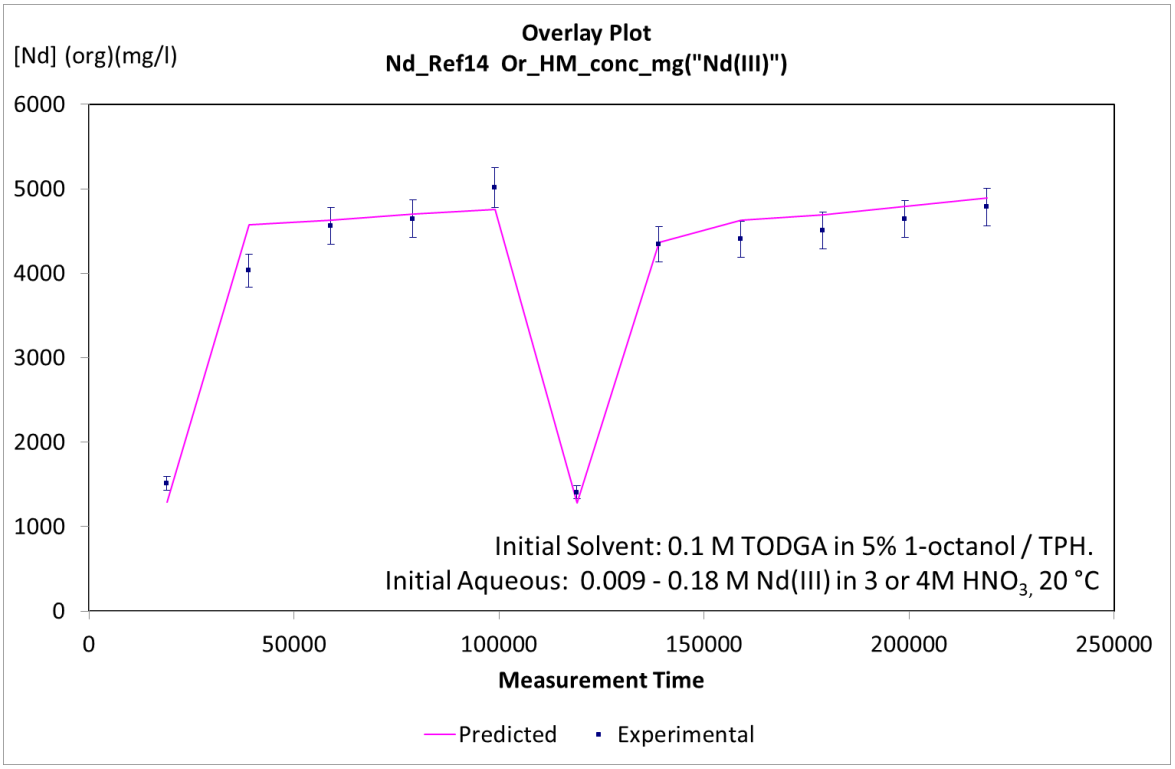

Figure 10: Fit of model to experimental data (Or Nd data series 4).

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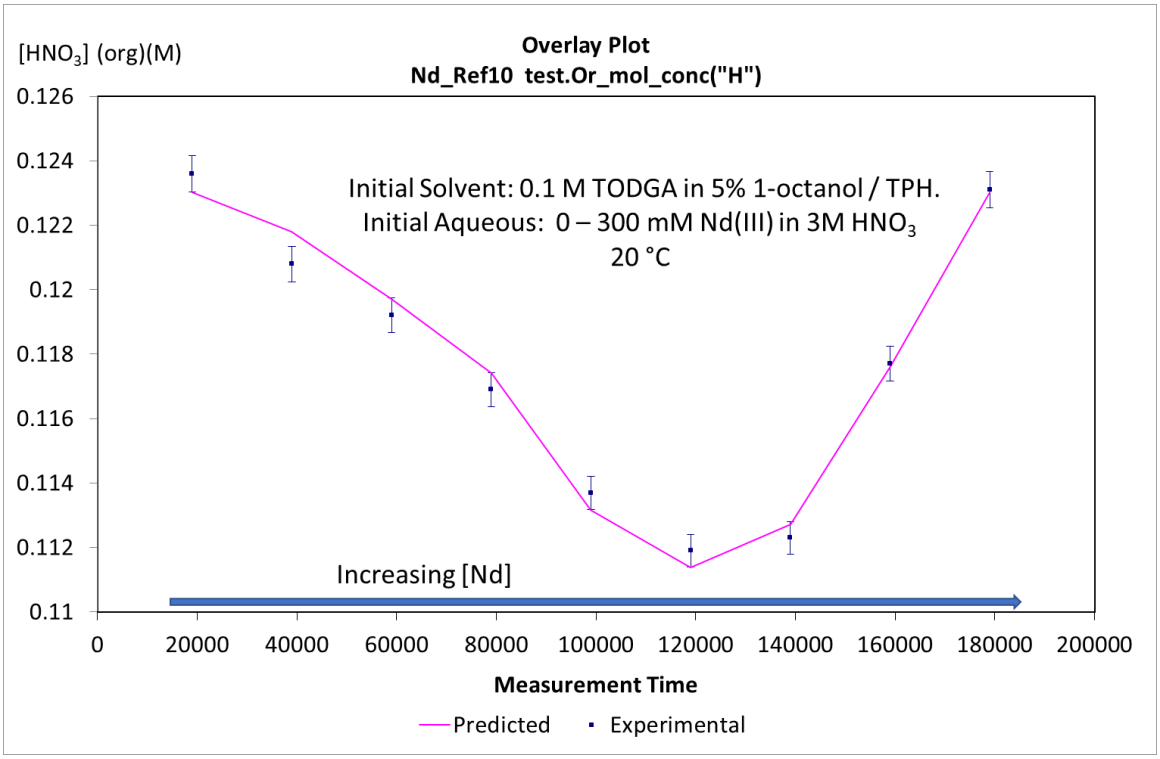

Figure 11: Fit of model to experimental data (Or HNO3 1).

These figures demonstrate a generally good fit to the available data, although it is important to note that as this is the data that were used to fit the model a good fit is to be expected. Testing of the model against data not used in the fitting would give a better assessment of the quality of the model, particularly if that data lies in ranges not covered by the data used in the fitting.

4.4. ORGANIC NEODYMIUM SPECIATION

To give some idea of the relative importance of the different complexes being proposed by this model, the model was run for extraction of Nd into 0.2M TODGA in 5% octanol / TPH at 20 °C for a range of aqueous acid and Nd concentrations. The molar concentrations of the different organic phase Nd complexes predicted by these runs are shown in Figure 12 through Figure 17 below.

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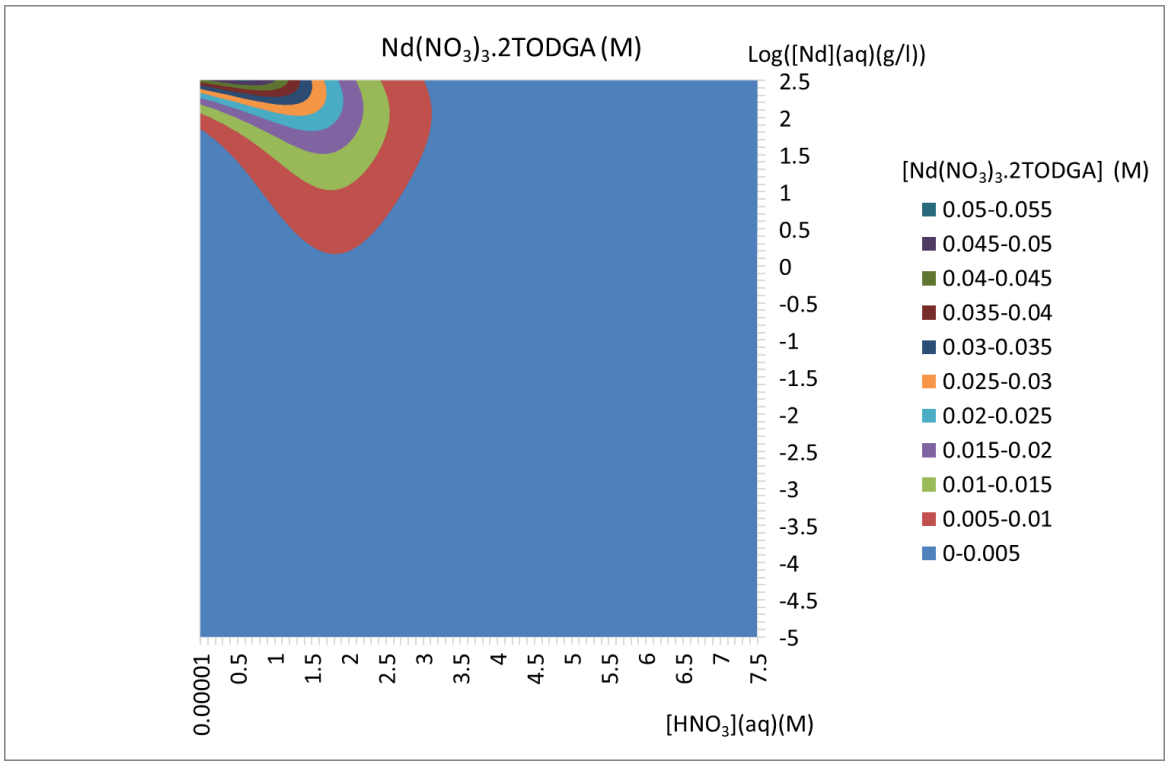

Figure 12: Predicted [$Nd(NO_3)_3$.2TODGA] in 0.2M TODGA in 5% octanol / TPH at 20 °C.

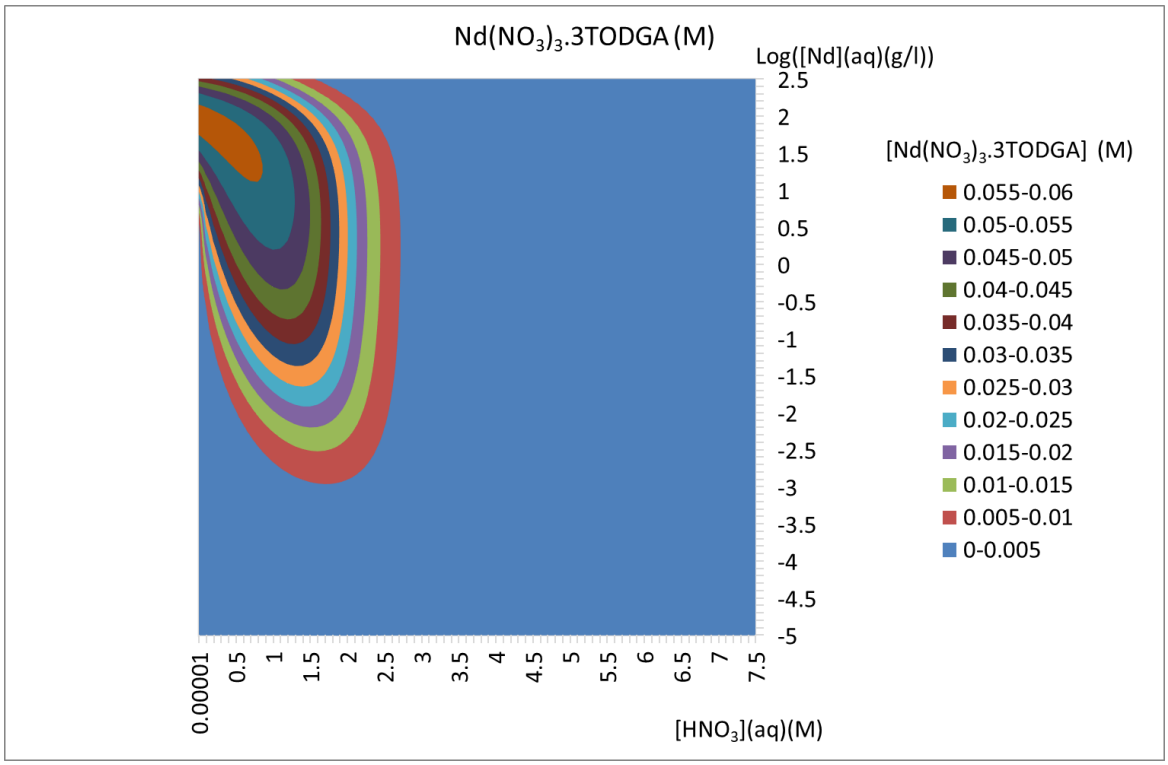

Figure 13: Predicted [$Nd(NO_3)_3$.3TODGA] in 0.2M TODGA in 5% octanol / TPH at 20 °C.

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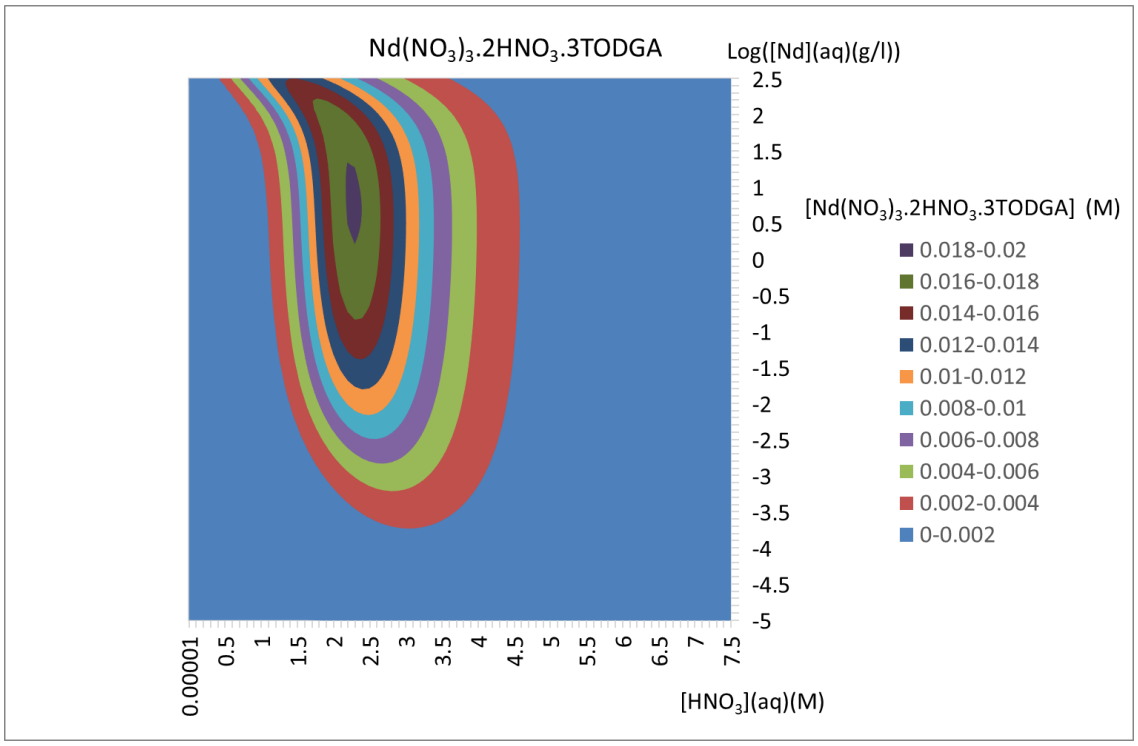

Figure 14: Predicted [$Nd(NO_3)_3.2HNO_3.3TODGA$] in 0.2M TODGA in 5% octanol / TPH at 20 °C.

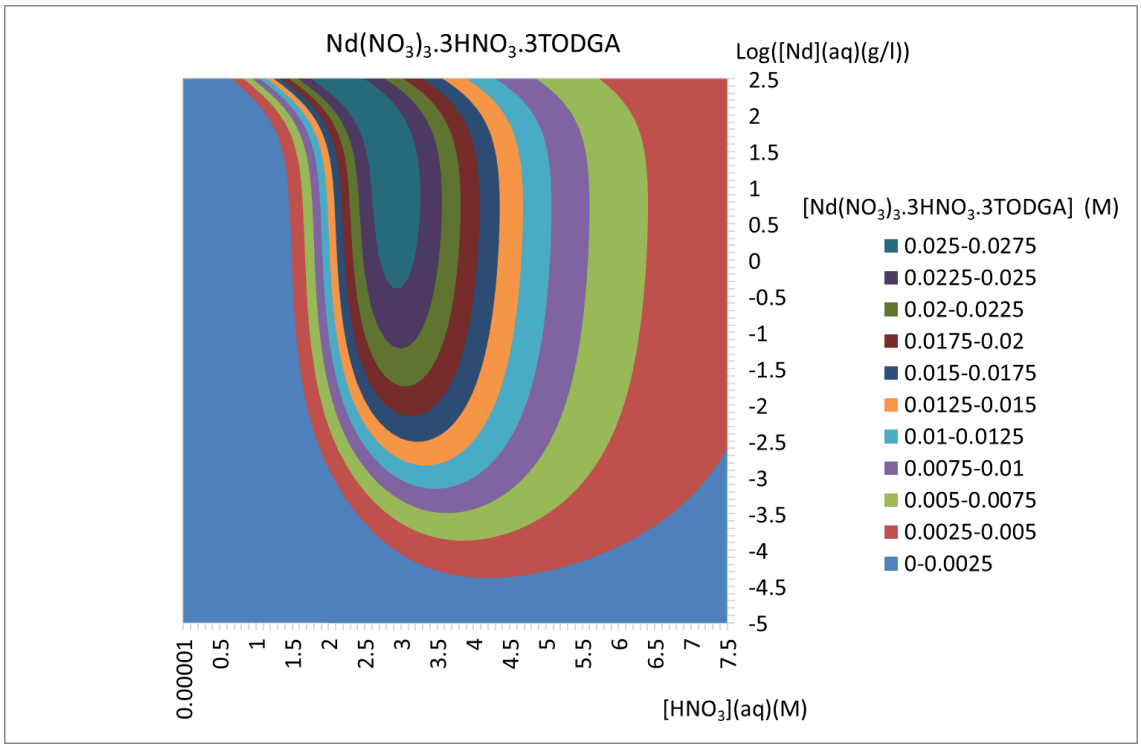

Figure 15: Predicted [$Nd(NO_3)_3.3HNO_3.3TODGA$] in 0.2M TODGA in 5% octanol / TPH at 20 °C.

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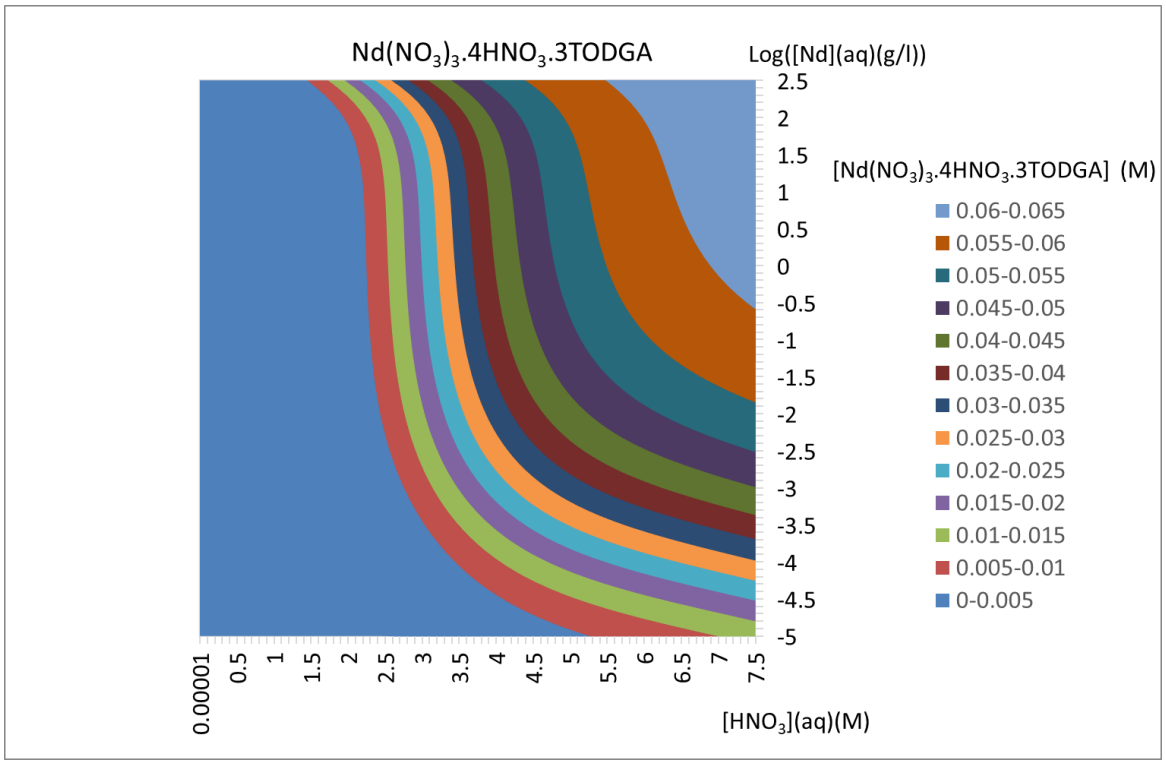

Figure 16: Predicted [$Nd(NO_3)_3.4HNO_3.3TODGA$] in 0.2M TODGA in 5% octanol / TPH at 20 °C.

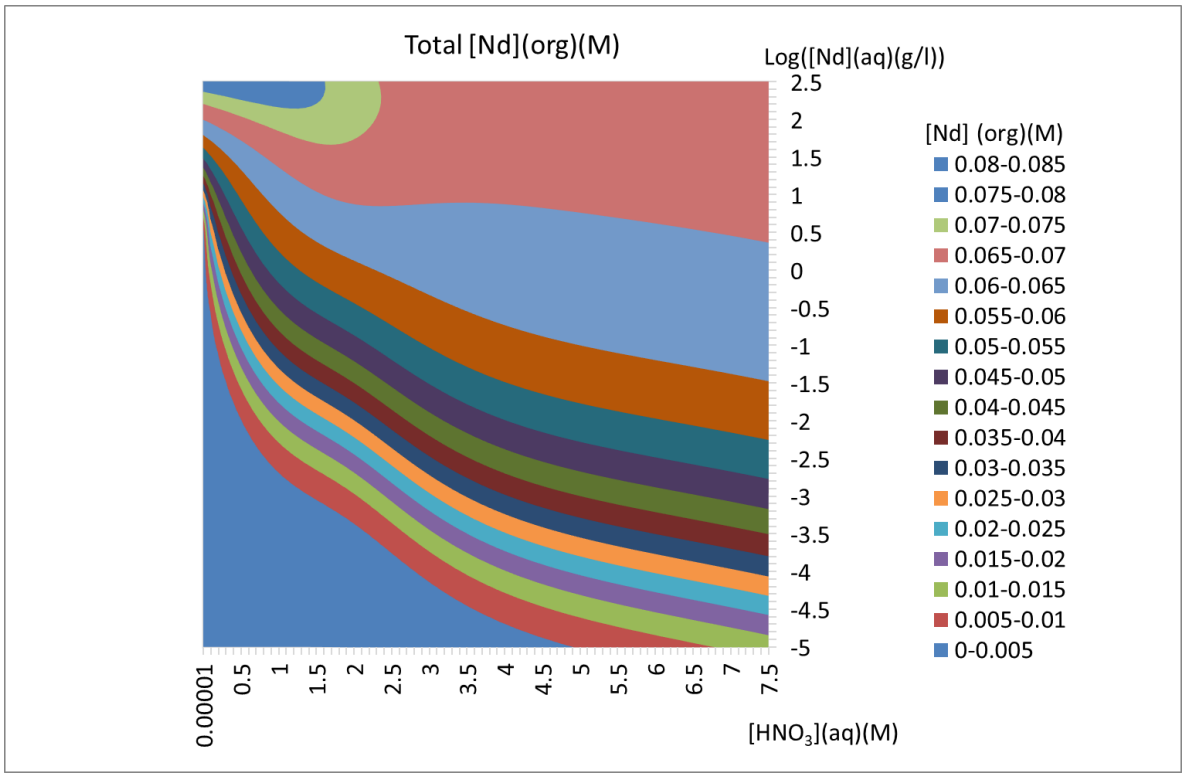

Figure 17: Predicted total organic [Nd] in 0.2M TODGA in 5% octanol / TPH at 20 °C.

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Table 4 below summarises the conditions under which each complex reaches maximum concentration when expressed as an absolute value and as a percentage of the extracted Nd.

Table 4: Relative importance of Nd Complexes in 0.2M TODGA in 5% octanol / TPH at 20 °C.

Complex	Max Concentration (M)	Acidity range for Max Concentration (M)	Aqueous [Nd] range for max concentration (g/l)
$Nd(NO_3)_3.2TODGA$	0.051	< 1.5	> 100
$Nd(NO_3)_3.3TODGA$	0.057	< 1.5	> 5
$Nd(NO_3)_3.2HNO_3.3TODGA$	0.018	2 – 3	> 0.1
$Nd(NO_3)_3.3HNO_3.3TODGA$	0.027	2.5 – 3.5	> 0.1
$Nd(NO_3)_3.4HNO_3.3TODGA$	0.063	> 5	> 0.1
	Max % Organic Nd	Acidity range for Max %Nd (M)	Aqueous [Nd] range for max % Nd (g/l)
$Nd(NO_3)_3.2TODGA$	61	< 1.5	> 100
$Nd(NO_3)_3.3TODGA$	99	< 1.5	< 100
$Nd(NO_3)_3.2HNO_3.3TODGA$	31	2 – 2.5	< 1
$Nd(NO_3)_3.3HNO_3.3TODGA$	43	2.5 – 3.5	< 1
$Nd(NO_3)_3.4HNO_3.3TODGA$	95	> 5	all

It is seen that under appropriate conditions any of the complexes can contribute significantly to the extracted Nd, although only $Nd(NO_3)_3.3TODGA$ and $Nd(NO_3)_3.4HNO_3.3TODGA$ become completely dominant in any region. In light of this the complexes were all assigned default weights (i.e. equal to their fitted value) for the purposes of the experimental design study.

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4.5. SCOPE FOR NEODYMIUM MODEL IMPROVEMENT

The model fits existing data well but the data do not cover the full problem space. Therefore, it would appear that there is potential for model improvement via expansion of the dataset. A number of areas in which additions to the existing data could be useful are apparent.

- There is a lack of solvent acid data for loaded systems. All the existing acid data relate to 0.1 M TODGA, 3M initial acid and 20 °C. Only initial Nd measurements are available from these experiments; no equilibrium Nd measurements were undertaken. To pin down the acid containing complexes with any degree of confidence will require solvent phase acidity to be measured over a wider range of conditions which should certainly include a range of acidities and a range of TODGA concentrations. The wider these ranges can be the better although potential problems could arise if extended beyond the known validity range of the acid extraction model (up to ~ 8M $[HNO_3]_{(aq)}$). The experiments would need to be undertaken with moderate or high Nd loadings.
- Also helpful for understanding the cross complexes would be some experiments aimed at separating out the effects of nitrate vs acidity. To this end, experiments that include an inextractable nitrate in the aqueous phase would be useful. We would need to satisfy ourselves that the nitrate in question does not coextract in any way with Nd – so some sort of initial experiment to check this would be appropriate. For example, inclusion of an inextractable nitrate like $NaNO_3$ to test for complexes like $Nd(NO_3)_3.2HNO_3.NaNO_3.3TODGA$. If we could then run experiments in which we had minimal acid present we should be able to separate out the acid free complexes from the acid / Nd cross complexes.
- We do not have any data for the temperature dependence of highly loaded systems. Some experiments in which the effect of temperature in such systems was explored would be useful. Measurements should include both Nd and acidity in both phases.
- A few measurements at extremes of acidity in loaded systems would be of value. At very low acidity we would learn something about the effect of nitrate by itself as distinct from acid (but see also above). Measurements at high acidity (which should include solvent phase acidity as well as Nd) could point us towards the existence of any previously unidentified complexes and might allow us to determine whether complexes with more than $4HNO_3$ exist or whether $4HNO_3$ is the limit. If a any complex with just one TODGA exists it might show up under these conditions. These measurements could also help identify the maximum acidity that can be used before third phase formation becomes an issue.
- All data collected to date have been at either 0.1 or 0.2M TODGA. Varying TODGA concentrations over a wider range would help with the identification of the number of TODGA ligands in the extracted complexes. We would benefit most from a series with trace Nd and a series in which there is enough Nd to saturate the solvent.

A general observation is that the error distribution associated with distribution value ‘measurements’ does not fit well with the distributions assumed in gPROMS due to it being a ratio of two actual measurements. Parameter estimation in gPROMS can be expected to work more reliably if it is fed the raw data i.e. aqueous and organic equilibrium concentrations. Equilibrium measurements will always be preferred to initial (pre-contact) measurements as these directly correspond to what is being calculated by the model.

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4.6. EXPERIMENT DESIGN FOR NEODYMIUM EXTRACTION

The model includes a number of fitted parameters including stability constants for the extracted complexes, the free energy associated with the complex formation and extraction and parameters associated with the definition of the activity coefficient correlation. The gPROMS experimental design capability was set up to look at design of experiments that would better define the stability constants and the free energy. Experiments specifically targeted at better definition of the activity coefficient correlation were not included due to the excessive number of variables involved.

4.6.1. GENERAL APPROACH TO GPROMS EXPERIMENT DESIGN

A considerable amount of effort was devoted to finding a procedure that would extract useful information from the experimental design feature of gPROMS. This section outlines the finally adopted procedure and the results for design of 'beaker' experiments to improve the existing model of Nd extraction.

A number of issues were identified with the experimental design as noted below:

1. The default tolerances for experimental design are too loose for this particular application. It is not known whether this applies more generally to other problems. The default setting is that the stationarity condition and Taylor conditions must be less than 10^{-3} for convergence to be considered to be attained. In practice it was found that this needs to be set considerably tighter as further significant evolution of the solution continued after the default tolerance was attained. For the work described below this tolerance was set at 10^{-7} [7]. The specified tolerance will not always be attained in the course of an experiment design with around half of all runs being terminated due to lack of progress (failure to improve the objective function between successive iterations). In such cases the best iteration of the design is reported and this was often found to be adequate.
2. The experiment design process is not guaranteed to find optimal designs and in general for anything other than the simplest cases the solution will not be optimal. This is probably a consequence of the high dimensionality of typical experiment design problems. In the work considered here for example an attempt to design a series of 10 beaker experiments with 4 control variables (initial concentrations of HNO_3, Nd and TODGA plus temperature) requires the minimisation of the objective function through manipulation of 40 degrees of freedom. This has two practical consequences, namely that run times can be very long and that the solution found is highly sensitive to the exact values of initial guesses employed.
3. It is important to note that the experiment design procedure will only suggest experiments that will allow improvement of an existing model without changing the structure of the model. It can therefore be expected to design an experimental program to provide better estimates of parameters within a model but it will not suggest experiments that would challenge the basic structure of the model (e.g. by showing the existence of a complex that is not included in the model). For example, consider a very simple model in which the relationship between a control variable, x, and measured variable y is described by the simple relationship y = kx + c. Experiment design is then used to define a series of

[7] In gPROMS this tolerance can be updated from solution parameters in the process used by the experiment design. Within solution parameters follow numerical solvers -> EDSolver -> MINLPSolver -> Optimisation Tolerance. The value entered here will apply to both the stationarity and Taylor conditions unless a non-zero value is specified for the latter in the same location. In general, it was found that the stationarity condition is the limiting tolerance.

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experiments to determine the values of k and c. The design will propose experiments in which x takes values of either x_{min} or x_{max} where x_{min} and x_{max} are bounds corresponding to the physical limits that can be investigated experimentally. The relative number of experiments at x_{min} and x_{max} will be determined by the variance model associated with the measured variable y. If the true behaviour of the system was non-linear then these proposed experiments would give no indication of the problem with the model because with experiments only carried out using only two values of x, a linear model will always be able to explain the two data points.

4. The objective function to be minimised during experiment design is a measure of the standard deviations of the parameters to be estimated that could be obtained by applying parameter estimation (model validation in gPROMS terminology) to the predicted results of the proposed experiments in conjunction with results of any previously conducted experiments. When there is only one parameter being determined the design is simply that which will allow the standard deviation of the parameter estimate to be minimised. When more than one parameter is to be estimated simultaneously, consideration needs to be given as to how the predicted standard deviations of the parameters are combined into a single objective function. In order to achieve this, weights are applied to each parameter being estimated. By default, weights are set equal to the expected value of the parameter[8] so that the objective function is a function of the standard deviation divided by the expected value of each parameter. The design will focus on producing experiments that minimise the weighted standard deviations of the parameters with the largest weighted standard deviation. The default weighting scheme is typically appropriate if each of the parameters is of equal importance in determining the output of the model, but it is not universally applicable. If a model contains a parameter to be estimated that makes only a very small contribution to the model output (say the stability constant of a complex that only ever accounts for a very small fraction of the extracted metal under consideration, and then only under a limited range of conditions) then the design with default weightings will focus experiments on better definition of this parameter (in the case of our minor extracted complex experiments would be suggested at conditions where the quantities of this complex are maximised). This would be the case despite accurate estimation of this parameter having very little bearing on overall model predictive capability. In such a case the weight associated with this parameter would need to be increased[9]. The other case in which weights might need to be manually adjusted is in the case where the accuracy with which we wish to determine a physical quantity is absolute rather than relative. An example might be the free energy associated with a complex where we would want to define it to tolerances of $\pm$ x kJ/mol rather $\pm$ x%. In general, it may be desirable to have weights associated with parameters informed by sensitivity studies to determine the relative importance of the different parameters in evaluation of ultimate model output.
5. The experiment design process is sensitive to the variance model associated measured variables, so consideration needs to be given to the accuracy with which measured quantities can be determined and how these accuracies depend on the absolute value of the measured variables. If a large variance is specified for a variable in a region of interest, then the experiment design is likely to suggest repeat experiments in this region in order to improve confidence in the value of the measured variable. Repeat experiments will not generally be suggested if the variance is small. When considering errors it should be noted that a significant deficiency of the gPROMS experiment design is that it does not allow for any variance of the control variables so that if we specify an experiment is to be run at 4 M

[8] gPROMS terminology can be rather misleading here. Setting a weight w of a parameter x results in the contribution to the objective function attributable to the standard deviation of x being divided by w. The weight set by the user is therefore the reciprocal of the weight used internally.

[9] Not decreased because gPROMS is effectively using the reciprocal of the weight.

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initial acidity gPROMS assumes that the experiment was run with initial acidity of 4.00000 M – not 4.00001 M.

6. In general, estimated parameters should be treated as a group. It is possible to perform experiment designs in which only a single parameter is being estimated at a time. In order to do this, the values of other parameters will be fixed in the design. Computationally this is much simpler than trying to design for determination of multiple parameters in parallel, but due to interaction between parameters, designs arising from such an approach are necessarily incomplete and optimal design of experiments needs to take account of uncertainty of all parameters under consideration simultaneously.

A number of different approaches were tried for application of experiment design in the case of the estimation of model parameters for the Nd extraction model. Taking everything at once to design a series of ten or twenty beaker experiments with determination of stability constants and free energy associated with the extraction of Nd was found to be impractical. Run times were extremely long (at least overnight) and resultant designs were clearly not optimal[10]. Running the design sufficiently often to obtain some indication of what may be near optimal in terms of the experiment design would be prohibitive in terms of computational time. An alternative approach of seeking to design for estimation of one or two model parameters at a time was found to be computationally tractable and results from this do offer some insights, but as noted above this approach is far from ideal due to failure to deal with interactions between uncertainties associated with parameters.

The approach eventually adopted is summarised below:

- Existing experimental results for distribution of Nd were taken into account in all designs so that the design would be focussed on aspects of the model that are poorly defined by existing experimental work.
- Experiment design was undertaken on an iterative basis with a single beaker experiment being designed during each iteration. At least three attempts at generating an experiment design were made for each iteration starting from different initial guesses, with the one that resulted in the smallest value of the objective function being accepted. After each iteration the control variable values in the newly designed experiment were rounded to experimentally convenient numbers and the resultant experiment was simulated, the results of the simulation being added as a pre-existing experiment for the next iteration. All model parameters to be estimated were included in every iteration of the design. Thus, at each iteration the single experiment that would most improve definition of the model parameters is designed on the assumption that previously designed experiments have been run and returned results in line with predictions of the model as currently formulated. An implication of this is that if an experiment throws up unexpected results then there would be potential to redesign subsequent experiments in light of the new information which would give a new better optimised set of experiments going forward. Whether any such redesign is worthwhile would need to be considered. after seeing how far the results of initial experiments diverge from those predicted by the model.
- Parameters to be estimated were the stability constants of complexes from Table 1 with non-zero stability constants:
    - $Nd(NO_3)_3.2TODGA$
    - $Nd(NO_3)_3.3TODGA$
    - $Nd(NO_3)_3.2HNO_3.3TODGA$

[10] Designed experiments and the objective functions associated with them were found to be highly sensitive to initial guesses and in many cases some of the proposed experiments were no different from the initial guesses.

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- $Nd(NO_3)_3.3HNO_3.3TODGA$
- $Nd(NO_3)_3.4HNO_3.3TODGA$

and ΔG for the Nd extraction. Weighting of the parameters adopted the gPROMS default with weights set equal to the nominal values as defined in Table 3. In all experiments it was assumed that the control variables were the temperature and initial concentrations of acid and Nd in the aqueous and of TODGA in the solvent. Initial acid concentrations were constrained to lie in the range 0.01 to 7 M, initial Nd concentrations in the range 0.01 to 150 g/L and TODGA concentrations in the range 0.01 to 0.3 M. Temperatures were limited to the range 10 – 50 °C. Experiments were assumed to comprise contact of solvent and aqueous in a 1:1 ratio with full equilibrium being attained. The solvent was assumed to be 5% octanol by volume. It was assumed that the solvent did not contain any extracted acid or metal at the start of the experiment.

- Measured variables were assumed to be nitric acid and neodymium concentrations in both phases, (the acid concentrations being expressed in mol/L and the metal concentrations in mg/L). Measurements are taken after the attainment of equilibrium. For measurement of metals a constant relative variance model was adopted with variance equal to 5% of the measured value in both phases. For acid measurement for both phases a heteroscedastic variance model was assumed with variance given by $0.05|x|^{0.6}$ where x is the measured value. This variance is summarised in Table 5 below for selected acidities.

Table 5: Assumed variance of nitric acid measurements.

$[HNO_3](M)$	Variance (M)	Variance (%)
0.01	0.003155	31.55
0.01585	0.004159	26.24
0.02512	0.005482	21.83
0.03981	0.007227	18.15
0.0631	0.009527	15.1
0.1	0.01256	12.56
0.1585	0.01656	10.45
0.2512	0.02183	8.689
0.3981	0.02877	7.227
0.631	0.03793	6.011
1	0.05	5
1.585	0.06591	4.159
2.512	0.08689	3.459
3.981	0.1145	2.877
6.31	0.151	2.393
10	0.1991	1.991

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4.6.2. RESULTS OF NEODYMIUM EXPERIMENT DESIGN

The process described in the previous section was run through 20 iterations. Table 6 below presents the initial conditions for the optimised experiment and the rounded version of these carried forward into subsequent calculations. Table 7 presents the predicted values of the measured variables for the optimised and rounded experiments. Table 8 then presents the standard deviation resulting from parameter estimation as each of the proposed experiments is added to the set of experiments used for the estimation.

Table 6: Control Variables for Beaker Trials from Experiment design.

Expt No	Initial values from Optimisation				Rounded Values carried forward			
	[TODGA] (M)	[HNO_3] (aq)(M)	[Nd](aq) (g/l)[11]	T (°C)	[TODGA] (M)	[HNO_3] (aq)(M)	[Nd](aq) (g/l)	T (°C)
1	0.02829	7	0.01	45.98	0.03	7	0.01	45
2	0.3	1.232	150	10	0.3	1.25	150	10
3	0.1145	3.008	0.01	50	0.1	3	0.01	50
4	0.02737	7	0.01	20.99	0.03	7	0.01	20
5	0.02821	7	0.01	29.37	0.03	7	0.01	30
6	0.01	0.4693	0.01	18.7	0.01	0.5	0.01	20
7	0.0436	3.16	0.01	25.14	0.04	3	0.01	25
8	0.02708	7	0.01	28.24	0.03	7	0.01	30
9	0.3	2.41	13.92	10	0.3	2.4	14	10
10	0.02508	7	0.01	22.4	0.025	7	0.01	20
11	0.02598	7	0.01	29.06	0.025	7	0.01	30
12	0.3	2.496	13.78	10	0.3	2.5	14	10
13	0.07598	3.371	0.01	50	0.075	3.5	0.01	50
14	0.3	0.539	142.7	10	0.3	0.5	150	10
15	0.02836	7	0.01	35.73	0.03	7	0.01	35
16	0.3	0.5259	140.9	10	0.3	0.5	150	10
17	0.05806	3.302	0.01	38.38	0.06	3.5	0.01	40
18	0.3	0.5394	141.3	10	0.3	0.5	150	10
19	0.3	2.945	13.48	10	0.3	3	14	10
20	0.0279	7	0.01	32.78	0.03	7	0.01	35

[11] In line with normal nuclear industry practice concentrations of heavy metals have been expressed in g/L. To convert to neodymium molarity divide by 144.242. It is assumed that experiments will use natural neodymium. Fission derived neodymium will have a slightly greater atomic weight.

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It is apparent that a number of these experiments are essentially repeats.

- Experiments 1, 4, 5, 8, 15 and 20 are all under the same chemical conditions (0.03M TODGA, 7 M HNO_3, trace Nd) albeit at different temperatures.
- Experiments 9, 12 and 19 are also under broadly similar conditions (0.3 M TODGA, 14 g/l Nd and 2.5 to 3.0 HNO_3, 10 °C).
- Experiments 16 and 18 are exact repeats (0.3 M TODGA, 0.5M HNO_3, 150 g/l Nd, 10 °C). Experiment 2 is at slightly higher acidity (1.25 M) but is otherwise similar.

Table 7: Predicted Values for Measured Variables of designed experiments.

Expt No	Experiment as first optimised				Experiment with rounded control variables			
	$[HNO_3]$ (aq) (M)	$[HNO_3]$ (org)(M)	[Nd](aq) (g/l)	[Nd] (org)(g/l)	$[HNO_3]$ (aq) (M)	$[HNO_3]$ (org)(M)	[Nd](aq) (g/l)	[Nd] (org)(g/l)
1	6.902	0.1252	0.05616	10.01	6.898	0.1303	0.04527	10.02
2	1.105	0.1323	133300	17300	1.12	0.1356	133400	17260
3	2.901	0.1172	0.02401	10.05	2.905	0.1039	0.03468	10.04
4	6.878	0.1549	0.02154	10.04	6.871	0.1625	0.01554	10.05
5	6.886	0.1443	0.02884	10.04	6.884	0.1476	0.02459	10.04
6	0.4685	0.000809	9.963	0.1369	0.4991	0.000878	9.961	0.1398
7	3.099	0.06776	0.07625	10.01	2.947	0.05874	0.1213	9.966
8	6.887	0.1432	0.03107	10.04	6.884	0.1476	0.02459	10.04
9	2.228	0.1964	550.6	13310	2.22	0.1945	592.5	13350
10	6.884	0.1474	0.03003	10.04	6.881	0.1511	0.02706	10.04
11	6.89	0.1395	0.03655	10.03	6.893	0.1359	0.04281	10.03
12	2.3	0.212	467.8	13250	2.304	0.212	575.1	13360
13	3.282	0.1001	0.03774	10.04	3.406	0.1051	0.03216	10.04
14	0.5167	0.02326	124600	18300	0.4794	0.02142	131700	18490
15	6.893	0.1364	0.03722	10.03	6.889	0.1412	0.03043	10.04
16	0.5051	0.02161	122800	18260	0.4794	0.02142	131700	18490
17	3.228	0.08278	0.05193	10.03	3.418	0.09201	0.0387	10.04
18	0.5174	0.02294	123300	18260	0.4794	0.02142	131700	18490
19	2.687	0.2809	271	13120	2.738	0.2861	495.5	13420
20	6.891	0.139	0.03456	10.03	6.889	0.1412	0.03043	10.04

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Table 8: Predicted standard deviations of parameters obtained from parameter estimation including the predicted results of successive designed experiments.

	Stability Constant					ΔG
Complex	$Nd(NO_3)_3$ .2TODGA	$Nd(NO_3)_3$ .3TODGA	$Nd(NO_3)_3$ .2HNO_3 .3TODGA	$Nd(NO_3)_3$ .3HNO_3 .3TODGA	$Nd(NO_3)_3$ .4HNO_3 .3TODGA	J/mol
Initial Value	1590.9	990308	80545	21809	714.99	-90761
Initial SD	257	26190	19330	4591	123.6	1411
Initial SD/value	16.15%	2.64%	24%	21.05%	17.29%	-1.55%
SD after Expt 1	171.1	25700	10120	3602	50.56	1409
" " " 2	150.3	25690	9984	3275	50.07	1408
" " " 3	147	25690	9855	2577	50.05	1396
" " " 4	139.3	25370	7457	2573	30.95	1160
" " " 5	137.2	25370	7026	2542	26.16	1156
" " " 6	133.2	23540	6962	2535	26.05	1149
" " " 7	132.2	23290	6717	2013	25.75	1044
" " " 8	131	23280	6490	1977	22.98	1043
" " " 9	121	23270	6461	1951	22.63	1023
" " " 10	120.7	23240	6167	1946	19.8	988.3
" " " 11	120.4	23240	6076	1925	18.53	987.8
" " " 12	114	23230	6043	1901	18.41	975.1
" " " 13	114	23190	6031	1843	18.25	933.2
" " " 14	109.2	23160	5885	1839	18.24	928.3
" " " 15	108.8	23130	5842	1805	17.49	920.3
" " " 16	104.6	23110	5714	1802	17.48	916.3
" " " 17	104.6	23110	5714	1725	17.47	915.7
" " " 18	101	23080	5603	1723	17.46	912.2
" " " 19	99.16	23070	5600	1691	17.37	893
" " " 20	98.9	23050	5564	1662	16.78	887.3
Final SD/Value	6.22%	2.33%	6.91%	7.62%	2.35%	-0.98%

It will be noted that standard deviations reduce after the addition of each experiment.

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5. LANTHANUM

5.1. AVAILABLE LANTHANUM EXTRACTION DATA

Three data series relating to the extraction of lanthanum (exemplar light lanthanide element) into TODGA / octanol mixtures were available as summarised below.

Series 1:

A series of 6 data points for extraction of trace (20 mg/l) lanthanum into 0.2 M TODGA in 5% octanol / TPH. Experiments were undertaken at 20 ℃ and covered the initial acidity range 0.15 – 1.0 M HNO_3. Other lanthanides and actinides were also present at trace levels. These are assumed in this work not to impact on the extraction of La. This is the same as series 1 of the Nd extraction experiments

Series 2:

A series of 40 data points giving distribution values for trace concentrations (10 mg/l initial aqueous concentration) of various actinides and lanthanides including La into 0.1 or 0.2 M TODGA / 5% octanol at 10, 20, 30, 40, 50 °C and initial HNO_3 (aqueous) concentrations of 0.11, 0.3, 0.98, 2.9M. This is the same as series 2 of the Nd extraction experiments, but unlike with Nd, distribution values were recorded for all permutations of temperature, acidity and TODGA concentration.

Series 3:

A series of 20 data points giving distribution values for lanthanum at various initial aqueous La concentrations in range 1.4 – 150 g/l into 0.1 M TODGA in 5% octanol / TPH at 20 ℃. Initial aqueous acid was 3.0 M HNO_3 in all cases.

5.2. FITTED LANTHANUM EXTRACTION MODEL

A model was fitted using gPROMS parameter estimation to work with the acid extraction model described in section 3 (model A). The La model was structured in a similar way to that for Nd described in the previous section.

Data handling was as for Nd; where both aqueous and organic equilibrium concentrations were reported, these were used in the fitting with the assumption that 100% mass balance applied (reported initial concentrations being ignored) and where initial concentrations and distribution values were reported these were converted into equilibrium aqueous and organic concentrations for use in the fitting, 100% mass balance being assumed.

The lanthanum concentration measurements were assumed to have a heteroscedastic variance, the parameters associated with this being fitted in the course of the gPROMS parameter estimation. Heteroscedastic variance has the form $\sigma = \omega |x|^{\gamma}$ where σ is the variance, ω and γ are fitted parameters and x is the value of the measurement. As for Nd, the same variance model was applied for all measurements. The fitted values are summarised in Table 9 below.

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Table 9: Variance model parameters for previously performed La distribution experiments.

Measured Quantity	Units	ω	γ
Lanthanum concentration	mg/L	0.083	0.9179
	mol/L	0.031395	0.9179

The fitting of the La distribution model itself included: fitting of an activity coefficient expression to use for La; the fitting of stability constants of the various solvent phase complexes; and the fitting of the free energy associated with formation of the complexes. The same free energy was assumed to apply to formation of all the complexes. The fitted activity coefficient expression is as below. Note that this is a function of the total nitrate concentration and is independent of the La concentration which will typically be much less than the nitrate concentration.

$$\gamma_{La} = \left[\frac{0.042418}{(0.28915 + [NO_3^-])^{2.28337}} + 0.41398 + 0.18565[NO_3^-] - 0.073348[NO_3^-]^2 + 0.018387[NO_3^-]^3\right]$$

Figure 18 below shows the relationship between the La activity coefficient and nitrate concentration given by this equation.

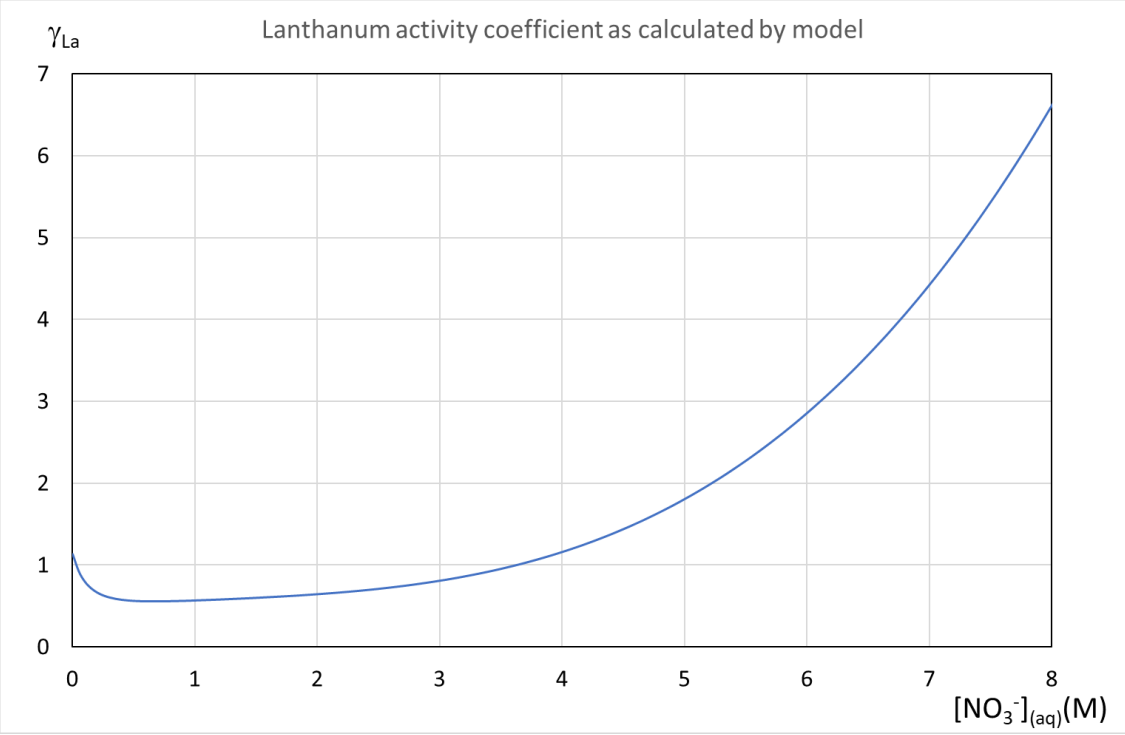

Figure 18: Calculation of the La activity coefficient.

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The activity coefficient from this equation is used to calculate the organic lanthanum in the same way organic neodymium was calculated in section 4.2.

The fitted stability constants used in the model were as in Table 10 below. Note that the model allows for the presence of a range of complexes for which the stability constants were fitted by gPROMS as zero.

Table 10: Fitted Stability constants for the La Distribution Model.

Complex	Constant	Value
$La(NO_3)_3$.TODGA	β_{La01}	0
$La(NO_3)_3$.2TODGA	β_{La02}	10788
$La(NO_3)_3$.3TODGA	β_{La03}	137400
$La(NO_3)_3$.4TODGA	β_{La04}	0
$La(NO_3)_3.HNO_3$.TODGA	β_{La11}	0
$La(NO_3)_3.HNO_3$.2TODGA	β_{La12}	0
$La(NO_3)_3.HNO_3$.3TODGA	β_{La13}	0
$La(NO_3)_3.HNO_3$.4TODGA	β_{La14}	0
$La(NO_3)_3.2HNO_3$.TODGA	β_{La21}	0
$La(NO_3)_3.2HNO_3$.2TODGA	β_{La31}	0
$La(NO_3)_3.2HNO_3$.3TODGA	β_{La23}	0
$La(NO_3)_3.2HNO_3$.4TODGA	β_{La24}	0
$La(NO_3)_3.3HNO_3$.TODGA	β_{La31}	0
$La(NO_3)_3.3HNO_3$.2TODGA	β_{La32}	0
$La(NO_3)_3.3HNO_3$.3TODGA	β_{La33}	0
$La(NO_3)_3.3HNO_3$.4TODGA	β_{La34}	0
$La(NO_3)_3.4HNO_3$.TODGA	β_{La41}	0
$La(NO_3)_3.4HNO_3$.2TODGA	β_{La42}	0.017646
$La(NO_3)_3.4HNO_3$.3TODGA	β_{La43}	339.89
$La(NO_3)_3.4HNO_3$.4TODGA	β_{La44}	0

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Temperature dependence was determined by an estimated value of ΔG = -80613.2, with the pre-exponential terms set such that the temperature correction factor evaluates to 1 at 20 °C.

5.3. LANTHANUM EXTRACTION MODEL PERFORMANCE

The model was run against the available data with results as shown in Figure 19 through Figure 25 below.

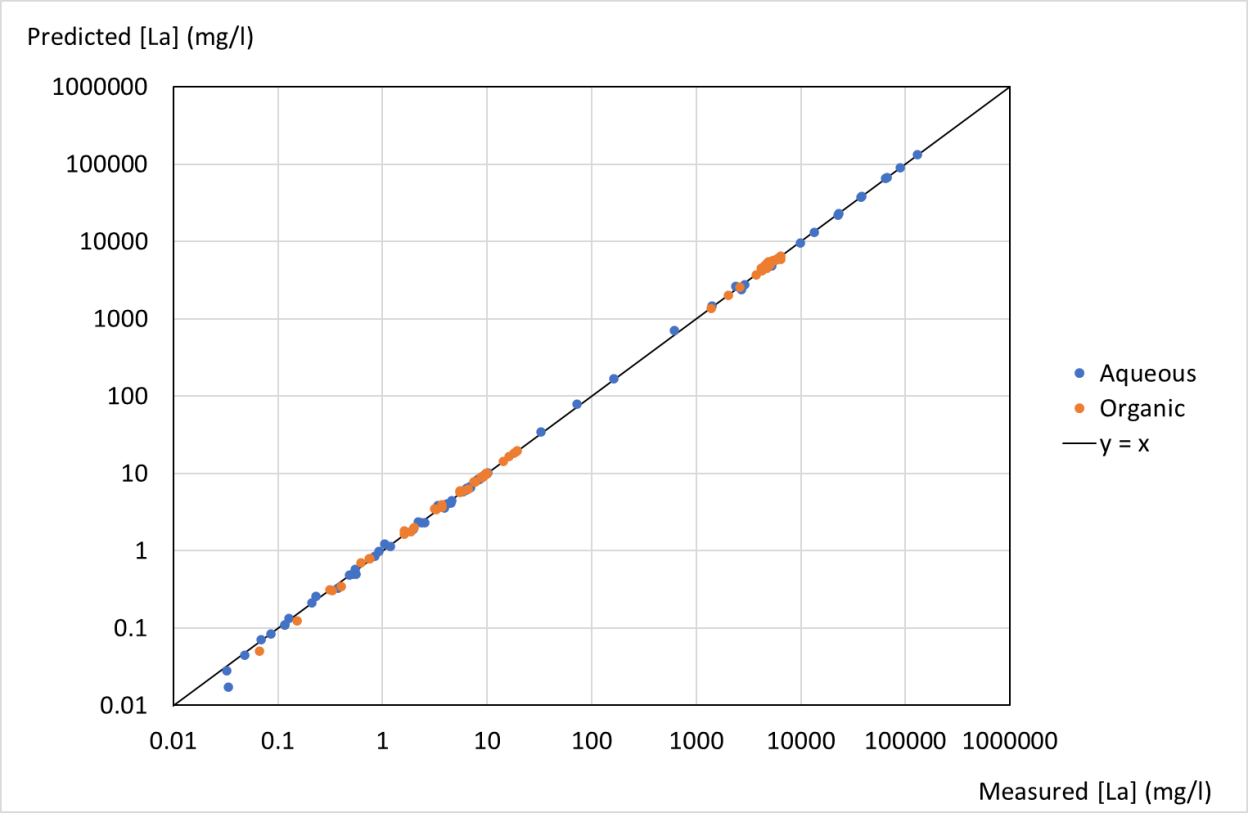

Figure 19: Modelled vs experimental La Concentrations.

In the below figures showing model predictions vs experimental data the error bars are the model-predicted variance of the measurement at the point in question.

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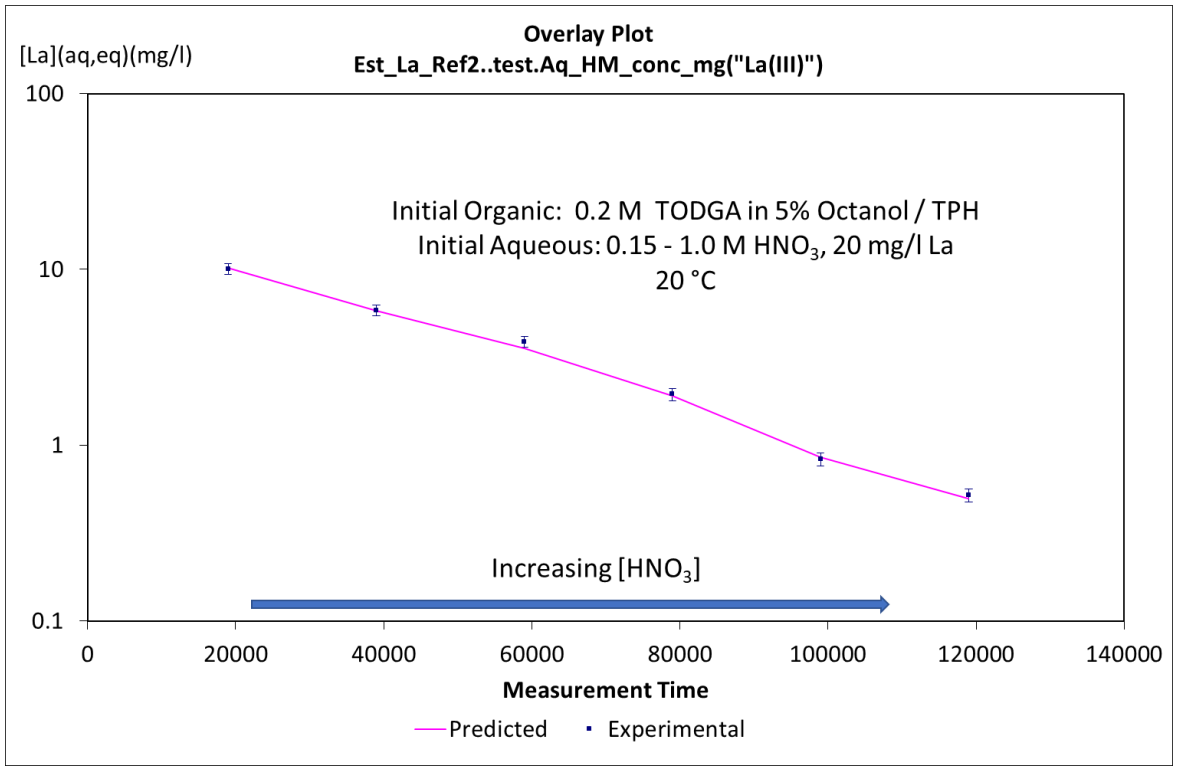

Figure 20: Fit of model to experimental data (Aq La data series 1).

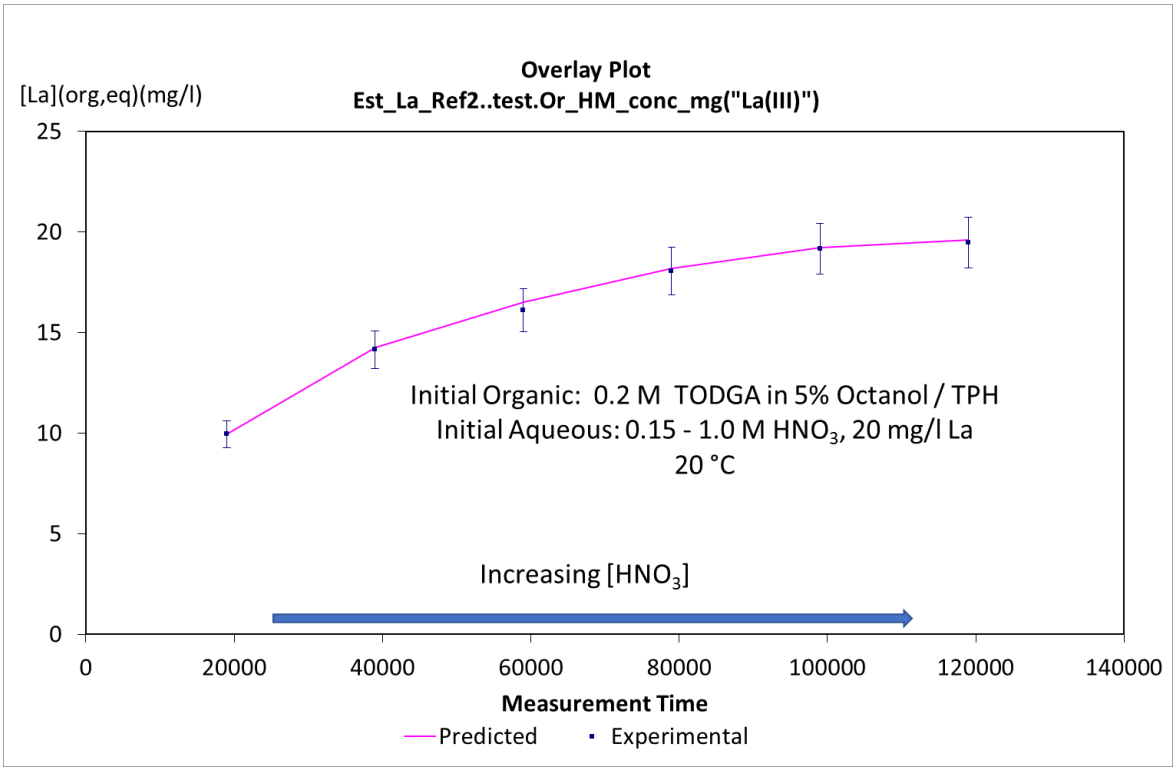

Figure 21: Fit of model to experimental data (Or La data series1).

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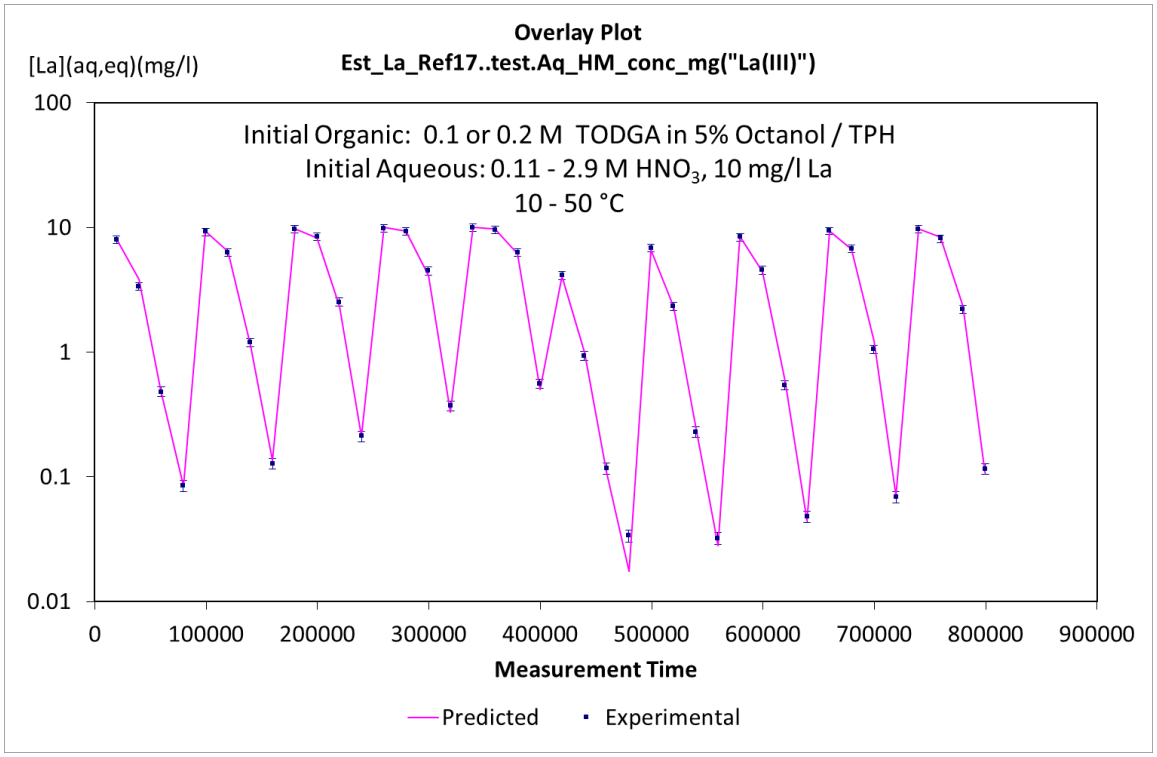

Figure 22: Fit of model to experimental data (Aq La data series 2).

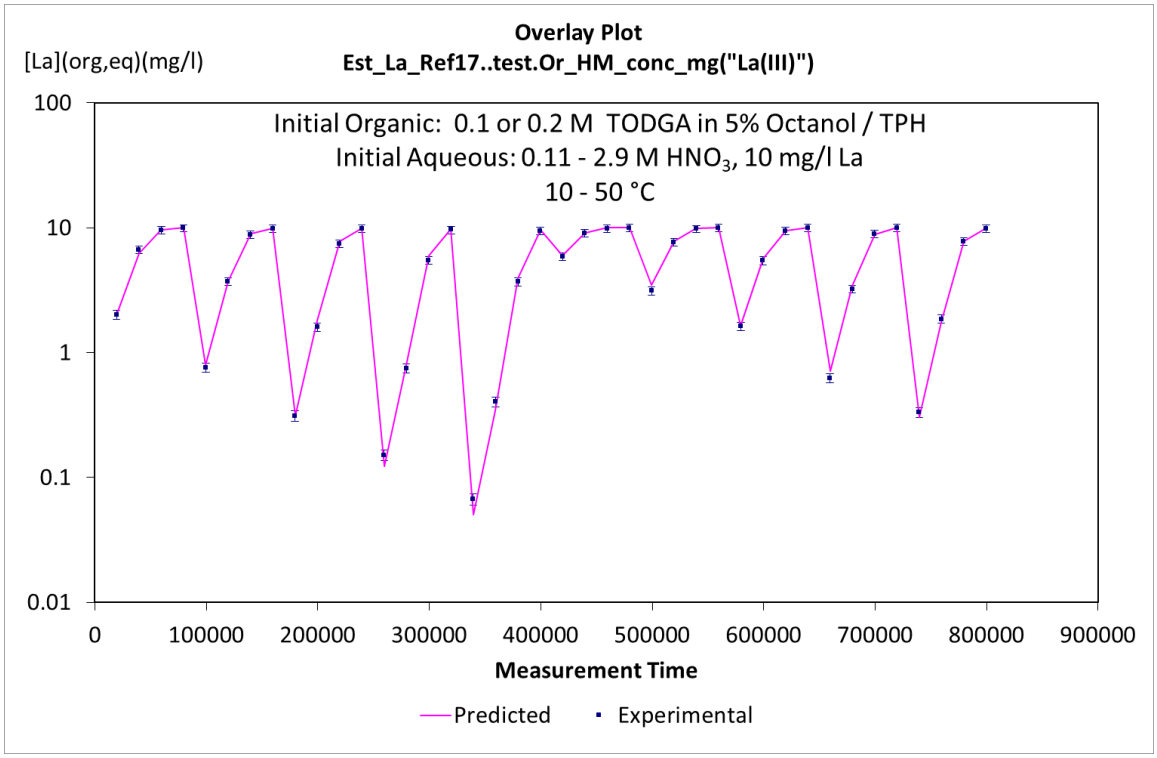

Figure 23: Fit of model to experimental data (Or La data series 2).

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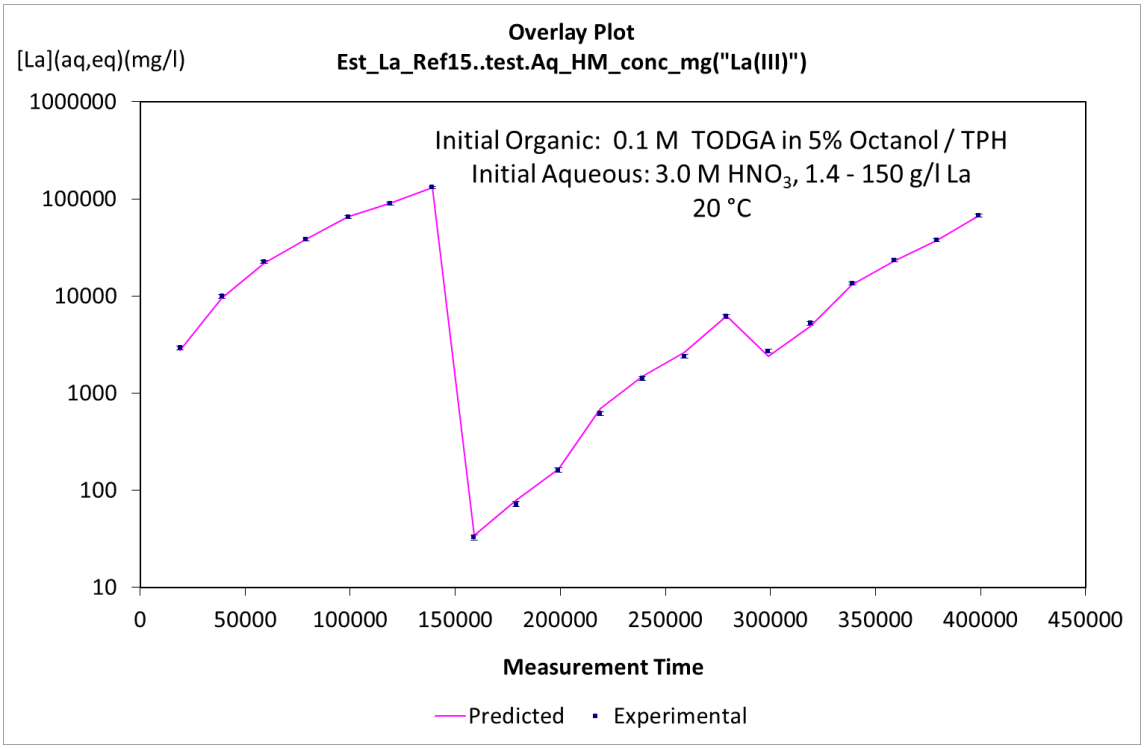

Figure 24: Fit of model to experimental data (Aq La data series 3).

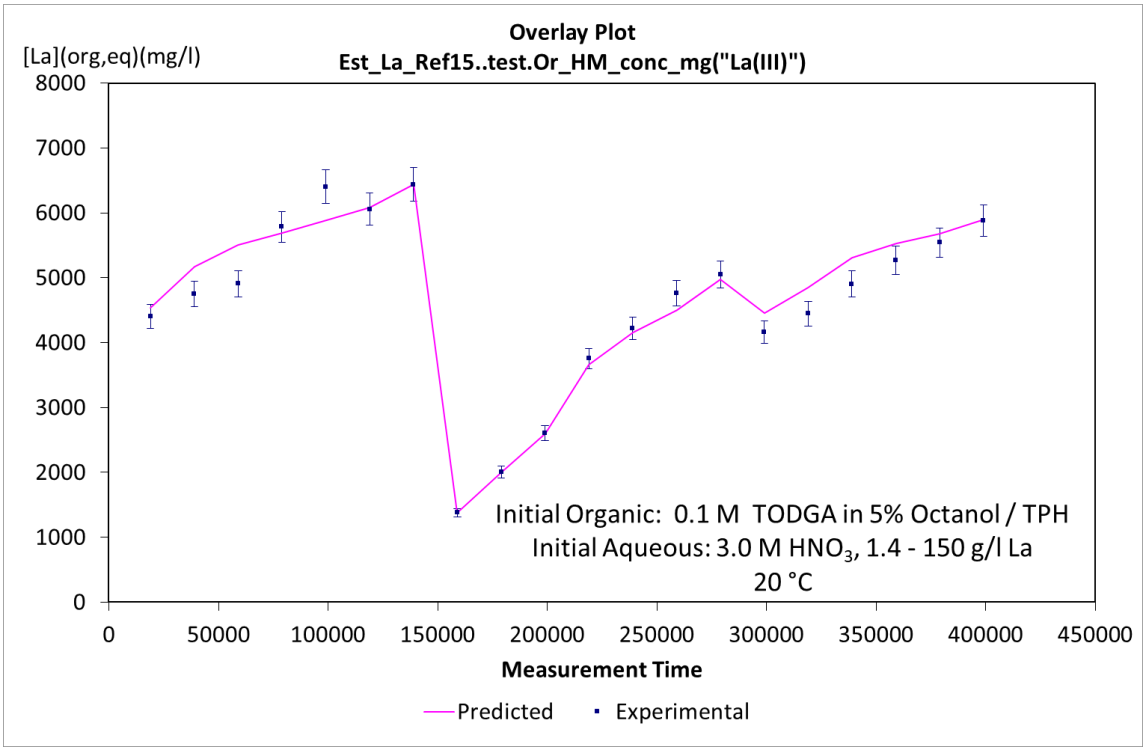

Figure 25: Fit of model to experimental data (Or La data series 3).

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These figures demonstrate a generally good fit to the available data, although it is important to note that as this is the data that was used to fit the model a good fit is to be expected. Testing of the model against data not used in the fitting would give a better assessment of the quality of the model, particularly if that data lies in ranges not covered by the data used in the fitting. A particular concern with regard to the La model (compared to the Nd model) is that there were no data available for the amount of acid extracted with high metal loadings. This makes it difficult to distinguish between the effect of the lanthanum activity coefficient and the amount of acid in lanthanum / acid / TODGA complexes.

5.4. ORGANIC LANTHANUM SPECIATION

To give some idea of the relative importance of the different complexes being proposed by this model, the model was run for extraction of La into 0.2M TODGA in 5% octanol / TPH at 20 °C for a range of aqueous acid and La concentrations. The molar concentrations of the different organic phase La complexes and the percentage of the extracted La accounted for by each complex predicted by these runs are shown in Figure 26 through Figure 34 below.

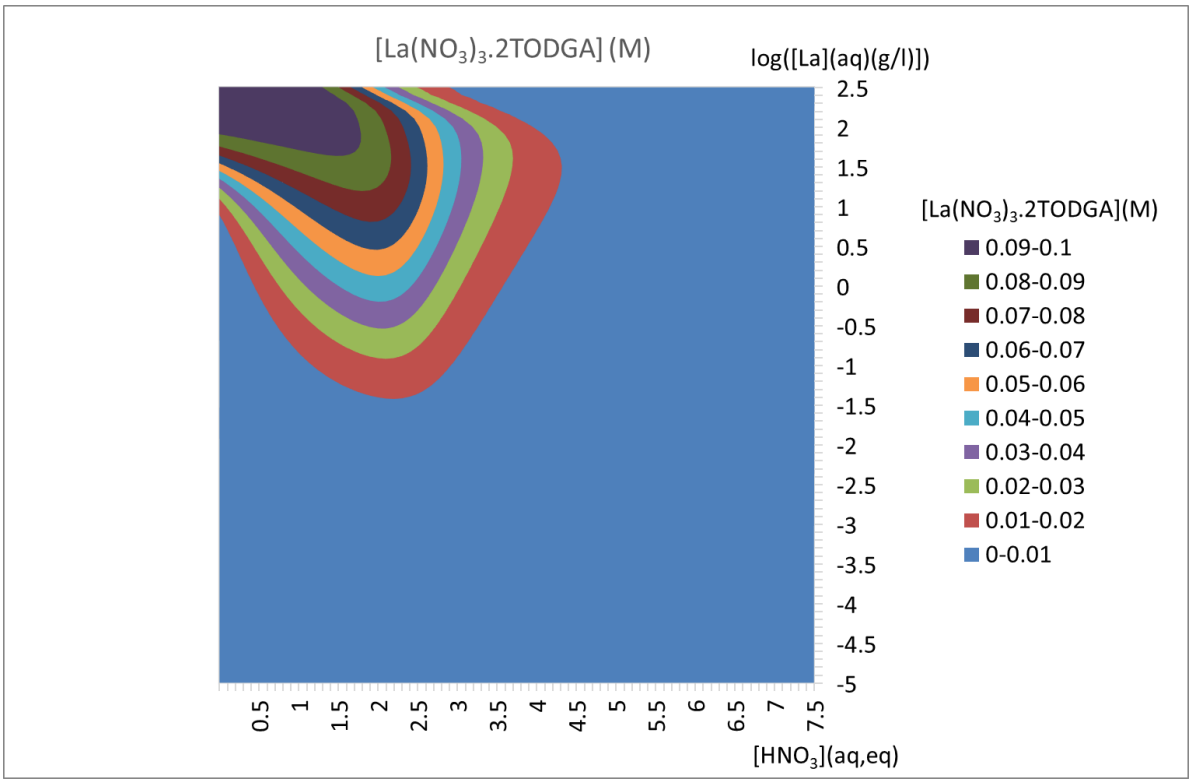

Figure 26: Predicted [La(NO₃)₃.2TODGA] in 0.2M TODGA in 5% octanol / TPH at 20 °C.

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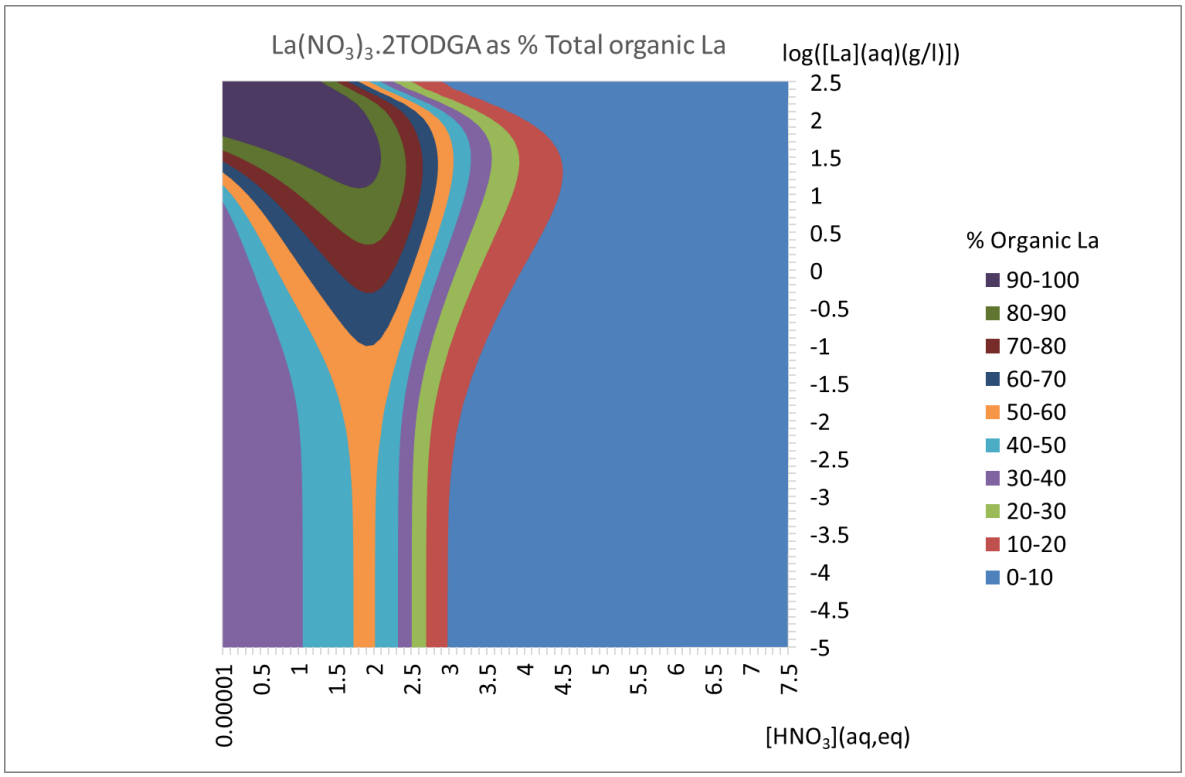

Figure 27: Predicted %$La(NO_3)_3$.2TODGA in 0.2M TODGA in 5% octanol / TPH at 20 °C.

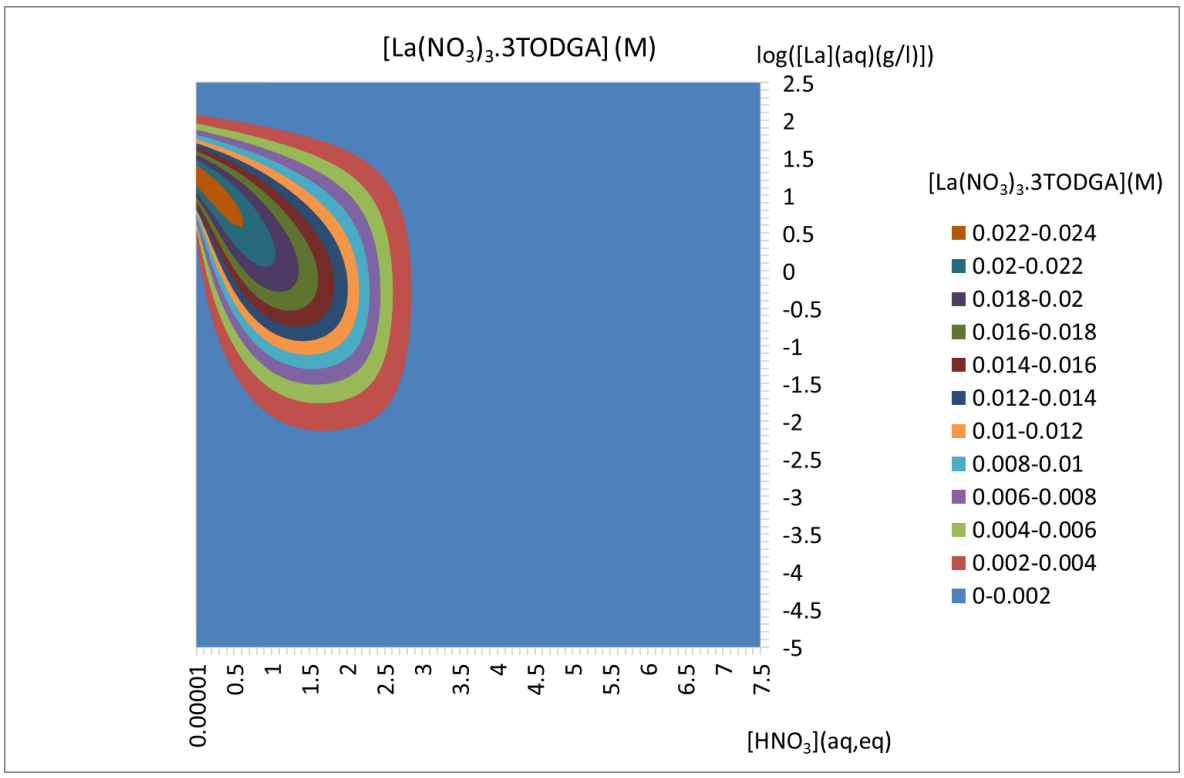

Figure 28: Predicted [$La(NO_3)_3$.3TODGA] in 0.2M TODGA in 5% octanol / TPH at 20 °C.

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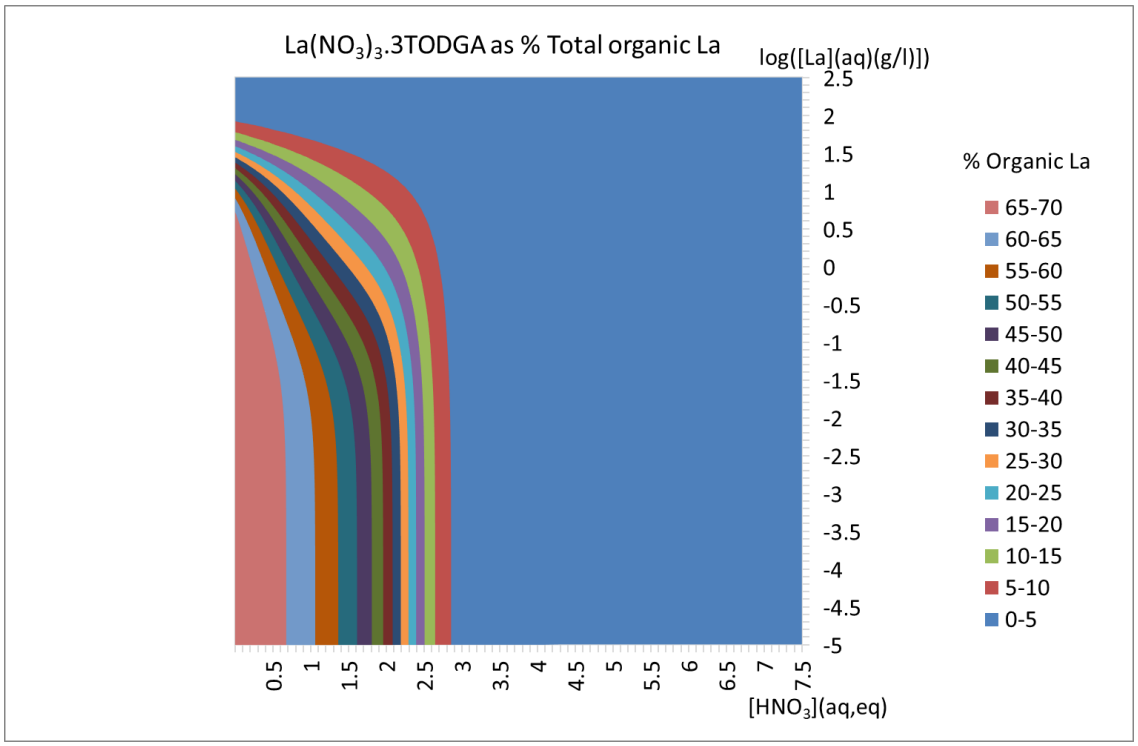

Figure 29: Predicted %$La(NO_3)_3$.3TODGA in 0.2M TODGA in 5% octanol / TPH at 20 °C.

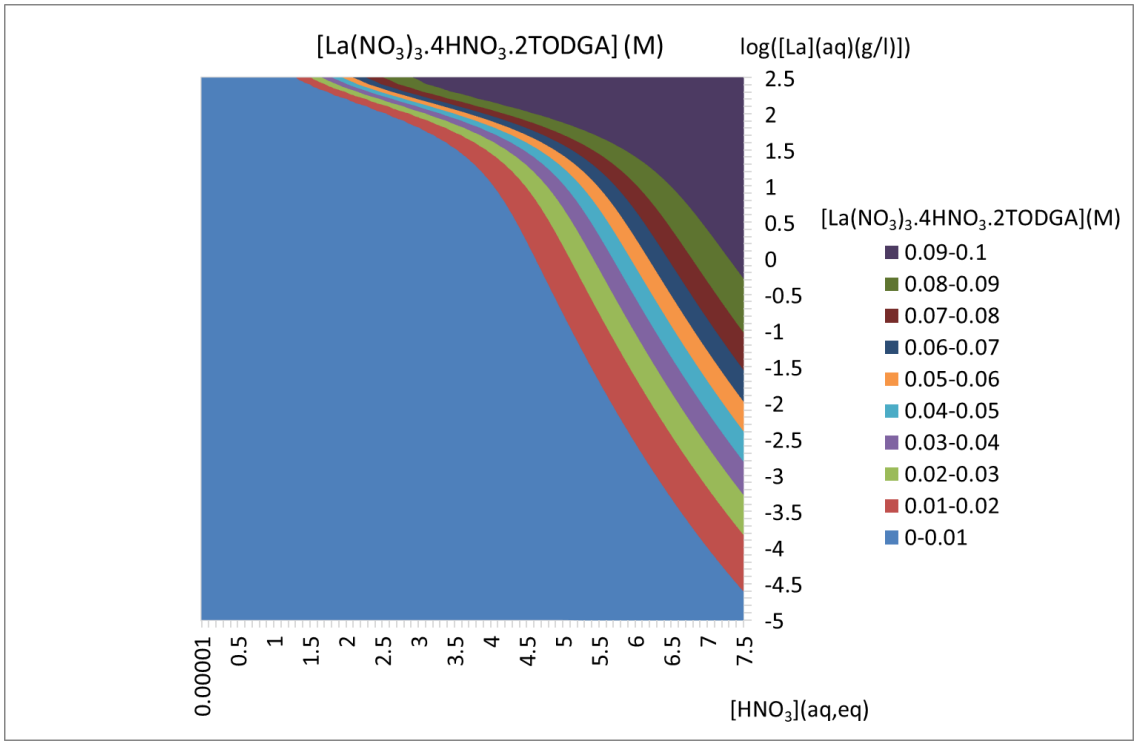

Figure 30: Predicted [$La(NO_3)_3$.4HNO_3.2TODGA in 0.2M TODGA in 5% octanol / TPH at 20 °C.

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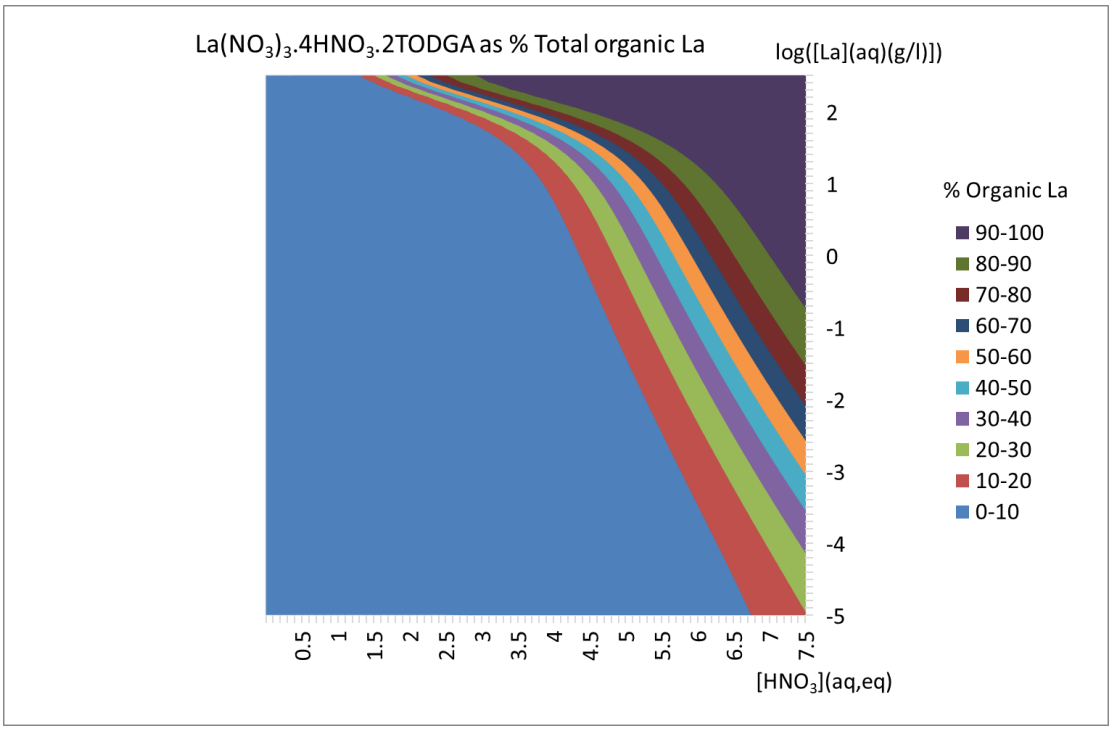

Figure 31: Predicted %$La(NO_3)_3.4HNO_3.2TODGA$ in 0.2M TODGA in 5% octanol / TPH at 20 °C.

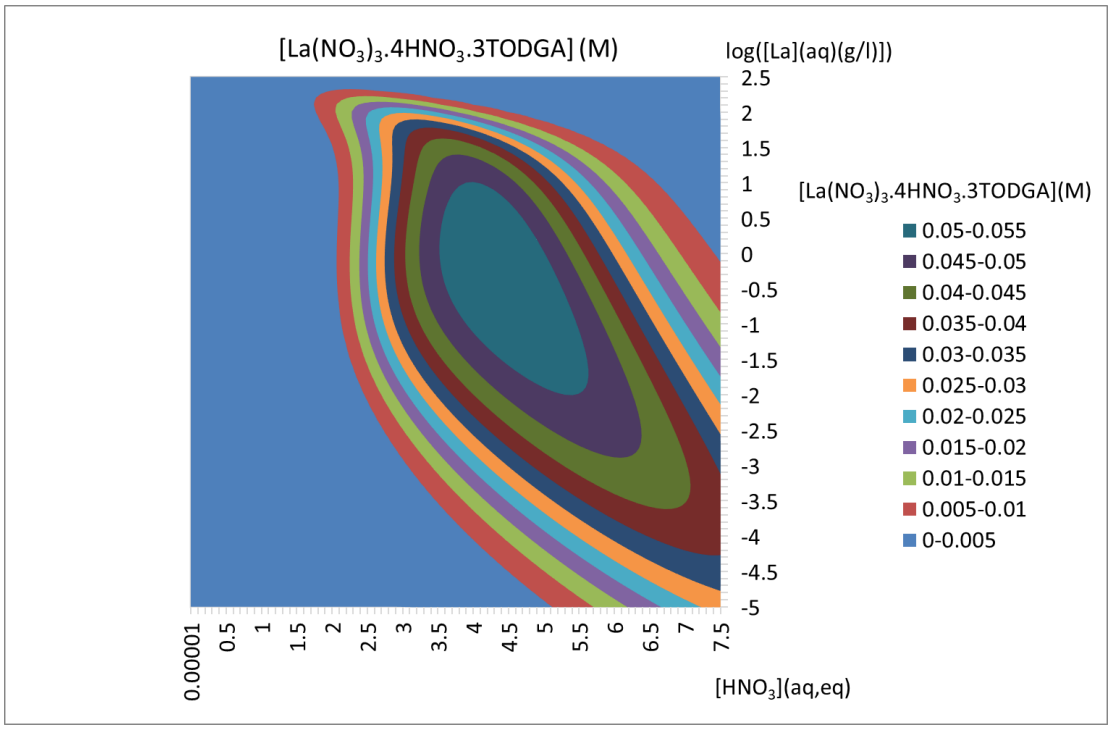

Figure 32: Predicted [$La(NO_3)_3.4HNO_3.3TODGA$ in 0.2M TODGA in 5% octanol / TPH at 20 °C.

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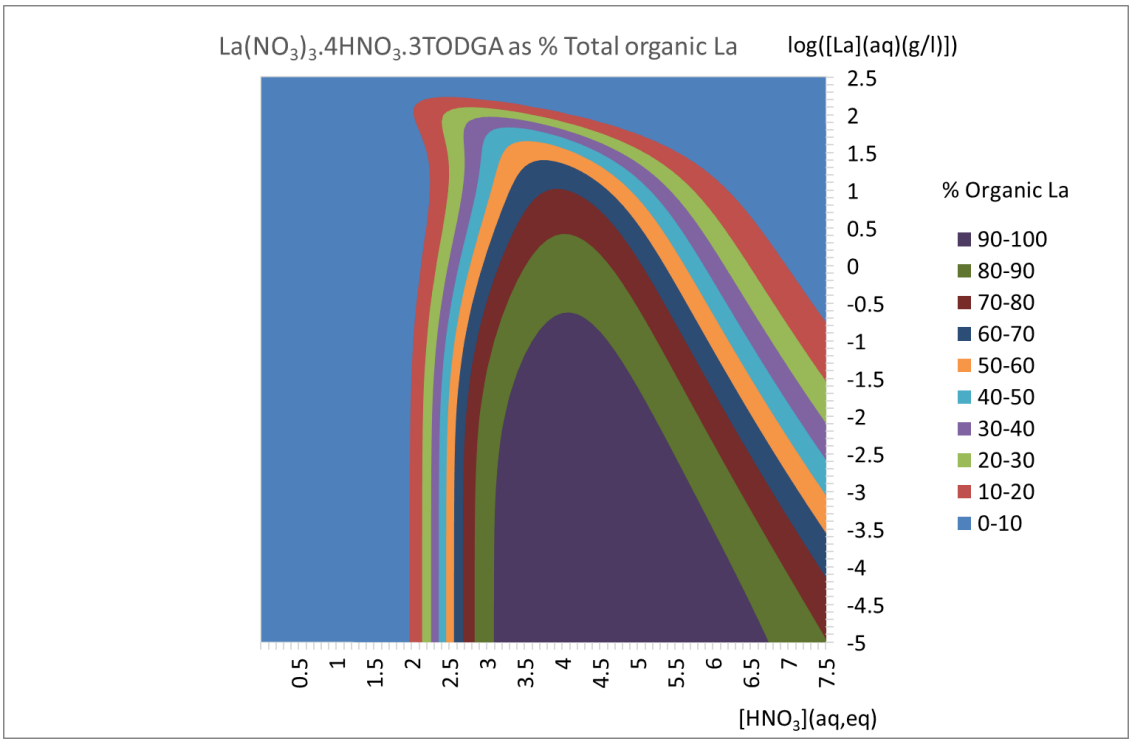

Figure 33: Predicted %La(NO₃)₃.4HNO₃.3TODGA in 0.2M TODGA in 5% octanol / TPH at 20 °C.

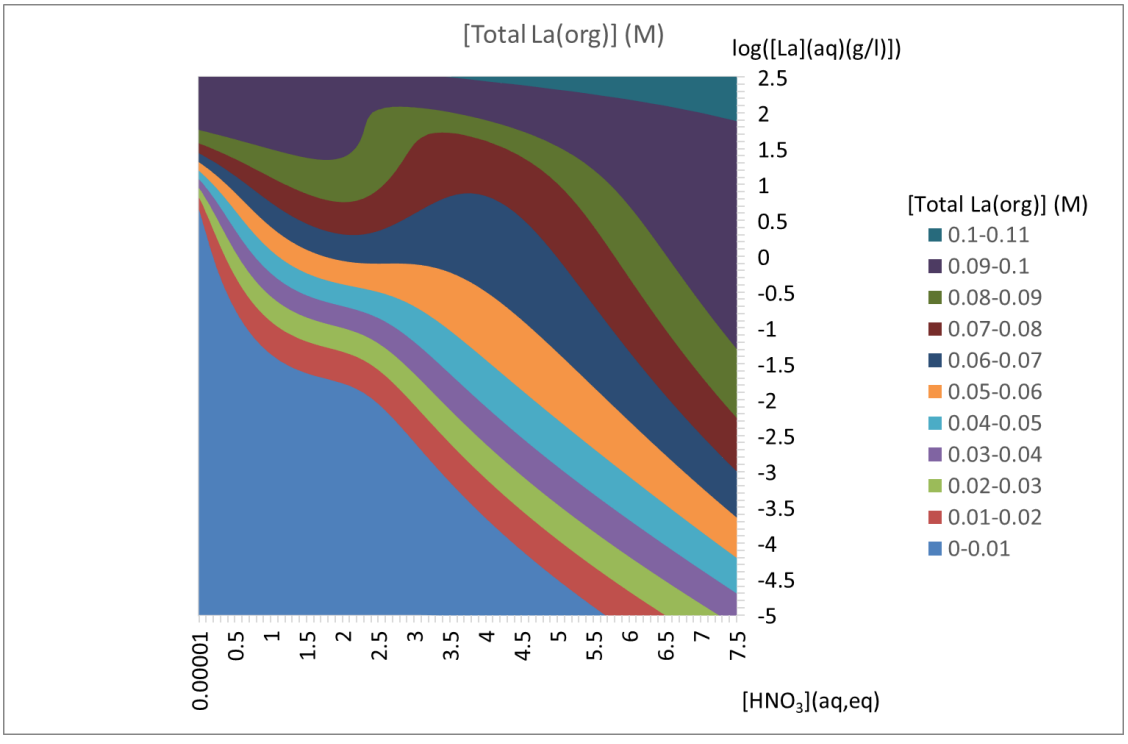

Figure 34: Predicted total organic [La] in 0.2M TODGA in 5% octanol / TPH at 20 °C.

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From these figures it can be seen that there are conditions under which each of the complexes is predicted to make up the majority of the extracted La, although given that $La(NO_3)_3.3TODGA$ is only dominant under low loading conditions the absolute amounts of this complex that can be present are less than for the other complexes.

5.5. SCOPE FOR LANTHANUM MODEL IMPROVEMENT

The model gives a good fit to the available data and the outstanding questions relate mainly to the applicability of the model in regions that are not covered by the data used to fit the model. From visual inspection of the data the obvious gaps are:

- Data at high acidity. Existing data is limited to 3 M HNO_3 or less. Higher acidity data will be required to better define the correlation for La activity.
- Data for co-extraction of HNO_3. The existence of La / HNO_3 / TODGA complexes is inferred from the relationship between La distribution and acidity, but a direct measure of acid extracted in the presence of significant La loading of the solvent would give more certainty regarding the existence and quantification of such complexes.
- Data with a wider range of TODGA concentrations. Existing data relates only to 0.1 and 0.2 M TODGA. Data over a wider range of TODGA concentrations would give more confidence in the split between complexes containing two TODGA ligands vs those containing three.

5.6. EXPERIMENT DESIGN FOR LANTHANUM EXTRACTION

The process described in the previous section for Nd was repeated for La and run through 7 iterations. The number of experiments designed was less than for Nd as the 95% t-values generated were larger than for Nd, indicating that confidence in the values of stability constants could be achieved with a lower number of experiments. This is probably due to the proposed Nd complexes including $Nd(NO_3)_3.nHNO_3.3TODGA$ for n = 2, 3, 4 which are difficult to distinguish experimentally. For La the initial model fit indicated good confidence in the values of all the stability constants except that for $La(NO_3)_3.4HNO_3.2TODGA$ where the 95% confidence limits span zero, suggesting that there is a possibility the complex does not actually exist. An aim of further experimental work would be to determine whether this complex actually exists and if so pin down its stability constant value with a greater level of confidence. The limits placed on the experimental conditions were as for the Nd experiment design i.e. 0.01 – 0.3 M [TODGA], 0.01 – 7.0 M initial [HNO_3], 0.01 – 150 g/l [La] and 10 – 50 °C.

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Table 11 below presents the initial conditions for the optimised experiment and the rounded version of these carried forward into subsequent calculations. Table 12 presents the predicted values of the measured variables for the optimised and rounded experiments. Table 13 then presents the standard deviations resulting from parameter estimation as each of the proposed experiments is added to the set of experiments used for the estimation.

Table 11: Control Variables for Beaker Trials from Experiment design.

Expt No	Initial values from Optimisation				Rounded Values carried forward			
	[TODGA] (M)	[HNO_3] (aq)(M)	[La](aq) (g/l)[12]	T (°C)	[TODGA] (M)	[HNO_3] (aq)(M)	[La](aq) (g/l)	T (°C)
1	0.3	7	13.02	10	0.3	7	13	10
2	0.3	0.01	0.01	10	0.3	0.01	0.01	10
3	0.0102	0.8569	0.05107	13.54	0.01	0.9	0.05	15
4	0.3	7	13.76	10	0.3	7	14	10
5	0.01	1.692	0.01	50	0.01	1.7	0.01	50
6	0.3	2.864	15.69	10	0.3	2.9	16	10
7	0.3	6.018	0.0168	10	0.3	6	0.01	10

The suggested experiments are at the extremes of the TODGA concentration range, at a range of different acidities and mostly at the extremes of the temperature range. Initial La concentrations are either effectively trace or in the range 13 -16 g/l. The latter is sufficient to bring the solvent close to saturation and is likely to have been identified as a suitable concentration due to its proximity to the boundary at which extracted La would switch from predominantly three TODGA complexes to predominantly two TODGA complexes.

[12] In line with normal nuclear industry practice heavy metal concentrations are expressed in g/l. To covert to mol/L divide by 138.905. This assumes natural lanthanum will be used for experiments. Fission derived lanthanum will have a slightly larger atomic weight.

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Table 12: Predicted Values for Measured Variables of designed experiments.

Expt No	Experiment as first optimised				Experiment with rounded control variables			
	$[HNO_3]$ (aq) (M)	$[HNO_3]$ (org)(M)	[La](aq) (g/l)	[La] (org)(g/l)	$[HNO_3]$ (aq) (M)	$[HNO_3]$ (org)(M)	[La](aq) (g/l)	[La] (org)(g/l)
1	6.536	0.5748	0.8751	12860	6.536	0.5748	0.8574	12840
2	0.009983	2.73E-05	9.959	0.1414	0.009983	2.73E-05	9.959	0.1414
3	0.8542	0.002808	47.46	3.713	0.8972	0.002938	46.68	3.429
4	6.536	0.5745	1.764	0.5745	6.536	0.5751	2.226	13830
5	1.687	0.005201	9.938	0.1635	1.695	0.005256	9.936	0.1652
6	2.665	0.2172	1055	14570	2.697	0.2212	1218	14720
7	5.452	0.67	2.162E-5	16.66	5.435	0.6685	1.329E-5	9.96

Table 13: Predicted standard deviations of parameters obtained from parameter estimation including the predicted results of successive designed experiments.

	Stability Constant				
Complex	$La(NO_3)_3$ .2TODGA	$La(NO_3)_3$ .3TODGA	$La(NO_3)_3$ .4HNO_3 .2TODGA	$La(NO_3)_3$ .4HNO_3 .3TODGA	ΔG
Initial Value	10790	137400	0.01765	339.9	-80610
Initial SD	473.5	5485	0.01351	14.96	864.8
Initial SD/value	4.39 %	3.99 %	76.6 %	4.40 %	-1.07 %
SD after Expt 1	424.9	5198	0.000881	14.53	861.4
" " " 2	417.6	4594	0.000878	14.41	791.7
" " " 3	355.9	4383	0.000877	14.26	788.6
" " " 4	355.7	4380	0.000549	14.05	785.9
" " " 5	314.6	4030	0.000547	13.7	692.8
" " " 6	279.5	3915	0.000544	13.3	685.6
" " " 7	279.2	3903	0.000542	10.44	662.3
Final SD/Value	2.59 %	2.84 %	3.07 %	3.07 %	-0.822 %

It will be noted that standard deviations reduce after the addition of each experiment.

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Table 14: 95% t-values obtained from parameter estimation including the predicted results of successive designed experiments.

	Stability Constant				ΔG
Complex	$La(NO_3)_3$ .2TODGA	$La(NO_3)_3$ .3TODGA	$La(NO_3)_3$ .4HNO_3 .2TODGA	$La(NO_3)_3$ .4HNO_3 .3TODGA	J/mol
Initial 95% t-value	11.51	12.65	0.6595	11.48	47.08
95% t-value after Expt 1	12.84	13.36	10.13	11.82	47.31
" " " " 2	13.06	15.12	10.16	11.93	51.47
" " " " 3	15.33	15.86	10.18	12.06	51.7
" " " " 4	15.34	15.87	16.27	12.24	51.88
" " " " 5	17.35	17.25	16.32	12.55	58.88
" " " " 6	19.53	17.76	16.41	12.93	59.5
" " " " 7	19.56	17.82	16.49	16.48	61.63

95% t-values[13] increase with each subsequent experiment. It will be noted that only experiment one is required to greatly improve the accuracy with which the stability constant of the $La(NO_3)_3.4HNO_3.2TODGA$ complex is known.

[13] 95% t-values are equal to the ratio of the mean value to the 95% confidence limit

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6. YTTERBIUM

6.1. AVAILABLE YTTERBIUM EXTRACTION DATA

Two data series relating to the extraction of ytterbium (an exemplar heavy lanthanide element) into TODGA / octanol mixtures were available as summarised below.

Series 1:

A series of 21 data points giving distribution values for trace concentrations (10 mg/l initial aqueous concentration) of various actinides and lanthanides including Yb into 0.1 or 0.2 M TODGA / 5% octanol at 10, 20, 30, 40, 50 °C and initial HNO_3 (aqueous) concentrations of 0.11, 0.3, 0.98 M. This is the same as series 2 of the Nd extraction experiments, but the conditions under which distribution values are available are much more limited. This is due to the highly extractable nature of Yb, which leads to limit of detection problems when measuring aqueous concentrations. No measurements were available at 2.9 M and even at 0.98 M acidity usable distribution values could only be obtained for extraction into 0.1M TODGA and even then only at the higher temperatures.

Series 2:

A series of 7 data points giving distribution values for ytterbium at various initial aqueous concentrations in range 5 – 15 g/l into 0.1 M TODGA in 5% octanol / TPH at 20 ℃. Initial aqueous acid was 3.0 M HNO_3 in all cases. Reported data were $[Yb]_{(aq,\ ini)}$, $[Yb]_{(org,\ eq)}$ and $D_{Yb.}$ Under these conditions the solvent will be nearly saturated.

6.2. FITTED YTTERBIUM EXTRACTION MODEL

A model was fitted using gPROMS parameter estimation to work with acid extraction model A described in section 3. The model was structured in a similar way to that for Nd described in section 4.2.

Data handling was as for Nd. In the case of the series 1 data, equilibrium aqueous and organic Yb concentrations were calculated from the initial aqueous concentration and the distribution values. These values were then used in the fitting. A similar approach is used for series 2 data. In this case the equilibrium organic concentration was reported as well as the distribution value giving some redundancy in the reported data. The equilibrium organic concentration reported differs slightly from the value calculated from the distribution value and initial aqueous concentration although the differences are small. The latter has been used in fitting of the model.

The ytterbium concentration measurements were assumed to have a heteroscedastic variance, the parameters associated with this being fitted in the course of the gPROMS parameter estimation. Heteroscedastic variance has the form $\sigma = \omega|x|^{\gamma}$ where σ is the variance, ω and γ are fitted parameters and x is the value of the measurement. The fitted values are summarised in Table 15 below

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Table 15: Variance model parameters for previously performed Yb distribution experiments.

Measured Quantity	Units	ω	γ
Ytterbium concentration	mg/L	0.17958	0.88013
	mol/L	0.042302	0.88013

The value of omega obtained here indicates that the fit obtained is not as good as for some other species. Variance amounts to 31% at 0.01 mg/l, 18% at 1 mg/l, 10% at 0.1 g/l and 6% at 6 g/l. The fitting of the Yb distribution model included; fitting of an activity coefficient expression to use for Yb, fitting of stability constants of the various solvent phase complexes and fitting of the free energy associated with formation of the complexes. The same free energy was assumed to apply to formation of all the complexes. The fitted activity coefficient expression is as below. Note that this is a function of the total nitrate concentration and is independent of the Yb concentration which will typically be much less than the nitrate concentration.

$$\gamma_{Yb} = \left[\frac{0.0897075}{(0.289781 + [NO_3^-])^{2.01053}} + 0.5 + 0.296845[NO_3^-] - 0.05[NO_3^-]^2 + 0.01[NO_3^-]^3\right]$$

Figure 35 below shows the relationship between the Yb activity coefficient and nitrate concentration given by this equation.

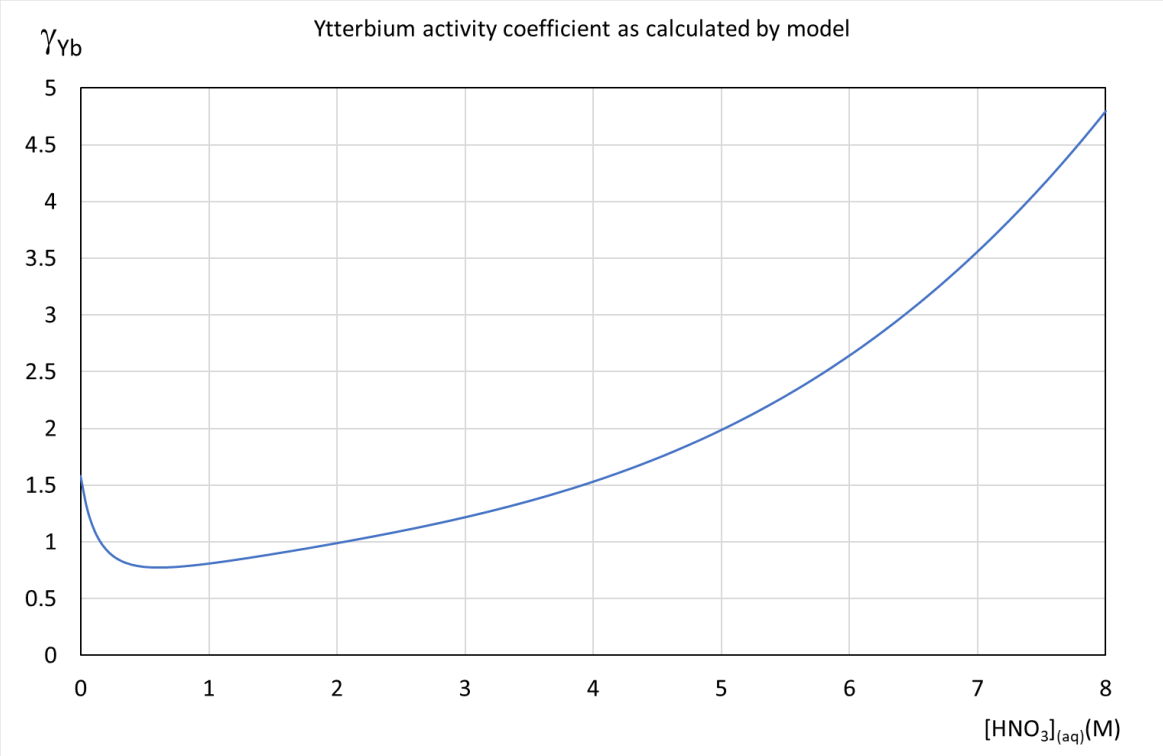

Figure 35: Calculation of the Yb activity coefficient.

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The activity coefficient from this equation is used to calculate the organic ytterbium in the same way organic neodymium was calculated in section 4.2.

The fitted stability constants used in the model were as in Table 16 below. Note that the model allows for the presence of a range of complexes for which the stability constants were fitted as zero.

Table 16: Fitted Stability constants for the Yb Distribution Model.

Complex	Constant	Value
$Yb(NO_3)_3$.TODGA	β_{Yb01}	0
$Yb(NO_3)_3$.2TODGA	β_{Yb02}	44283
$Yb(NO_3)_3$.3TODGA	β_{Yb03}	3.0045 E7
$Yb(NO_3)_3$.4TODGA	β_{Yb04}	0
$Yb(NO_3)_3.HNO_3$.TODGA	β_{Yb11}	0
$Yb(NO_3)_3.HNO_3$.2TODGA	β_{Yb12}	0
$Yb(NO_3)_3.HNO_3$.3TODGA	β_{Yb13}	1.9050 E7
$Yb(NO_3)_3.HNO_3$.4TODGA	β_{Yb14}	0
$Yb(NO_3)_3.2HNO_3$.TODGA	β_{Yb21}	0
$Yb(NO_3)_3.2HNO_3$.2TODGA	β_{Yb31}	0
$Yb(NO_3)_3.2HNO_3$.3TODGA	β_{Yb23}	0
$Yb(NO_3)_3.2HNO_3$.4TODGA	β_{Yb24}	0
$Yb(NO_3)_3.3HNO_3$.TODGA	β_{Yb31}	0
$Yb(NO_3)_3.3HNO_3$.2TODGA	β_{Yb32}	0
$Yb(NO_3)_3.3HNO_3$.3TODGA	β_{Yb33}	0
$Yb(NO_3)_3.3HNO_3$.4TODGA	β_{Yb34}	0
$Yb(NO_3)_3.4HNO_3$.TODGA	β_{Yb41}	0
$Yb(NO_3)_3.4HNO_3$.2TODGA	β_{Yb42}	0
$Yb(NO_3)_3.4HNO_3$.3TODGA	β_{Yb43}	287985
$Yb(NO_3)_3.4HNO_3$.4TODGA	β_{Yb44}	0

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Temperature dependence was determined by a fitted value of ΔG = -96164.3, with the pre-exponential terms set such that the temperature correction factor evaluates to 1 at 20 °C.

6.3. YTTERBIUM EXTRACTION MODEL PERFORMANCE

The model was run against the available data with results as shown in Figure 36 through Figure 40 below.

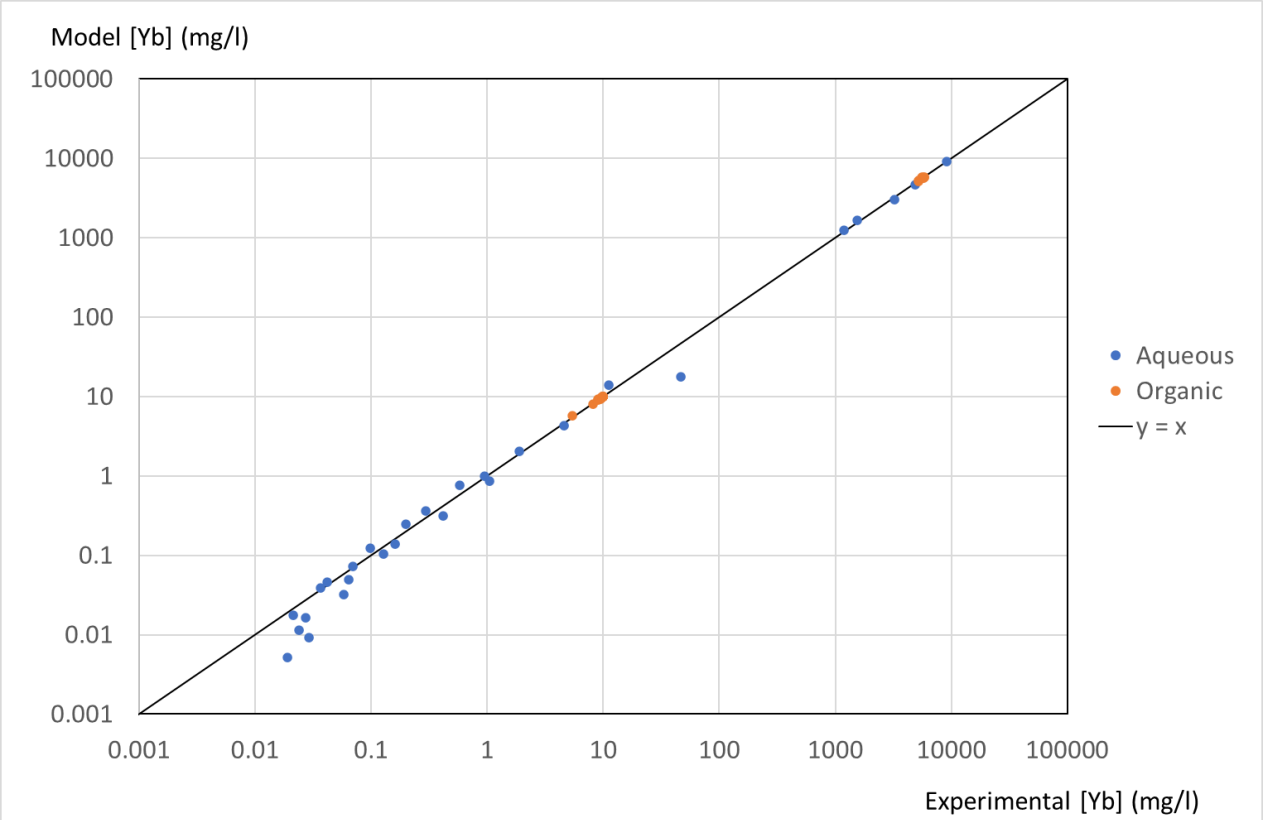

Figure 36: Modelled vs experimental Yb Concentrations.

The scatter plot in Figure 36 above shows that the model has a tendency to underpredict very low aqueous Yb concentrations. This may reflect difficulties associated with measurement when distribution values are very high (and aqueous concentrations very low) where any imperfect phase separation would result in a big relative error in the aqueous phase measurement.

In the below figures showing model predictions vs experimental data the error bars are the model-predicted variance of the measurement at the point in question.

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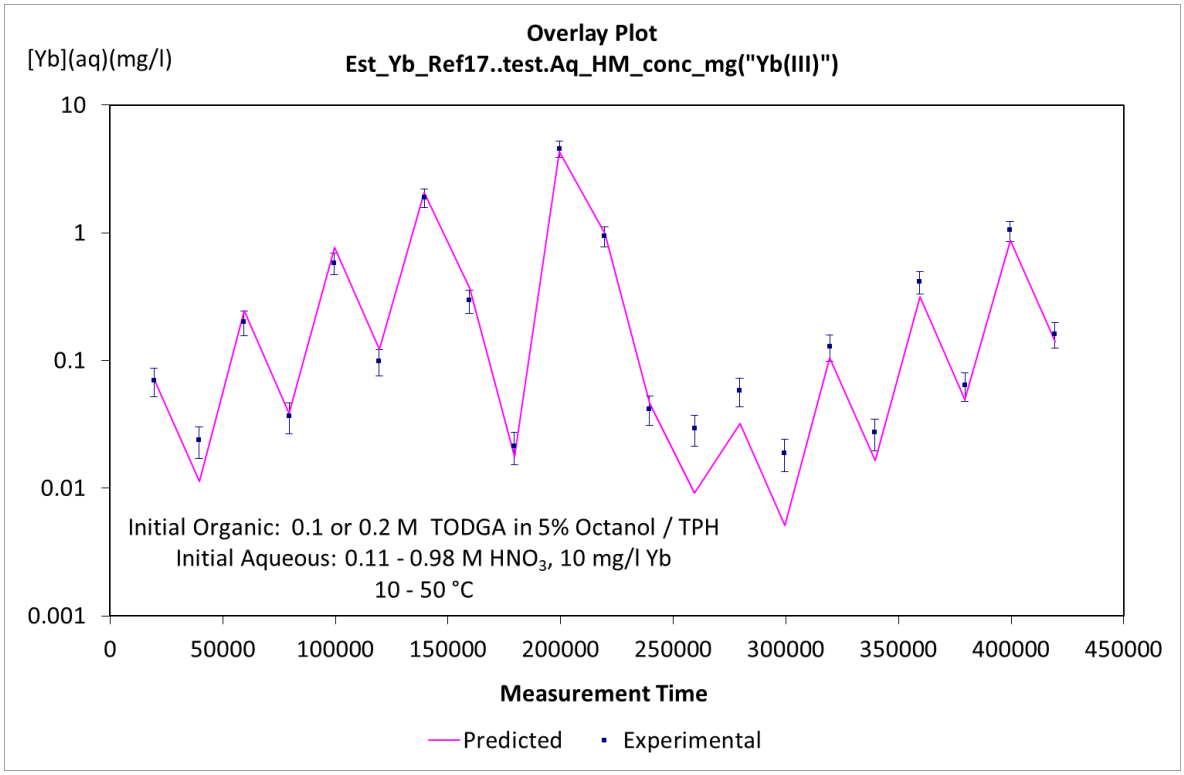

Figure 37: Fit of model to experimental data (Aq Yb data series 1).

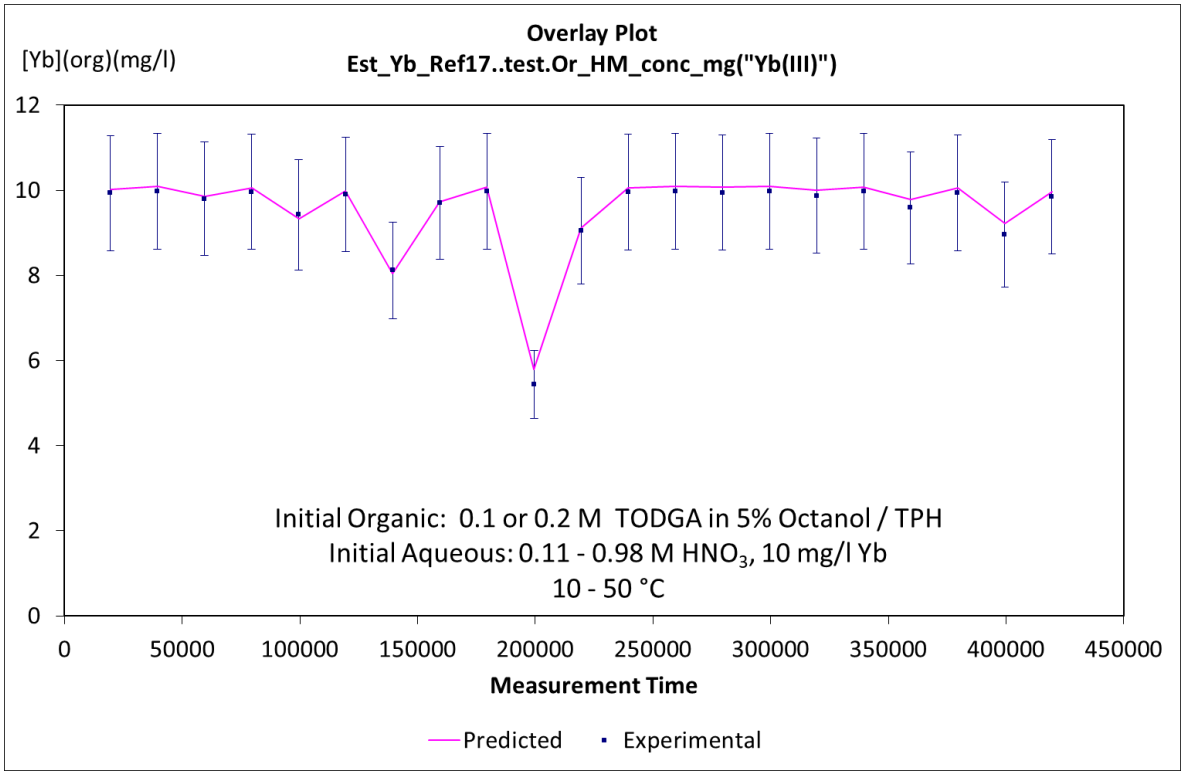

Figure 38: Fit of model to experimental data (Or Yb data series 1).

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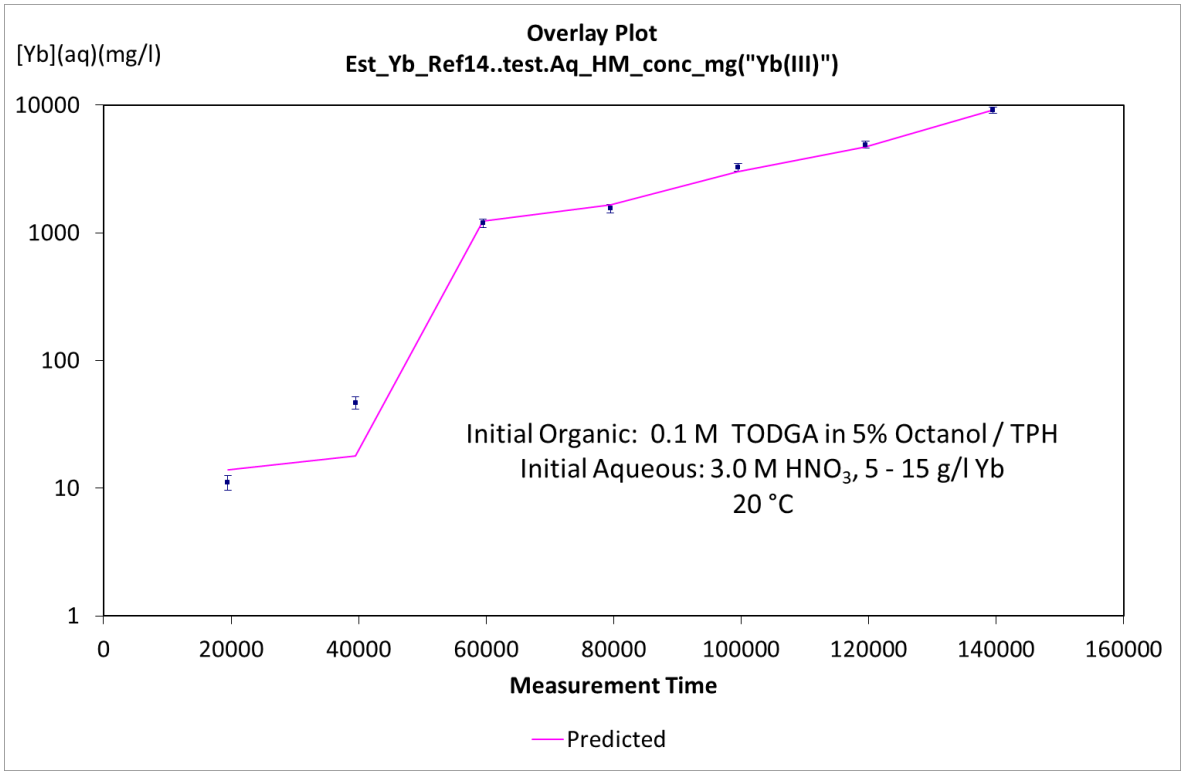

Figure 39: Fit of model to experimental data (Aq Yb data series 2).

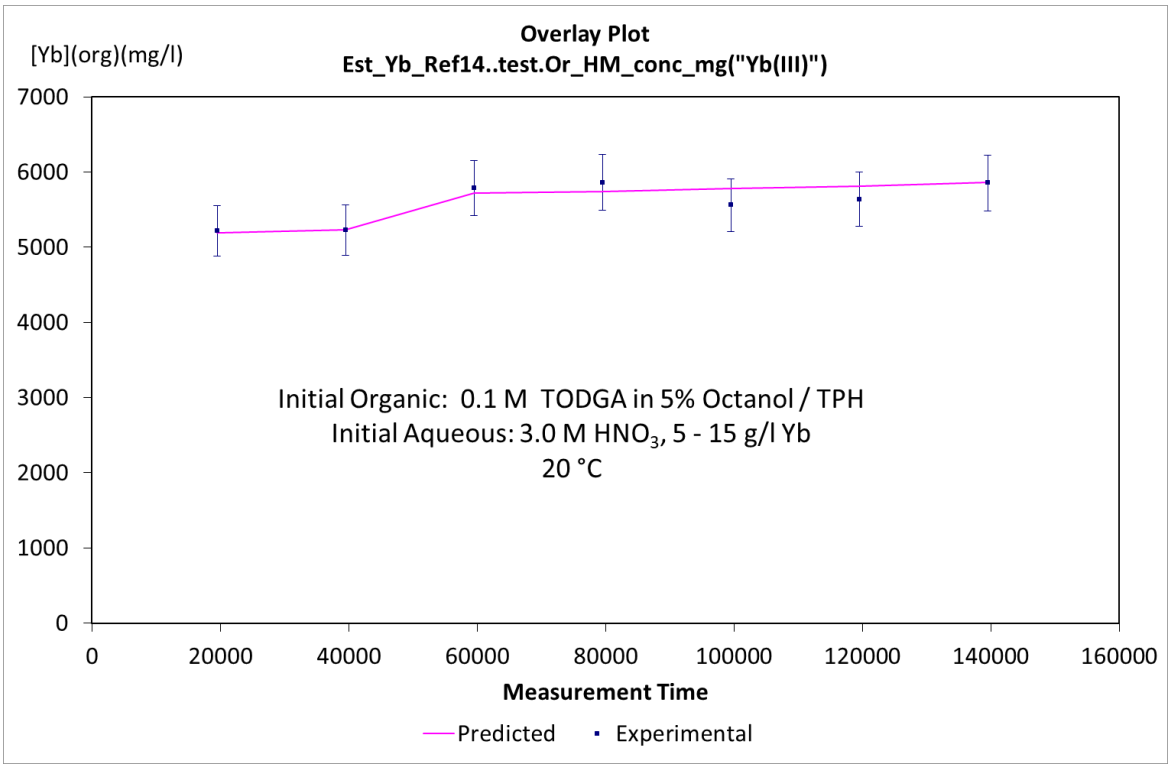

Figure 40: Fit of model to experimental data (Or Yb data series 2).

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These figures demonstrate a generally reasonable fit to the available data, although not as good as was obtained for either Nd or La. There is a clear concern with the rather limited range of data used to generate the fit. In particular, there is a lack of higher acidity data and a lack of solvent phase acidity measurements in Yb loaded systems

6.4. ORGANIC YTTERBIUM SPECIATION

To give some idea of the relative importance of the different complexes being proposed by this model, the model was run for extraction of Yb into 0.2M TODGA in 5% octanol / TPH at 20 °C for a range of aqueous acid and Yb concentrations. The molar concentrations of the different organic phase Yb complexes and the percentage of the extracted Yb accounted for by each complex predicted by these runs are shown in Figure 41 through Figure 49 below.

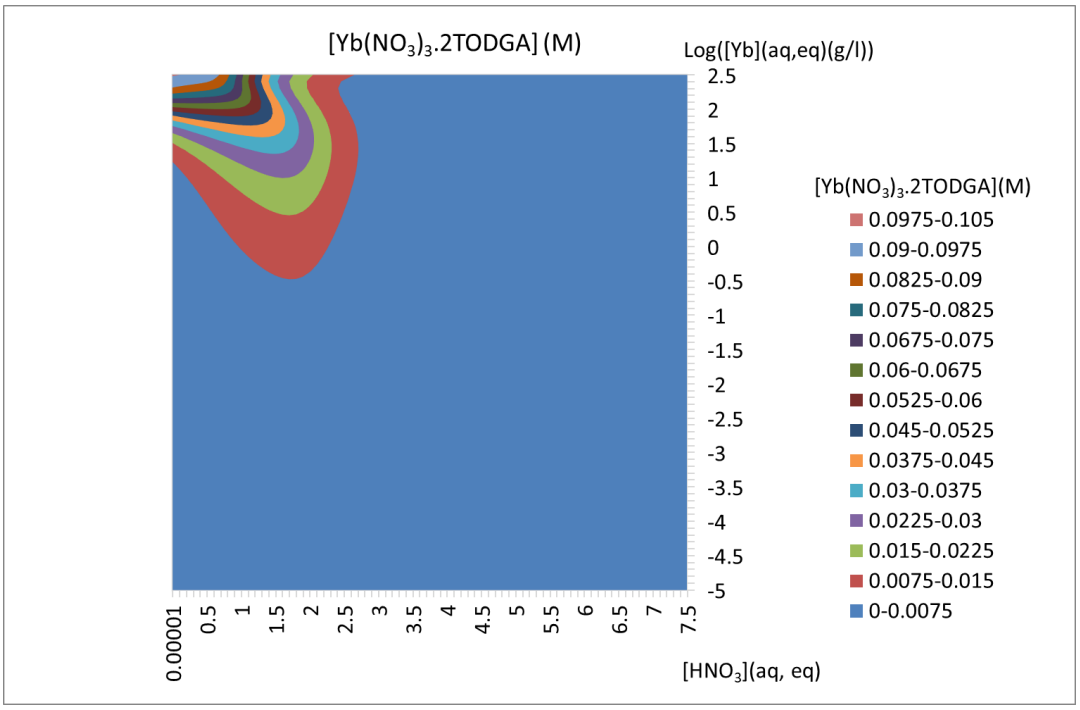

Figure 41: Predicted [Yb(NO3)3.2TODGA] in 0.2M TODGA in 5% octanol / TPH at 20 °C.

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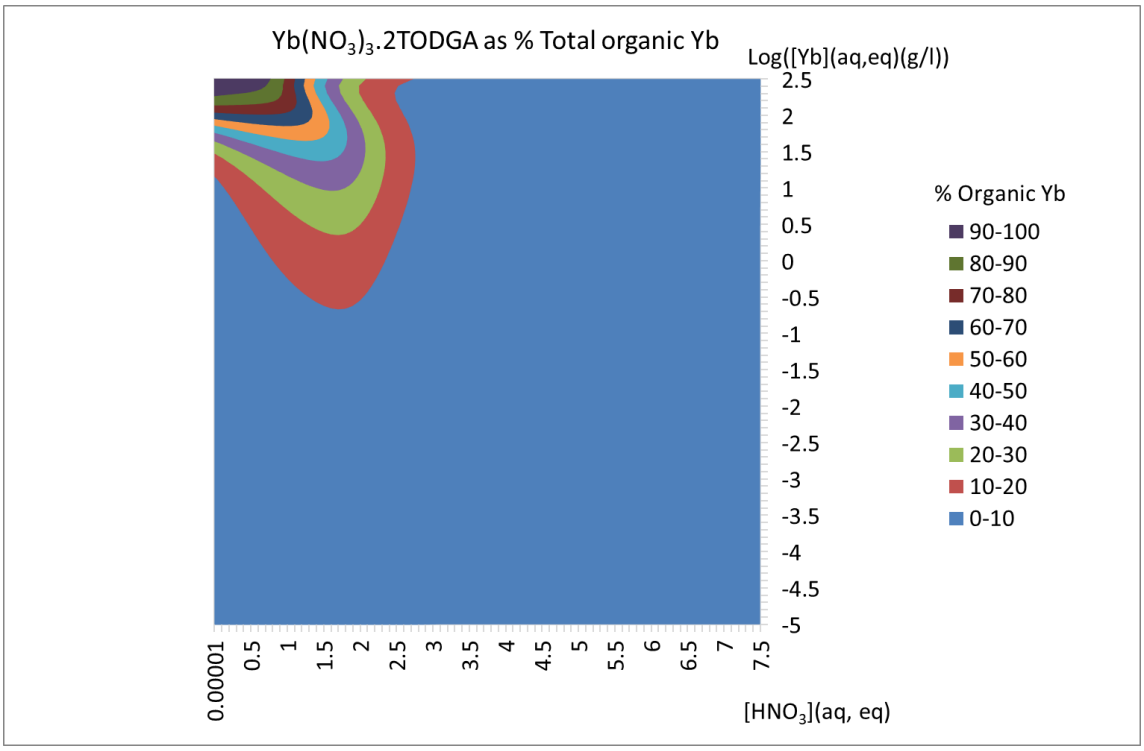

Figure 42: Predicted %$Yb(NO_3)_3$.2TODGA in 0.2M TODGA in 5% octanol / TPH at 20 °C.

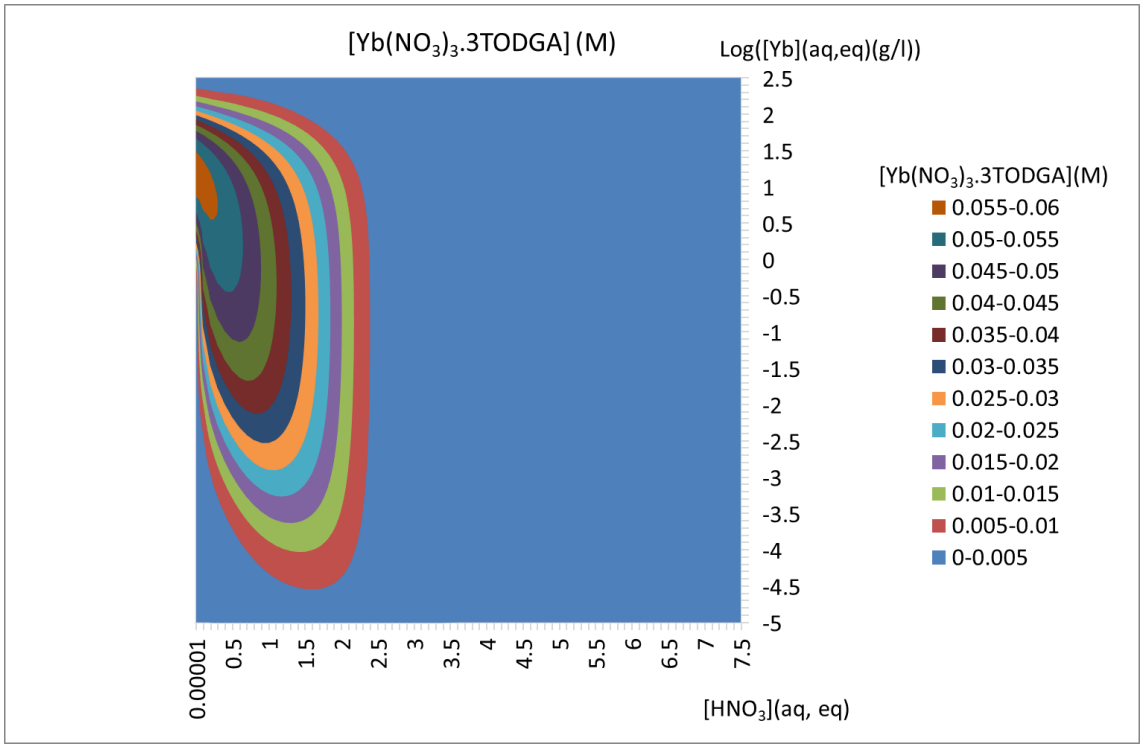

Figure 43: Predicted [$Yb(NO_3)_3$.3TODGA] in 0.2M TODGA in 5% octanol / TPH at 20 °C.

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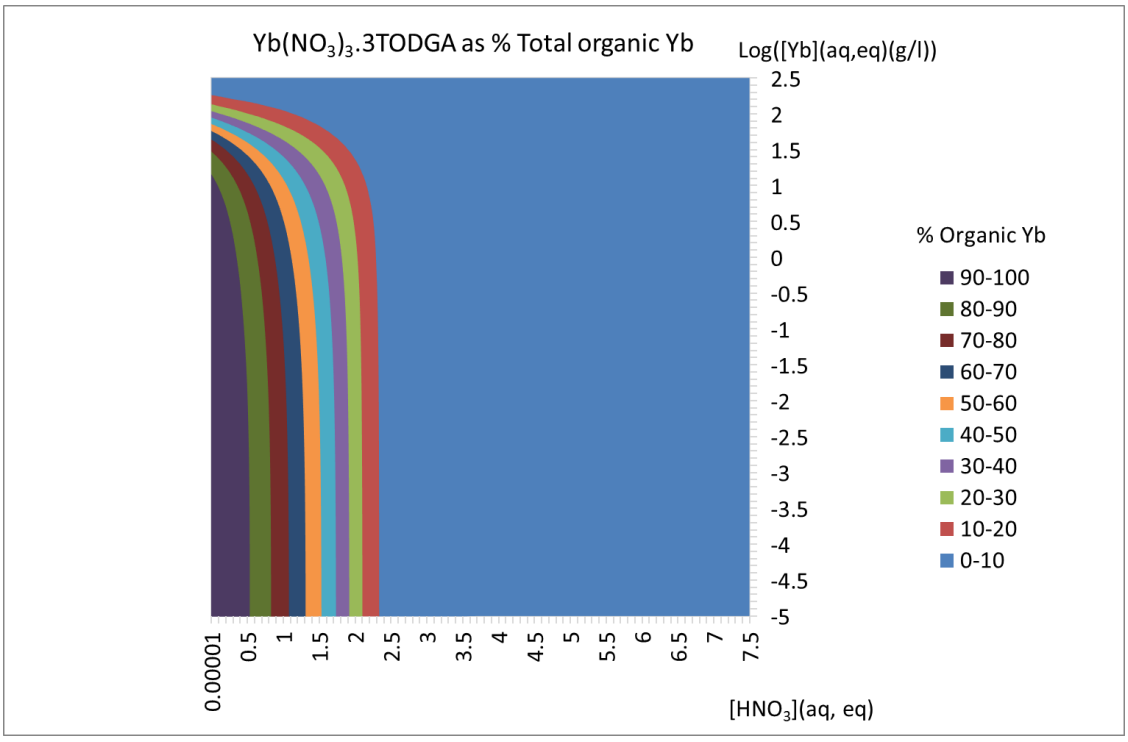

Figure 44: Predicted %$Yb(NO_3)_3$.3TODGA in 0.2M TODGA in 5% octanol / TPH at 20 °C .

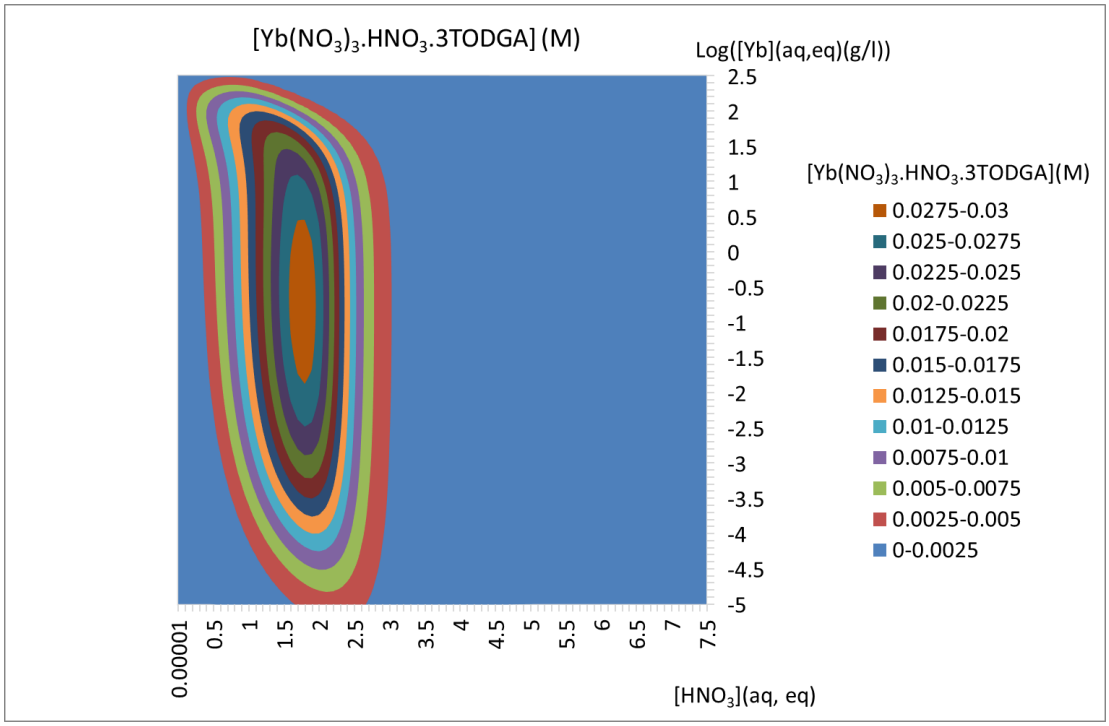

Figure 45: Predicted [$Yb(NO_3)_3$.HNO_3.3TODGA] in 0.2M TODGA in 5% octanol / TPH at 20 °C.

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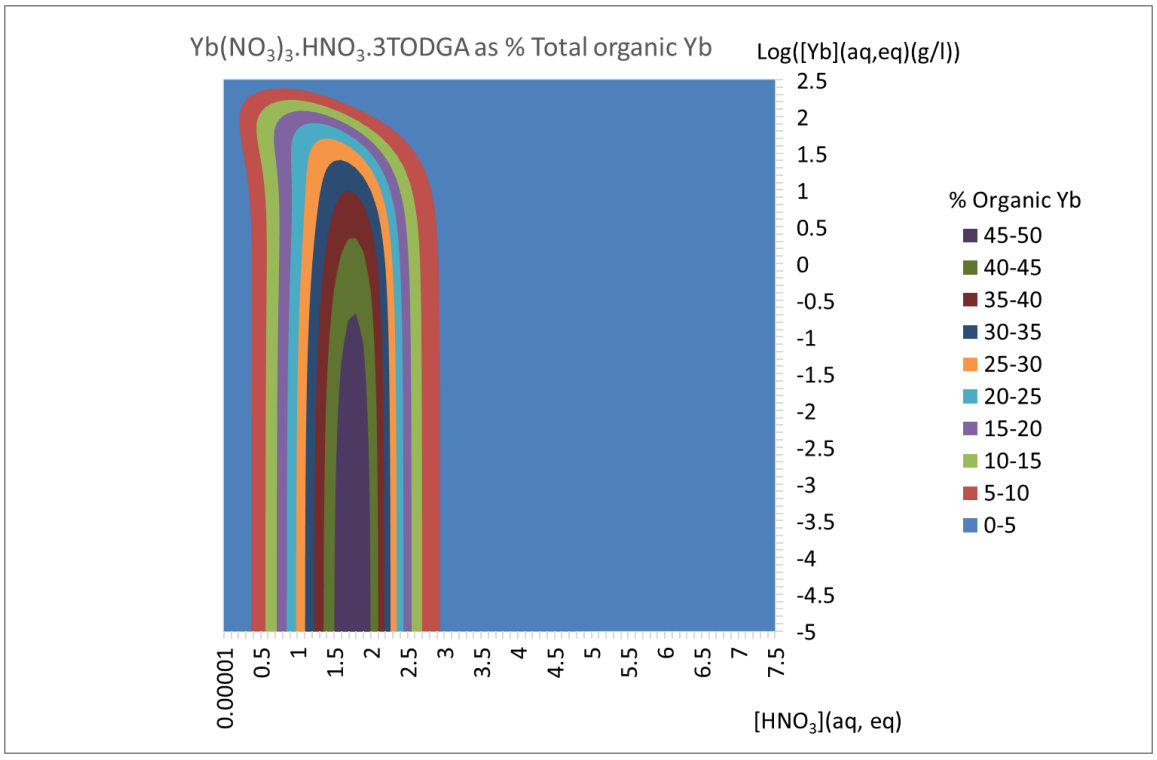

Figure 46: Predicted %$Yb(NO_3)_3$. HNO_3.3TODGA in 0.2M TODGA in 5% octanol / TPH at 20 °C.

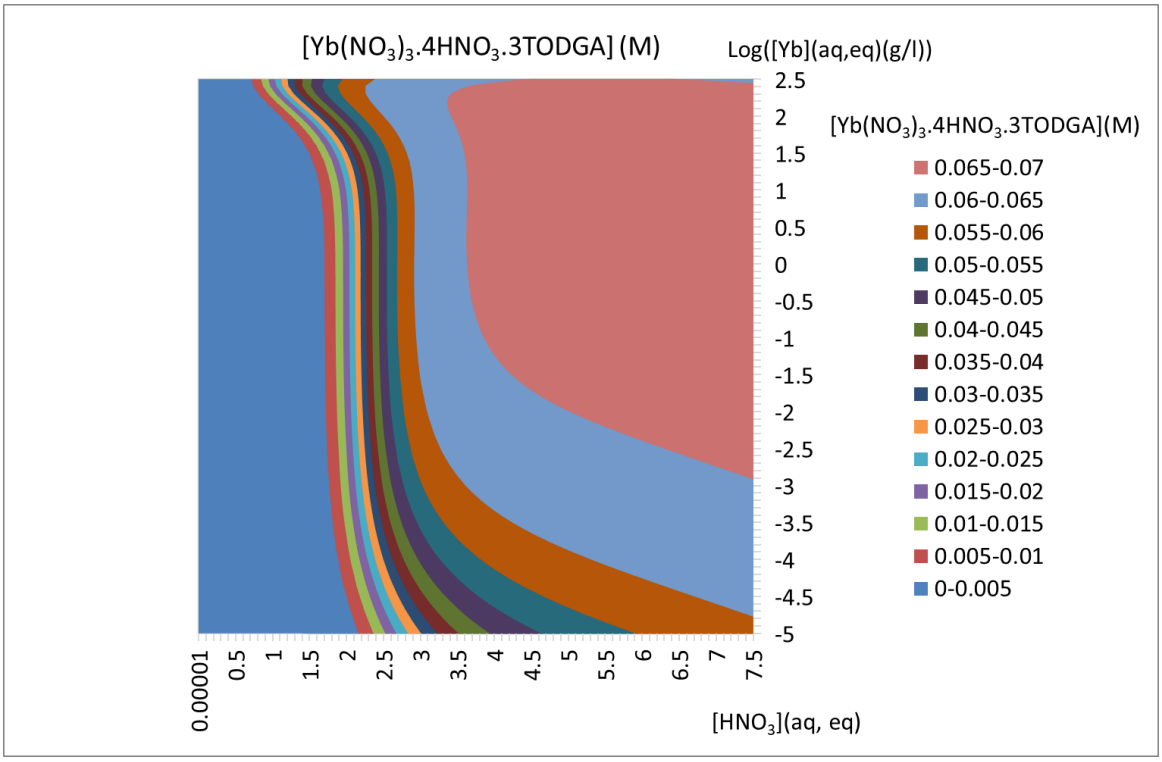

Figure 47: Predicted [$Yb(NO_3)_3$.4HNO_3.3TODGA] in 0.2M TODGA in 5% octanol / TPH at 20 °C.

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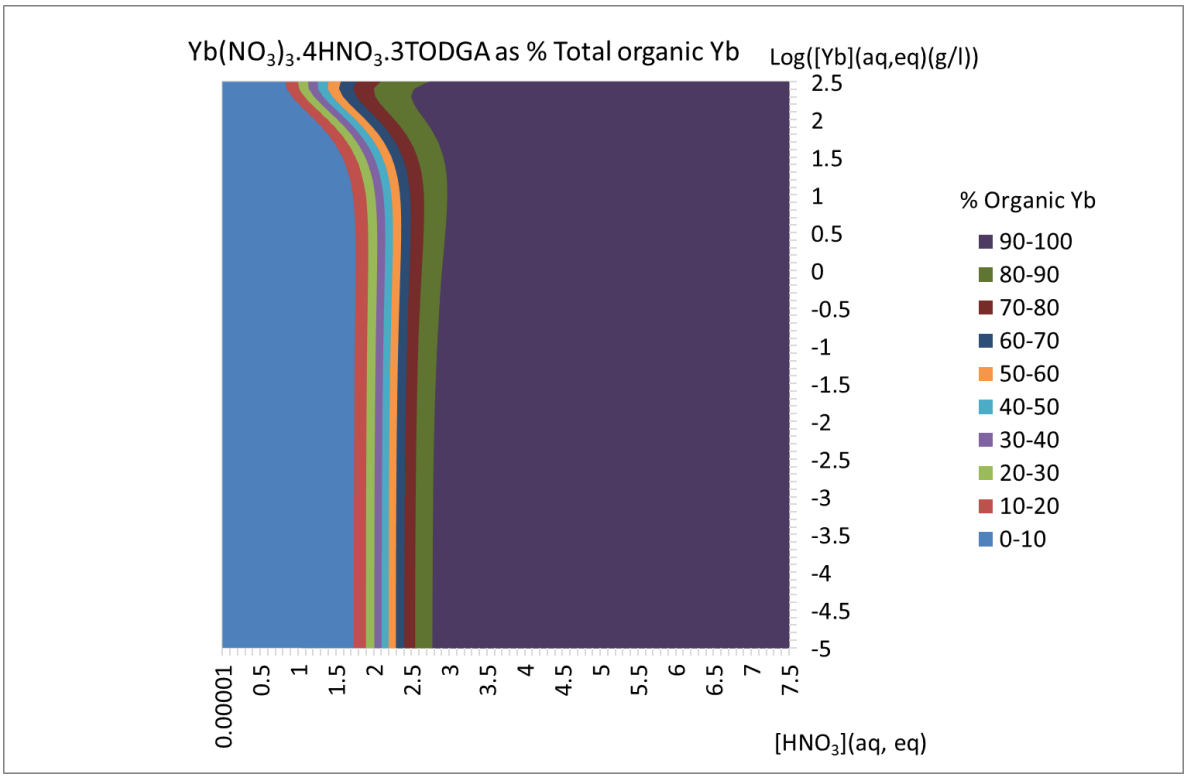

Figure 48: Predicted %$Yb(NO_3)_3.4HNO_3.3TODGA$ in 0.2M TODGA in 5% octanol / TPH at 20 °C.

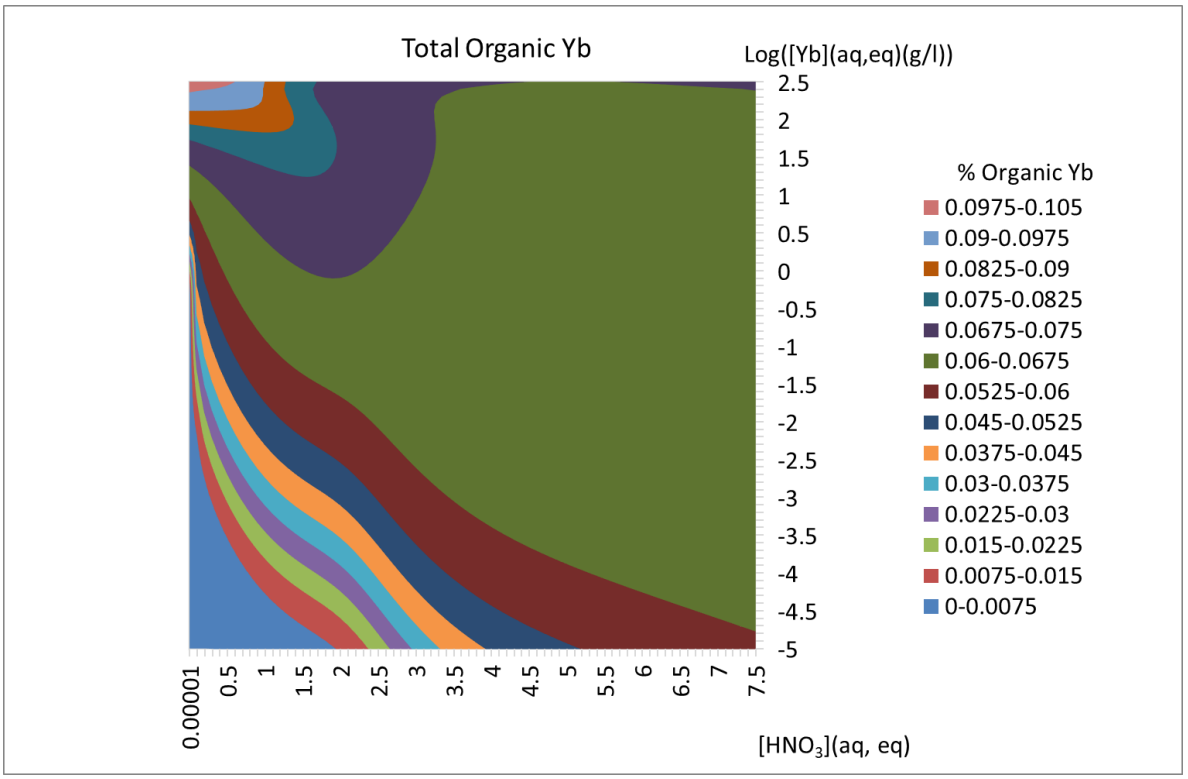

Figure 49: Predicted total organic [Yb] in 0.2M TODGA in 5% octanol / TPH at 20 °C.

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From these figures it can be seen that there are conditions under which each of the complexes is predicted to make up the majority of the extracted Yb, although given that $Yb(NO_3)_3.3TODGA$ and $Yb(NO_3)_3.HNO_3.3TODGA$ are only dominant under low loading conditions the absolute amounts of these complexes that can be present are less than for the other complexes. It is also seen that due to $Yb(NO_3)_3.4HNO_3.3TODGA$ dominating under high acidity conditions, higher Yb loading of the solvent is predicted to be possible at moderate acidity (where $Yb(NO_3)_3.2TODGA$ is present) than at high acidity. None of the available data would confirm or refute this.

6.5. SCOPE FOR YTTERBIUM MODEL IMPROVEMENT

The model gives a reasonable fit to the available data with the fit being least good under conditions which have been predicted to give high distribution values. There are experimental difficulties associated with the measurement of very high distribution values and it is possible that the relatively poor fit under these conditions is a consequence of scatter and systematic undermeasurement of high distribution values. Despite this, the main outstanding questions relate to the applicability of the model in regions that are not covered by the data used to fit the model. From visual inspection of the data the obvious gaps are:

- Data at high acidity. Existing data is limited to 3 M HNO_3 or less and at low loading is limited to less than 1 M HNO_3. Higher acidity data will be required to better define the correlation for Yb activity. Given the difficulties associated with measurement of the extremely high distribution values expected at high acidity it is likely that measurement of extraction into very low TODGA concentrations will be required. Whilst the model as it stands at present will correctly predict that (subject to saturation limits) Yb will be almost entirely extracted into the solvent at high acidity, the question of whether those saturation limits are determined by 2 TODGA or 3 TODGA complexes is still subject to uncertainty. It is also necessary to understand what the expected behaviour will be in an oversaturated system containing a number of highly extractable species. In this case there will be a requirement to say how the extracting species will compete for the available TODGA. This requires good estimation of the stability constants of the extracting species. It is not enough to say that the constants take very high values; their relative magnitudes must be known.
- Data for co-extraction of HNO_3. The existence of Yb / HNO_3 / TODGA complexes is inferred from the relationship between Yb distribution and acidity but direct measurement of acid extracted in the presence of significant Yb loading of the solvent would give more certainty regarding the existence and quantification of such complexes.
- Data with a wider range of TODGA concentrations. Existing data relates only to 0.1 and 0.2 M TODGA. Data over a wider range of TODGA concentrations would give more confidence in the split between complexes containing two TODGA ligands vs those containing three.
- Data at high Yb loading and high acidity. This would be required to determine whether a $Yb(NO_3)_3.nHNO_3.2TODGA$ complex exists.

6.6. EXPERIMENT DESIGN YTTERBIUM EXTRACTION

The process described in the previous sections for Nd and La was repeated for Yb and run through 10 iterations. The initial parameter estimation suggested that there was reasonable confidence in the values of the stability constants for the $Yb(NO_3)_3.3TODGA$ and $Yb(NO_3)_3.4HNO_3.3TODGA$ complexes, but the stability constants for the $Yb(NO_3)_3.2TODGA$ and $Yb(NO_3)_3.HNO_3.3TODGA$ complexes are less well defined as evidenced

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by low 95% t-values. An aim of any further experimental work would be to confirm or refute the existence of these complexes.

The limits placed on the experimental conditions were as for the Nd experiment design i.e. 0.01 – 0.3 M [TODGA], 0.01 – 7.0 M initial [HNO_3], 0.01 – 150 g/l [Yb] and 10 – 50 °C.

Table 17 below presents the initial conditions for the optimised experiment and the rounded version of these carried forward into subsequent calculations. Table 18 presents the predicted values of the measured variables for the optimised and rounded experiments. Table 19 and Table 20 then present the standard deviations and 95% t-values resulting from parameter estimation as each of the proposed experiments is added to the set of experiments used for the estimation.

Table 17: Control Variables for Yb Beaker Trials from Experiment Design.

Expt No	Initial values from Optimisation				Rounded Values carried forward			
	[TODGA] (M)	[HNO_3] (aq)(M)	[Yb](aq) (g/l)[14]	T (°C)	[TODGA] (M)	[HNO_3] (aq)(M)	[Yb](aq) (g/l)	T (°C)
1	0.3	1.029	18.41	37.62	0.3	1	18	40
2	0.3	1.026	17.93	35.55	0.3	1	18	35
3	0.3	1.12	15.77	43.92	0.3	1.1	16	45
4	0.3	1.025	16.85	32.25	0.3	1	17	30
5	0.3	2.253	15.55	32.6	0.3	2.25	16	35
6	0.3	2.31	15.18	36.42	0.3	2.25	15	35
7	0.3	2.307	13.68	43.47	0.3	2.25	14	45
8	0.3	2.33	19.77	29.42	0.3	2.35	20	30
9	0.183	2.362	9.419	48.58	0.2	2.4	10	50
10	0.3	0.9884	31.43	24.48	0.3	1	30	25

The suggested experiments are mostly at the upper limit of the TODGA concentration range, at either ~1 M or 2.3 M HNO_3 and mostly in the higher part of the temperature range. Initial Yb concentrations are mostly in the range 15 - 20 g/l. This is sufficient to bring the solvent close to saturation and is likely to have been identified as a suitable concentration due to its proximity to the boundary at which extracted Yb would switch from predominantly three TODGA complexes to predominantly two TODGA complexes.

[14] In line with normal nuclear industry practice heavy metal concentrations are expressed in g/l. To covert to mol/L divide by 173.04. This assumes natural ytterbium will be used for experiments. Fission derived ytterbium will have a slightly larger atomic weight.

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Table 18: Predicted Values for Measured Variables of Designed Experiments.

Expt No	Experiment as first optimised				Experiment with rounded control variables			
	$[HNO_3]$ (aq) (M)	$[HNO_3]$ (org)(M)	[Yb](aq) (mg/l)	[Yb] (org) (mg/l)	$[HNO_3]$ (aq) (M)	$[HNO_3]$ (org)(M)	[Yb](aq) (mg/l)	[Yb] (org) (mg/l)
1	1.006	0.0282	1704	16620	0.9775	0.02703	1517	16400
2	1.003	0.02807	1296	16550	0.9776	0.02693	1357	16560
3	1.092	0.03338	341.1	15350	1.073	0.03217	453.5	15460
4	1.001	0.02842	560.2	16210	0.9772	0.02724	599	16320
5	2.079	0.1925	19.04	15400	2.077	0.1912	40.64	15820
6	2.122	0.2073	13.75	15030	2.077	0.1917	11.52	14860
7	2.122	0.2038	5.551	13560	2.079	0.1893	8.829	13870
8	2.14	0.2108	2061	0.2108	2.155	0.2167	2274	17580
9	2.228	0.1487	66.99	9292	2.25	0.1664	37.44	9892
10	0.9661	0.02703	13100	18300	0.9774	0.02733	11760	18200

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Table 19: Predicted standard deviations of parameters obtained from parameter estimation including the predicted results of successive designed experiments.

	Stability Constant				ΔG
Complex	$Yb(NO_3)_3$ .2TODGA	$Yb(NO_3)_3$ .3TODGA	$Yb(NO_3)_3$ .4HNO_3 .3TODGA	$Yb(NO_3)_3$ .HNO_3 .3TODGA	J/mol
Initial Value	44282.9	3.00E+07	287985	1.91E+07	-96164.3
Initial SD	23110	2677000	44660	18240000	3882
Initial SD/value	52.19%	8.91%	15.51%	95.75%	-4.04%
SD after Expt 1	13340	2641000	37020	6473000	3584
" " " 2	9414	2640000	35810	4854000	3567
" " " 3	9250	2615000	35650	4142000	3306
" " " 4	6498	2580000	35060	3709000	3157
" " " 5	6452	2497000	32000	2990000	3046
" " " 6	6285	2443000	29740	2522000	2981
" " " 7	5749	2291000	28450	2434000	2565
" " " 8	5048	2246000	27020	2320000	2527
" " " 9	4936	2018000	26030	2120000	2057
" " " 10	4791	2008000	25990	2044000	2047
Final SD/Value	10.82%	6.68%	9.02%	10.73%	-2.13%

It will be noted that standard deviations reduce after the addition of each experiment.

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Table 20: 95% t-values obtained from parameter estimation including the predicted results of successive designed experiments.

	Stability Constant				
Complex	$Yb(NO_3)_3$ .2TODGA	$Yb(NO_3)_3$ .3TODGA	$Yb(NO_3)_3$ .4HNO_3 .3TODGA	$Yb(NO_3)_3$ .HNO_3 .3TODGA	ΔG
Initial 95% t-value	0.9515	5.572	3.202	0.5186	12.3
95% t-value after Expt 1	1.656	5.677	3.882	1.469	13.39
" " " " 2	2.351	5.688	4.019	1.961	13.47
" " " " 3	2.395	5.75	4.042	2.302	14.55
" " " " 4	3.415	5.836	4.116	2.574	15.27
" " " " 5	3.445	6.033	4.517	3.198	15.83
" " " " 6	3.539	6.175	4.864	3.797	16.19
" " " " 7	3.873	6.588	5.088	3.936	18.83
" " " " 8	4.414	6.729	5.363	4.135	19.13
" " " " 9	4.517	7.493	5.568	4.526	23.52
" " " " 10	4.656	7.535	5.58	4.696	23.65

95% t-values increase with each subsequent experiment.

Some reservations must be expressed about the proposed experiments. As described above, gPROMS suggests experiments based on optimisation of the existing model. It will not suggest experiments that would be relevant if the model structure is wrong (through e.g. omission of a complex that is present in significant quantities under some conditions not covered by the original dataset). As the data to which the model was fitted had rather limited coverage it is possible that such omissions do occur. There is also scope for the activity coefficient correlation to be significantly wrong at higher acidities. A particular concern is that there may be a $Yb(NO_3)_3.nHNO_3.2TODGA$ complex for some $n > 0$. To investigate the possible existence of such a complex would require experiments designed to drive the system into high saturation at high acidity. If such complexes existed experiments of this nature would show the TODGA:Yb ratio to be less than 3 at high acidity. Measurement of the solvent phase acidity under such conditions would give evidence with regard to the number of acid adducts associated with the complex.

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7. AMERICIUM

7.1. AVAILABLE AMERICIUM EXTRACTION DATA

Seven data series relating to the extraction of americium into TODGA / octanol mixtures were available as summarised below.

Series 1:

A series of 6 data points relating to extraction of trace americium (actual concentration unknown, but for fitting purposes taken to be 10 mg/l) into 0.2 M TODGA / 5% octanol in TPH at 20 °C and initial HNO_3 (aqueous) concentrations in the range 0.15 to 1.0 M. Various lanthanides were also present at trace concentrations. These were assumed not to affect the extraction of americium. This series is from the same experiments as series 1 of the Nd extraction data. Measurements were by gamma counting with separate analysis by alpha counting in 4 cases. For fitting purposes, the alpha and gamma results have been treated as separate experiments giving a total of 10 data points. Differences between distribution values obtained using the two measurement techniques vary from 4 to 24 %. A related data point at 0.198 M HNO_3 was excluded from the fitting due to use of Fluka kerosene as a diluent which appears to affect the distribution values.

Series 2:

A series of 7 data points giving distribution values for trace americium (actual concentration unknown, but for fitting purposes taken to be 10 mg/l) into various concentrations of TODGA (0.001 to 0.1 M) in 5% octanol / TPH from 2.0 M initial HNO_3 at 20 °C.

Series 3:

A series of 12 data points giving distribution values for trace americium (actual concentration unknown, but for fitting purposes taken to be 10 mg/l) into 0.05M TODGA in 5% octanol / TPH from various initial HNO_3 concentrations (0.1 – 4.9 M) at 20 °C. Values at the highest acidities are need to be treated with caution due to experimental difficulties associated with measurement of very high distribution values.

Series 4:

A series of 100 data points giving distribution values for trace americium (1 – 100 kBq/ml) extracted into 0.1, 0.2 or 0.3 M TODGA in 5% octanol / TPH from 0.1 to 4.9 M HNO_3 at 20 °C. In light of problems associated with measurement of very high distribution values only data points associated with a measured distribution value of less than 1000 were used in the fitting. This left 33 data points.

Series 5:

A series of 7 data points for extraction of trace americium (actual concentration unknown, but for fitting purposes taken to be 10 mg/l) into 0.1 M TODGA in 5% octanol / TPH from 3.0 M initial HNO_3 containing 7 – 150 g/l lanthanum at 20 °C. These are the same experiments as for series 3 of the lanthanum data.

Series 6:

A series of 11 data points for extraction of trace americium (actual concentration unknown, but for fitting purposes taken to be 10 mg/l) into 0.1 M TODGA in 5% octanol / TPH from 1.0 M initial HNO_3 containing 1.4 –

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150 g/l (0.01 – 1.0 M) neodymium at 20 °C. These are the same experiments as for series 3 of the neodymium data.

Series 7:

A series of 35 data points giving distribution values for trace concentrations (10 mg/l initial aqueous concentration for Ln) of various actinides and lanthanides including Am (1kBq/ml) into 0.1 or 0.2 M TODGA / 5% octanol at 10, 20, 30, 40, 50 °C and initial HNO_3 (aqueous) concentrations of 0.11, 0.3, 0.98, 2.9M. Some permutations that would give very high distribution values were omitted due to known experimental difficulties associated with measurement of very high distribution values. These are the same experiments as series 2 of the neodymium dataset.

Two other datasets containing americium distribution data were available but were not used in fitting. These data sets are described below:

Unused Series 1:

A series of 3 data points giving distribution values for trace americium into 0.2 M TODGA / 5% octanol in TPH from 4.63 M HNO_3 (it is assumed that this is initial concentration) and temperatures of 5, 22, and 55 °C. Other data were available from the same source in which americium distribution was measured in the context of a high level waste simulant. These data were too complex to analyse for fitting purposes. There was also significant uncertainty with regard to the very high distribution values associated with the extraction of trace americium from high acidity aqueous phases. Errors associated with these are likely to be very large and for this reason this data set was ultimately excluded from the fitting.

Unused series 2:

A collection of 45 data points giving distribution values for americium into TODGA / TBP / octanol / TPH mixtures from aqueous solutions containing Th(IV). These were not used due to the presence of Th(IV) which is significantly extractable into both TBP and TODGA.

Notably compared to other species there are no data relating to high americium loading and related to this there are no data that will give a direct measure of co-extracted acid. Due to practical issues associated with handling of large americium concentrations it may not be feasible to obtain such data

7.2. FITTED AMERICIUM EXTRACTION MODEL

A model was fitted using gPROMS parameter estimation to work with the acid extraction model A described in section 3. The model was structured in a similar way to that for Nd described in the section 4.2.

The data can be divided into two classes, one in which the quantities of americium used in the experiments are known (generally expressed in kBq/ml) and one in which only distribution values were reported. In fitting the model it was assumed that in the latter case an initial americium concentration of 10 mg/l was used. This allowed calculation of equilibrium aqueous and organic concentrations from the distribution values.

The americium concentration measurements were assumed to have a heteroscedastic variance, the parameters associated with this being fitted in the course of the model fitting. Heteroscedastic variance has the form $\sigma = \omega|x|^{\gamma}$ where σ is the variance, ω and γ are fitted parameters and x is the value of the measurement. The fitted values are summarised in Table 21 below. Separate values were found for cases

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where the americium concentrations were known and those where they were calculated from distribution values using an assumed nominal initial aqueous concentration.

Table 21: Variance model parameters for previously performed Am distribution experiments.

Measured Quantity	Units[15]	ω	γ
Americium concentration (expts where initial Am concentrations reported)	mg/l	0.0290204	0.492513
	mol/L	5.38765E-05	0.492513
Americium concentration (expts where initial Am concentrations assumed)	mg/l	0.0872208	0.267657
	mol/L	9.98016E-06	0.267657

The values reported here indicate that the fit is good for higher americium concentrations but poor where concentrations are very low (<< 1 mg/L). In the case of the experiments where the initial Am concentration was reported the variance amounts to 30% at 0.01 mg/L, 2.9% at 1 mg/L and 0.28% at 0.1 g/l. The corresponding figures for the cases where the initial total americium has had to be assumed (at 10 mg/L) are 250%, 8.7% and 0.3%.

The fitting of the Am distribution model itself included: fitting of an activity coefficient expression to use for Am, fitting of stability constants of the various solvent phase complexes and fitting of the free energy associated with formation of the complexes. The same free energy was assumed to apply to formation of all the complexes. The fitted activity coefficient expression is as below. Note that this is a function of the total nitrate concentration and is independent of the Am concentration which will typically be much less than the nitrate concentration.

$$\gamma_{Am} = \left[\frac{0.885469}{(0.202348 + [NO_3^-])} + 0.42829 + 0.15[NO_3^-] - 0.05[NO_3^-]^2 + 0.00931731[NO_3^-]^3\right]$$

Figure 50 below shows the relationship between the Am activity coefficient and nitrate concentration given by this equation.

[15] Conversion from mg/l to mol/L assumes an atomic weight of 241. This would be representative of americium separated from aged plutonium. Americium separated from spent fuel would have a slightly larger atomic weight.

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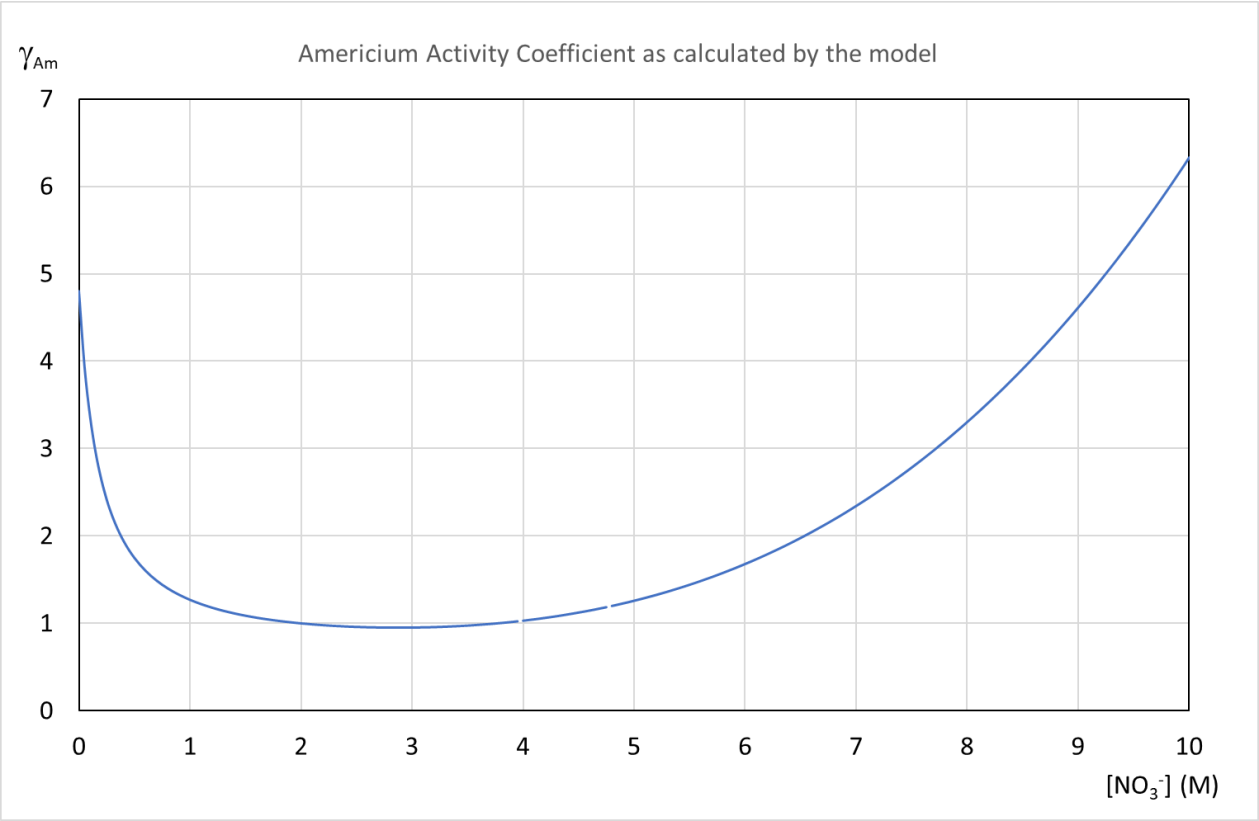

Figure 50: Calculation of the Am activity coefficient.

Fitted stability constants used in the model were as in Table 22 below. Note that the model allows for the presence of a range of complexes for which the stability constants were fitted as zero.

The activity coefficient from this equation is used to calculate the organic americium in the same way organic neodymium was calculated in section 4.2.

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Table 22: Fitted Stability constants for the Am Distribution Model.

Complex	Constant	Value
$Am(NO_3)_3$.TODGA	β_{Am01}	0
$Am(NO_3)_3$.2TODGA	β_{Am02}	495.28
$Am(NO_3)_3$.3TODGA	β_{Am03}	2250
$Am(NO_3)_3$.4TODGA	β_{Am04}	0
$Am(NO_3)_3.HNO_3$.TODGA	β_{Am11}	0
$Am(NO_3)_3.HNO_3$.2TODGA	β_{Am12}	0
$Am(NO_3)_3.HNO_3$.3TODGA	β_{Am13}	146217
$Am(NO_3)_3.HNO_3$.4TODGA	β_{Am14}	0
$Am(NO_3)_3.2HNO_3$.TODGA	β_{Am21}	0
$Am(NO_3)_3.2HNO_3$.2TODGA	β_{Am31}	159.043
$Am(NO_3)_3.2HNO_3$.3TODGA	β_{Am23}	0
$Am(NO_3)_3.2HNO_3$.4TODGA	β_{Am24}	0
$Am(NO_3)_3.3HNO_3$.TODGA	β_{Am31}	0
$Am(NO_3)_3.3HNO_3$.2TODGA	β_{Am32}	0
$Am(NO_3)_3.3HNO_3$.3TODGA	β_{Am33}	284607
$Am(NO_3)_3.3HNO_3$.4TODGA	β_{Am34}	0
$Am(NO_3)_3.4HNO_3$.TODGA	β_{Am41}	0
$Am(NO_3)_3.4HNO_3$.2TODGA	β_{Am42}	9.78337
$Am(NO_3)_3.4HNO_3$.3TODGA	β_{Am43}	2196.04
$Am(NO_3)_3.4HNO_3$.4TODGA	β_{Am44}	0

Temperature dependence was determined by a fitted value of ΔG = -92088, with the pre-exponential terms set such that the temperature correction factor evaluates to 1 at 20 °C.

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7.3. AMERICIUM EXTRACTION MODEL PERFORMANCE

The model was run against the available data (both that used in fitting and that not used in the fitting) with results shown in Figure 51 through Figure 72.

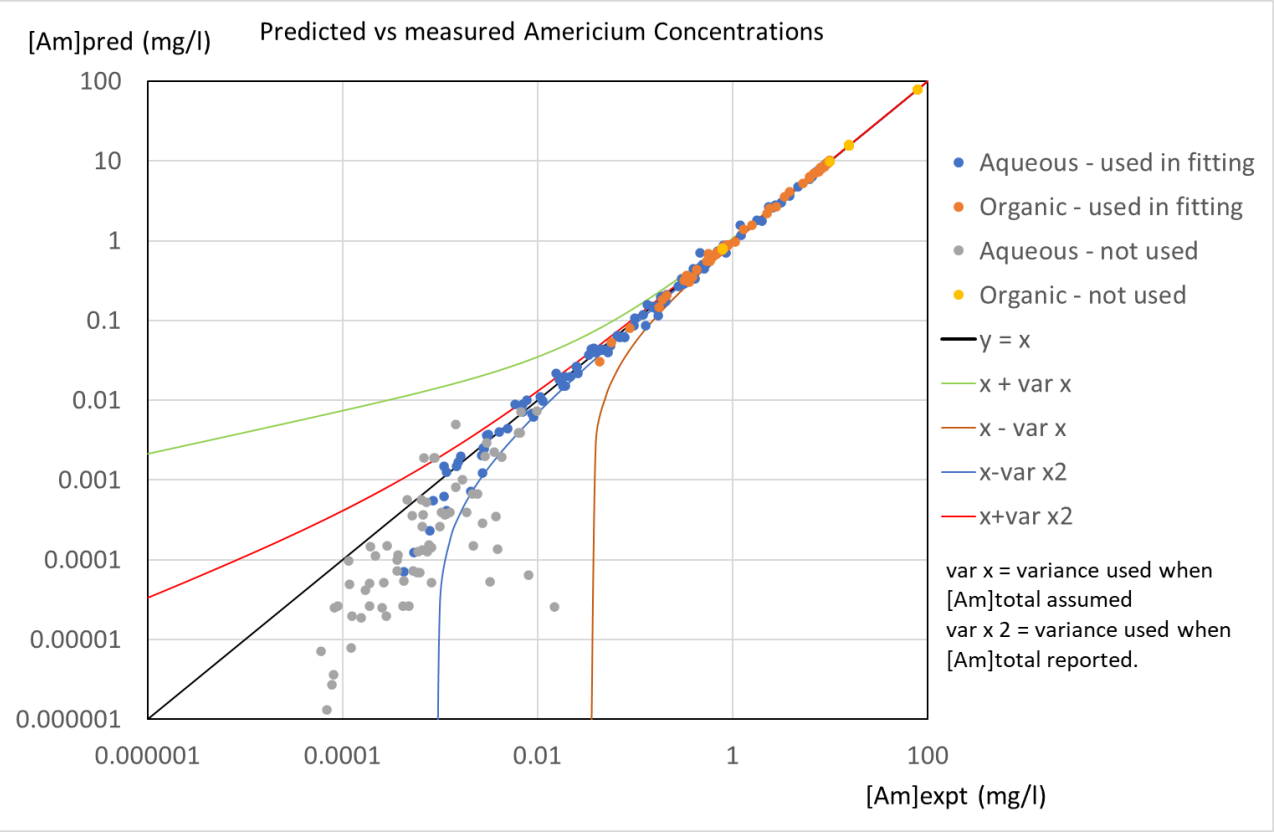

Figure 51: Predicted vs measured values for americium distribution constants.

Note that in Figure 51 above and Figure 52 below the continuous lines give the bounds defined by plus or minus the variances given in Table 22, two different variance models having been used depending on whether the total concentration of americium was reported or had to be assumed as a nominal trace concentration (applied when only he distribution value was reported).

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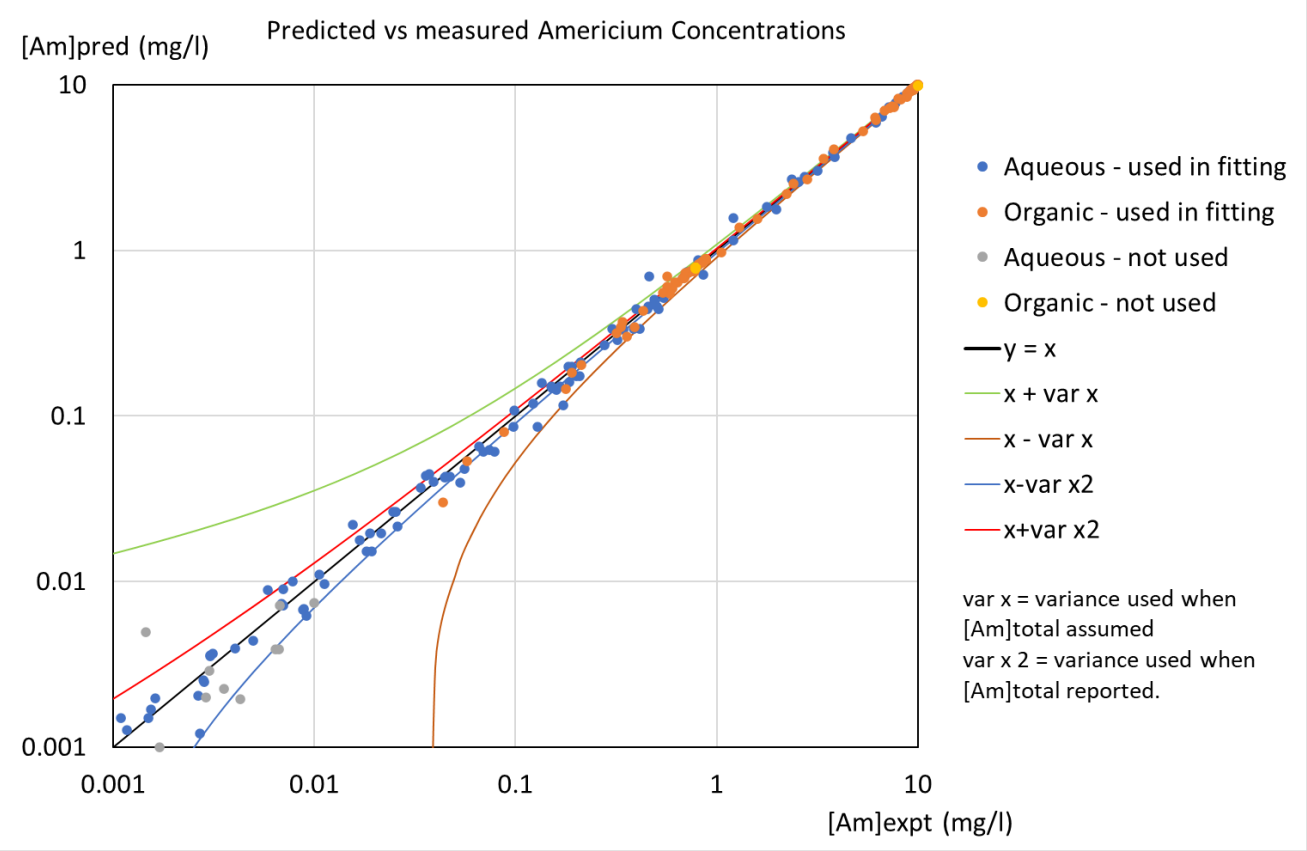

Figure 52: Predicted vs measured values for americium distribution constants (subset).

Figure 51 and Figure 52 suggest that the fitted variance models are probably overstating variance at very low concentrations. This may be an indication of the heteroscedastic variance model being a poor fit to the actual variance which may have some other relationship to the magnitude of the value. As the other variance models supported by gPROMS are special cases of the heteroscedastic model, there is no prospect of the current gPROMS implementation supplying a better fit. As distribution values for americium are typically high, the variance associated with distribution values mostly reflects variance in the measurement of the underlying aqueous concentration, this normally being very much smaller than the corresponding organic concentration.

It will be seen from these figures that the model tends to underpredict extraction when concentrations (specifically in the aqueous) are very low. This does not necessarily reflect a bias in the model but may instead reflect experimental difficulties in obtaining the very high quality phase separation required to measure the highest distribution values.

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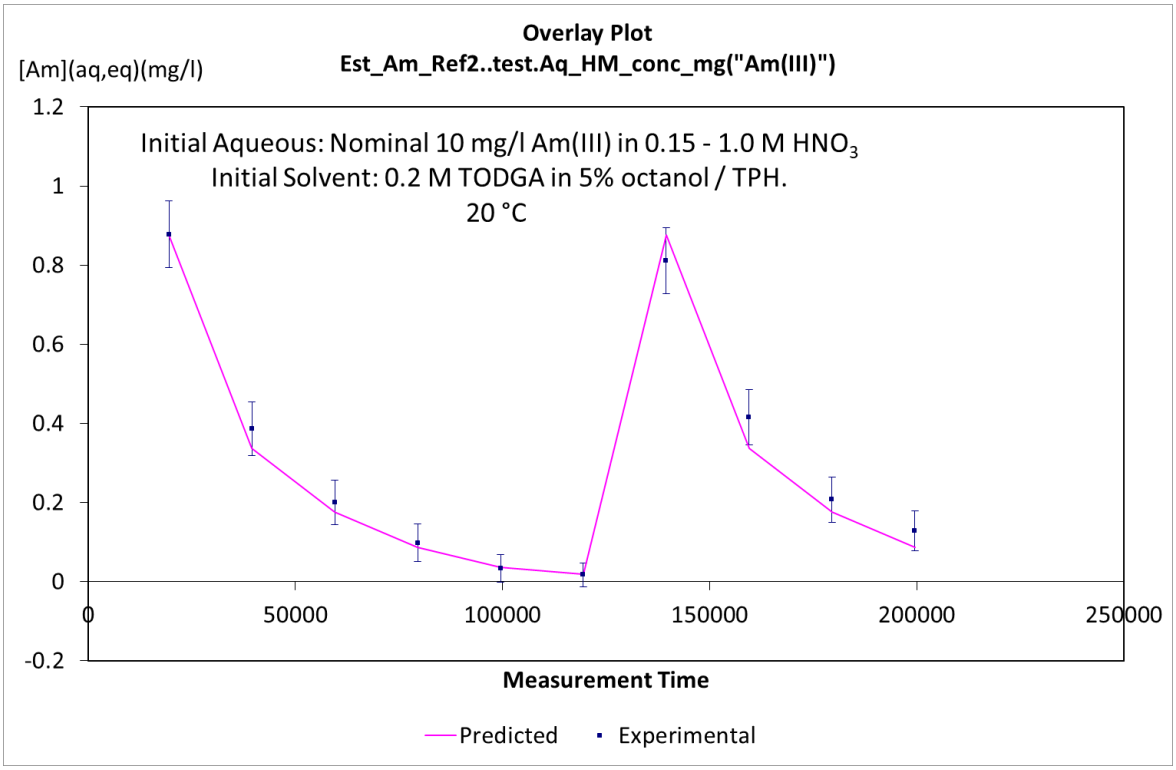

Figure 53: Fit of Am distribution model to experimental data (Aq Am data series 1).

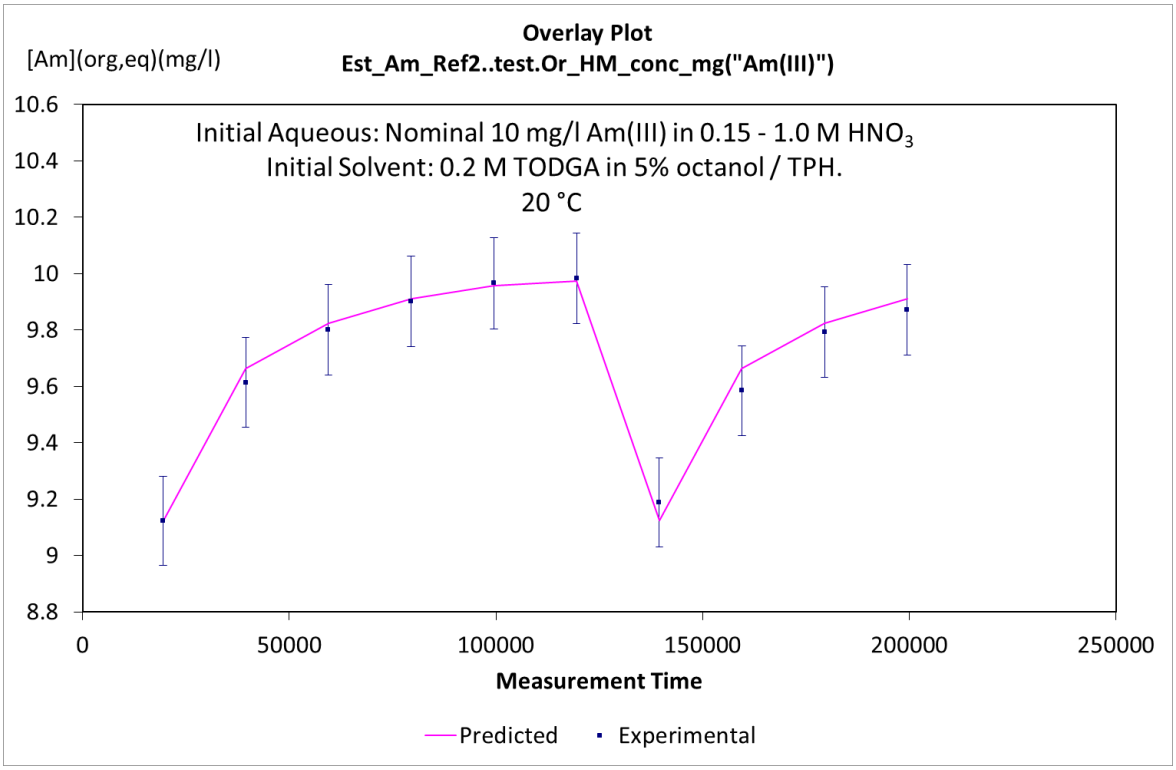

Figure 54: Fit of Am distribution model to experimental data (Or Am data series 1).

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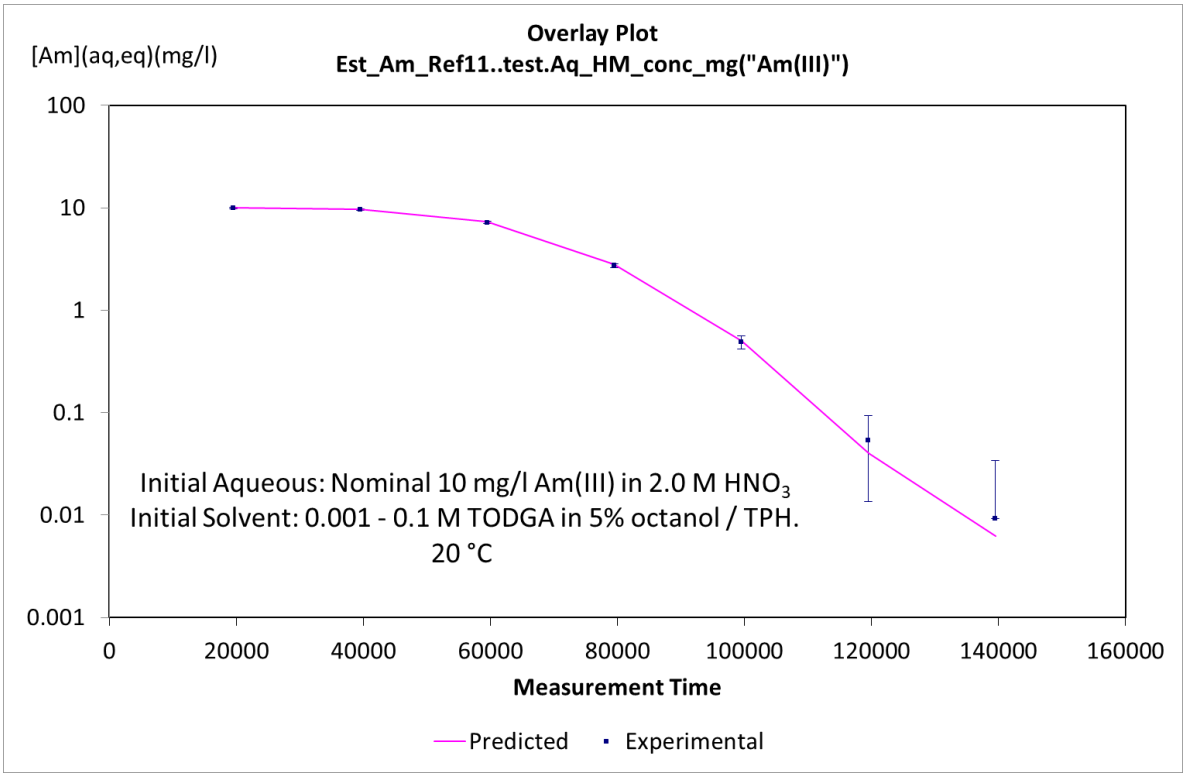

Figure 55: Fit of Am distribution model to experimental data (Aq Am data series 2).

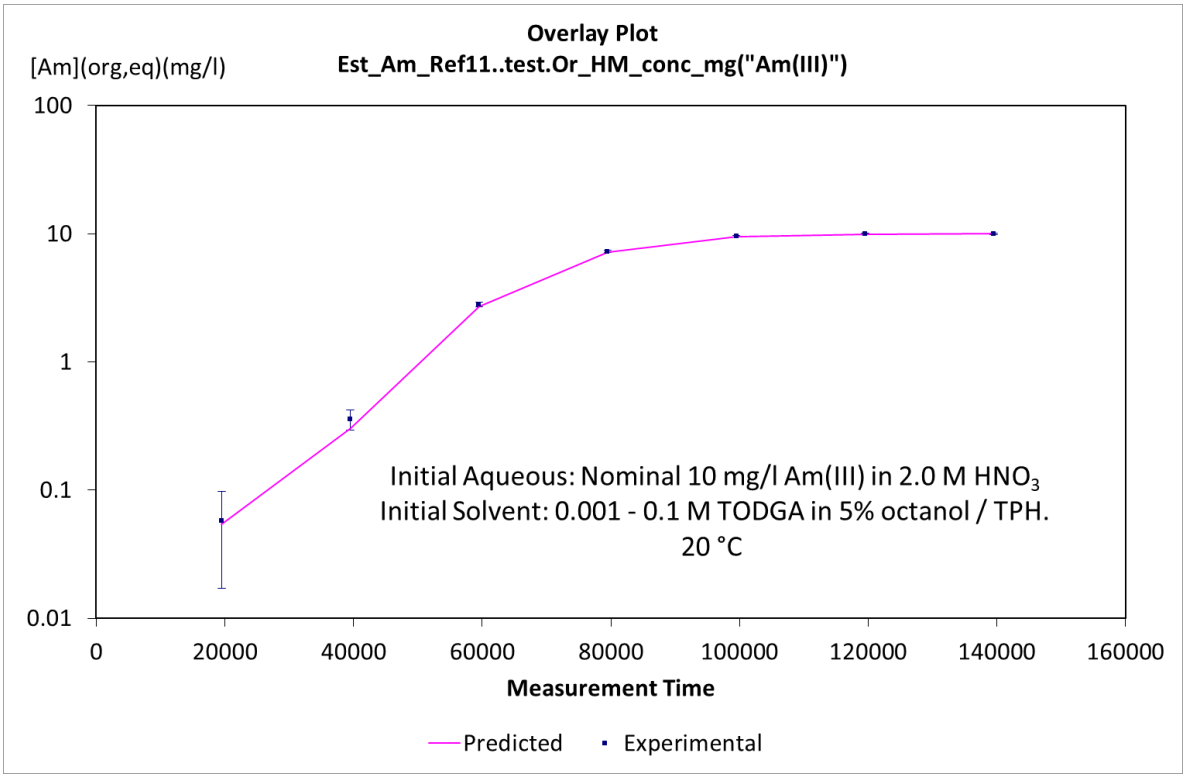

Figure 56: Fit of Am distribution model to experimental data (Or Am data series 2).

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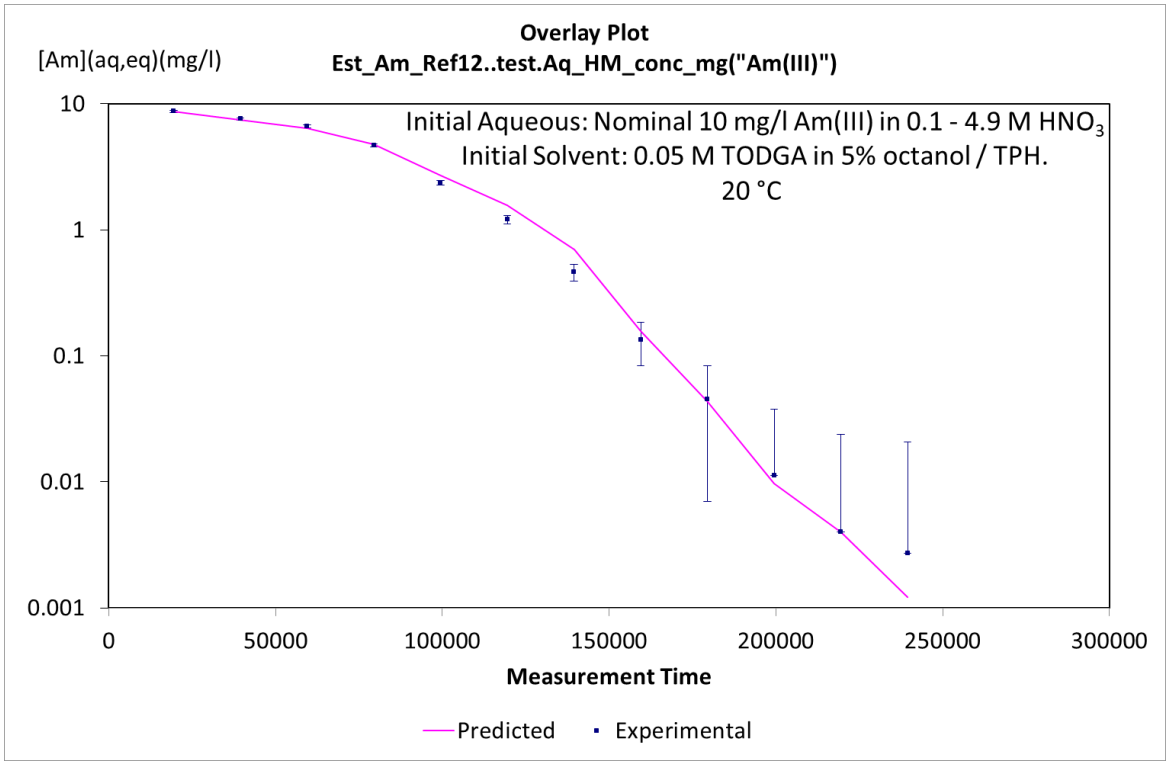

Figure 57: Fit of Am distribution model to experimental data (Aq Am data series 3).

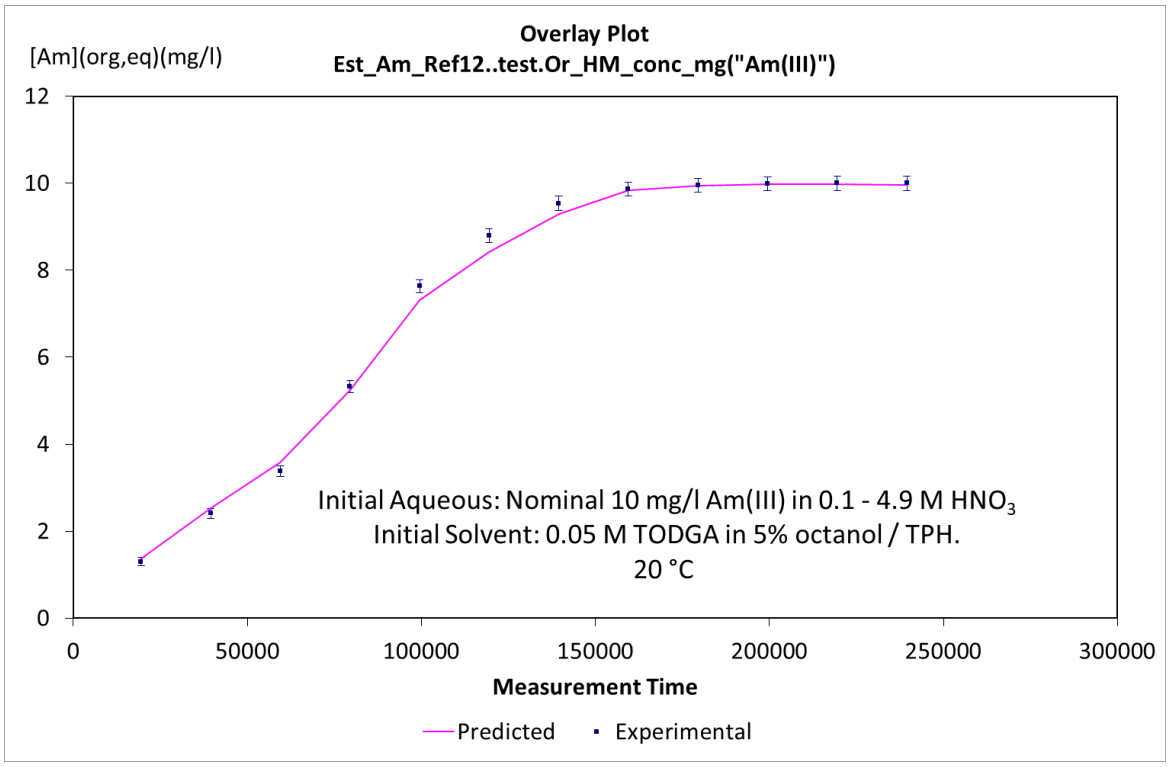

Figure 58: Fit of Am distribution model to experimental data (Or Am data series 3).

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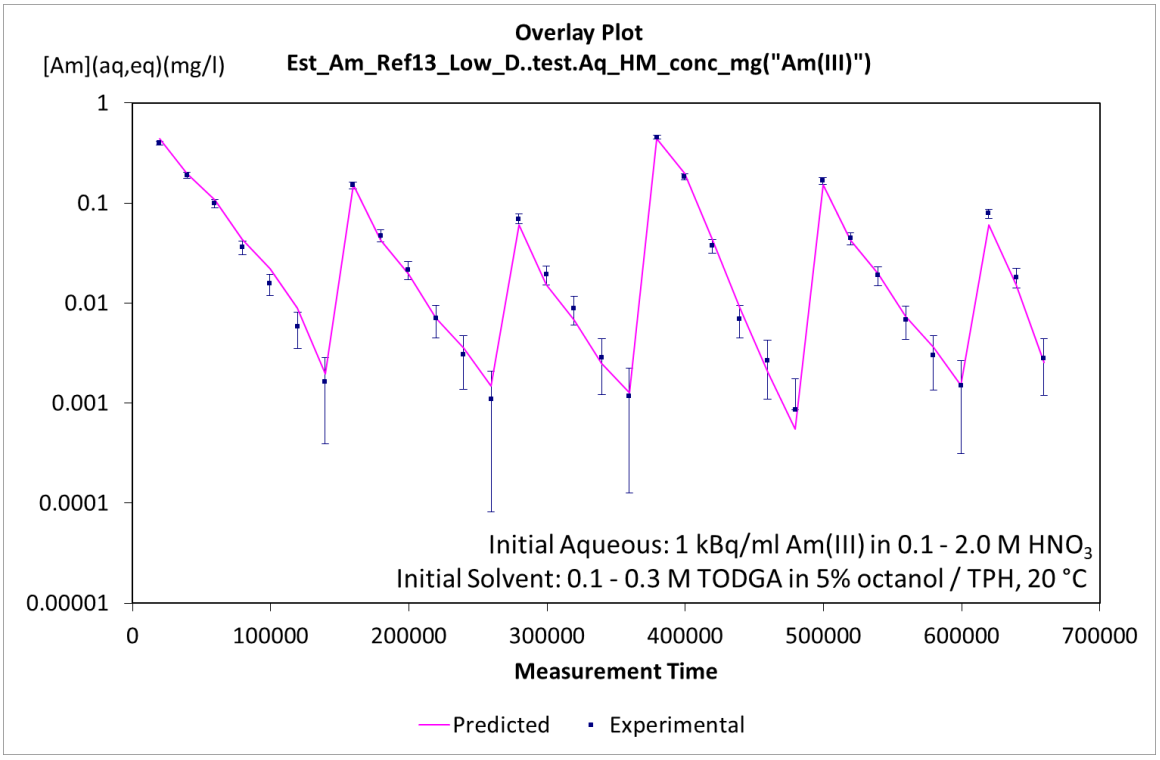

Figure 59: Fit of Am distribution model to experimental data (Aq Am data series 4).

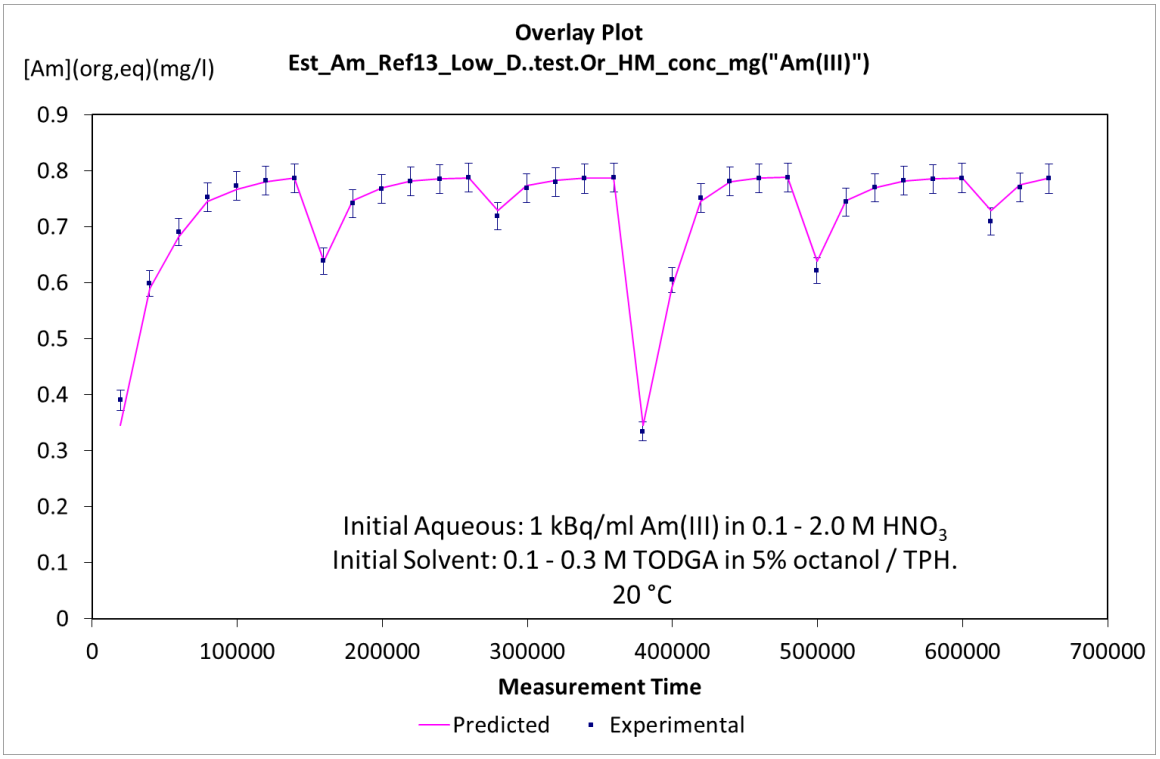

Figure 60: Fit of Am distribution model to experimental data (Or Am data series 4).

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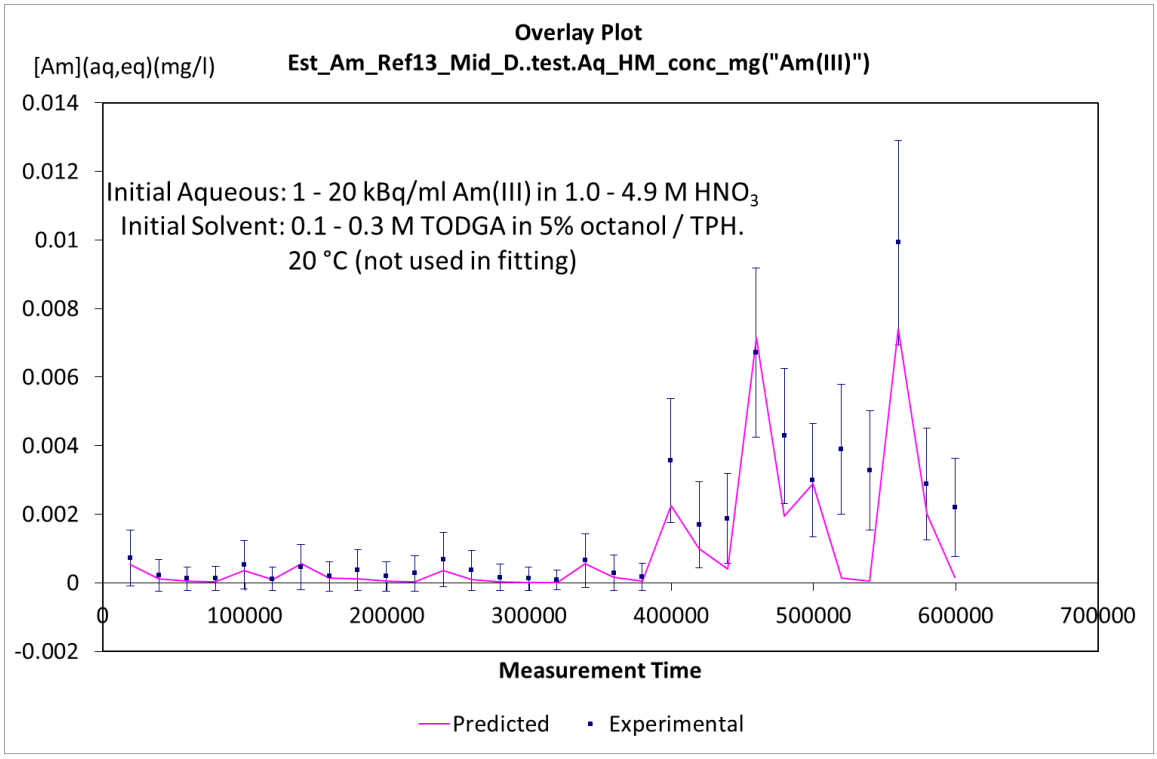

Figure 61: Fit of Am distribution model to experimental data (Aq Am data series 4 – Mid D unused).

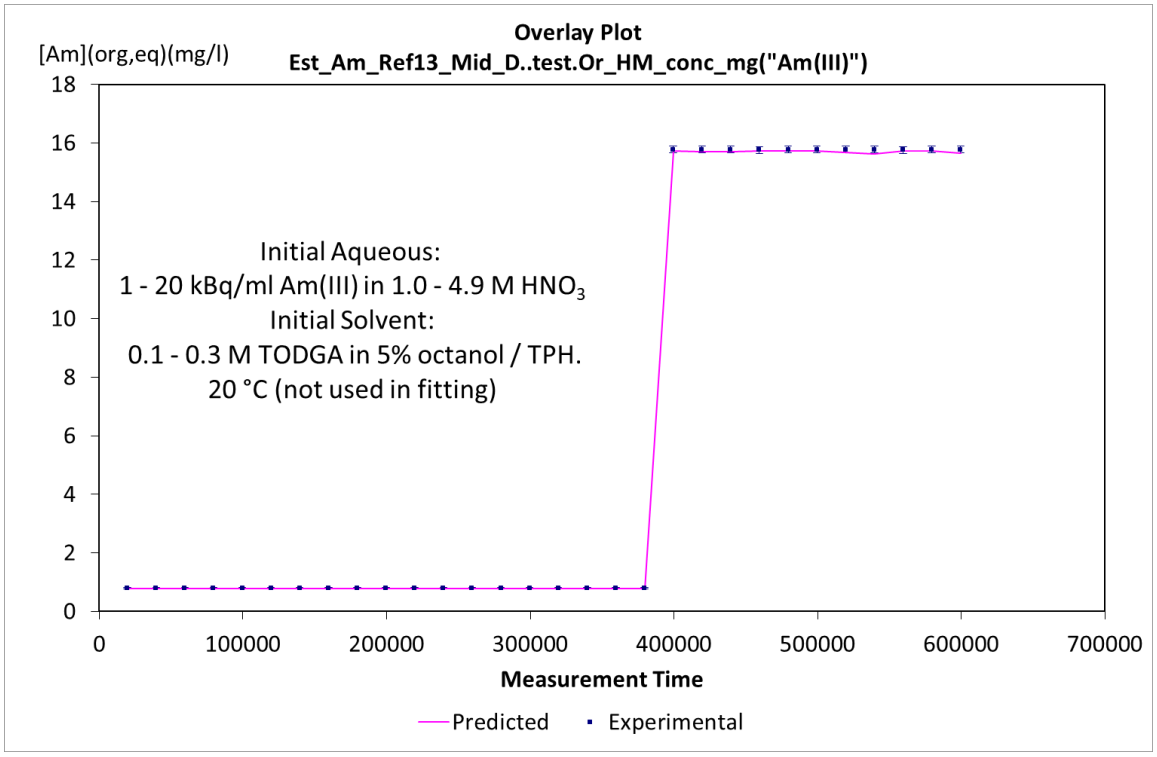

Figure 62: Fit of Am distribution model to experimental data (Or Am data series 4 – Mid D unused).

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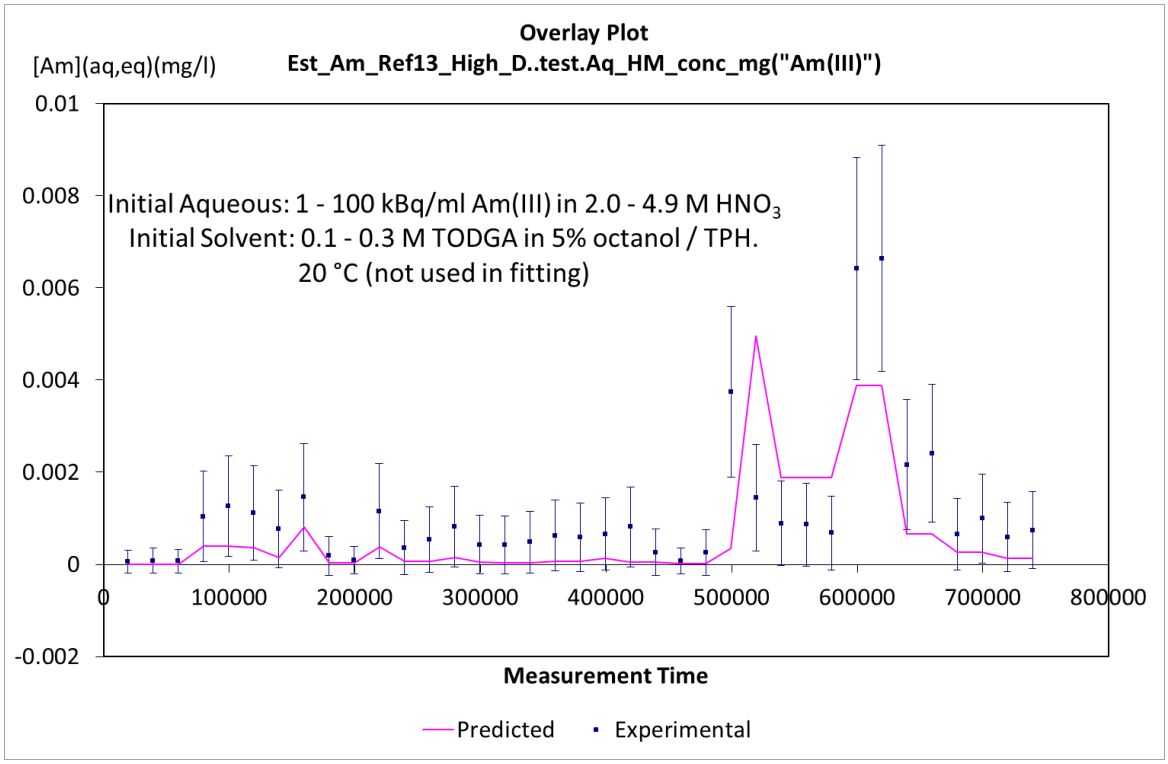

Figure 63: Fit of Am distribution model to experimental data (Aq Am data series 4 – High D unused).

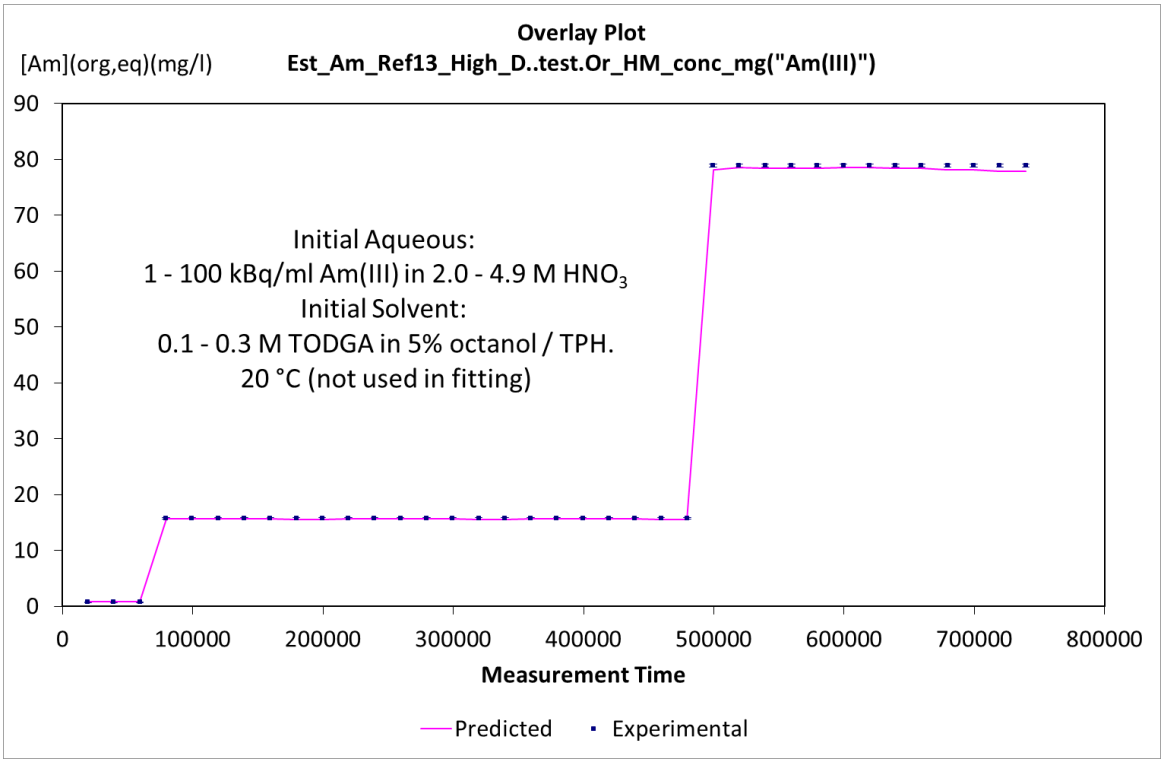

Figure 64: Fit of Am distribution model to experimental data (Or Am data series 4 – High D unused).

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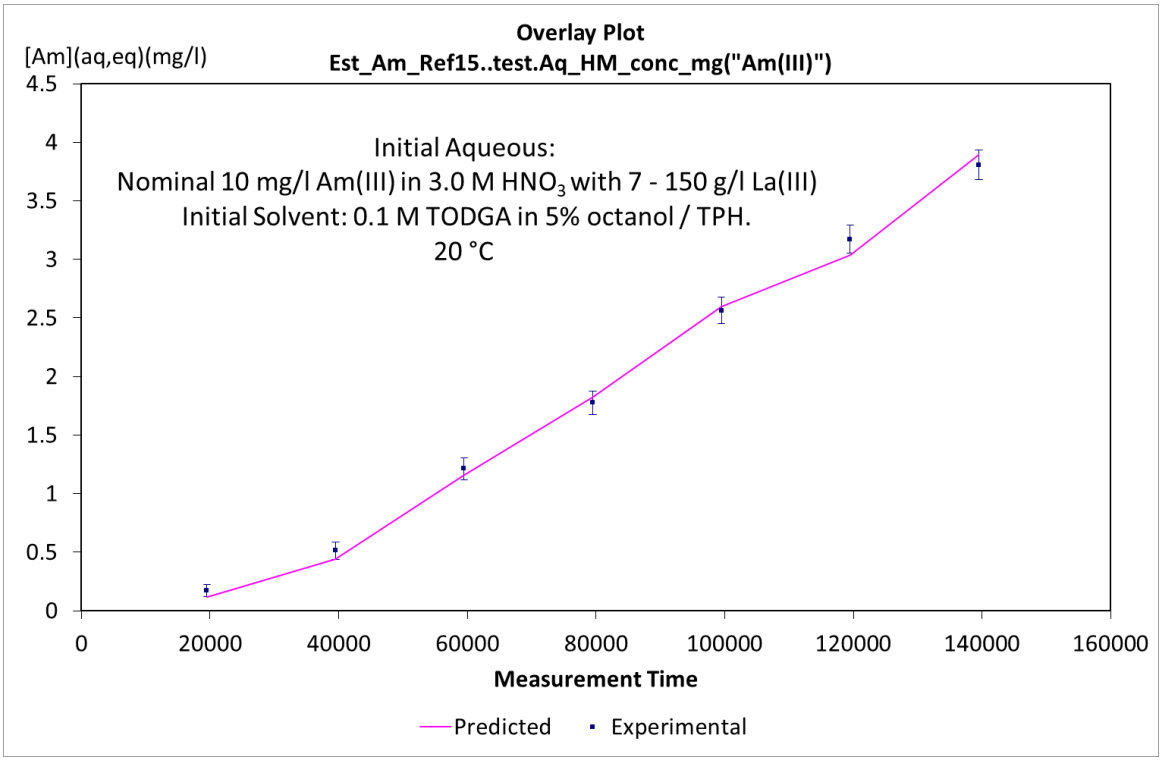

Figure 65: Fit of Am distribution model to experimental data (Aq Am data series 5).

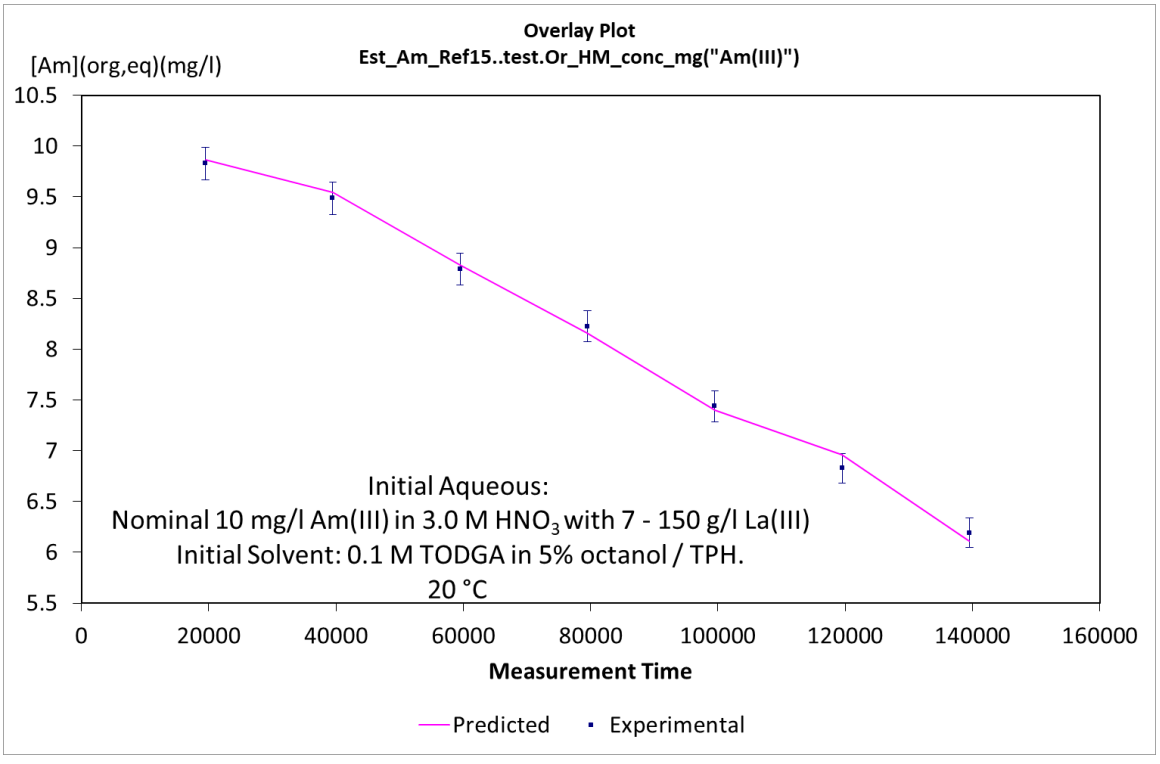

Figure 66: Fit of Am distribution model to experimental data (Or Am data series 5).

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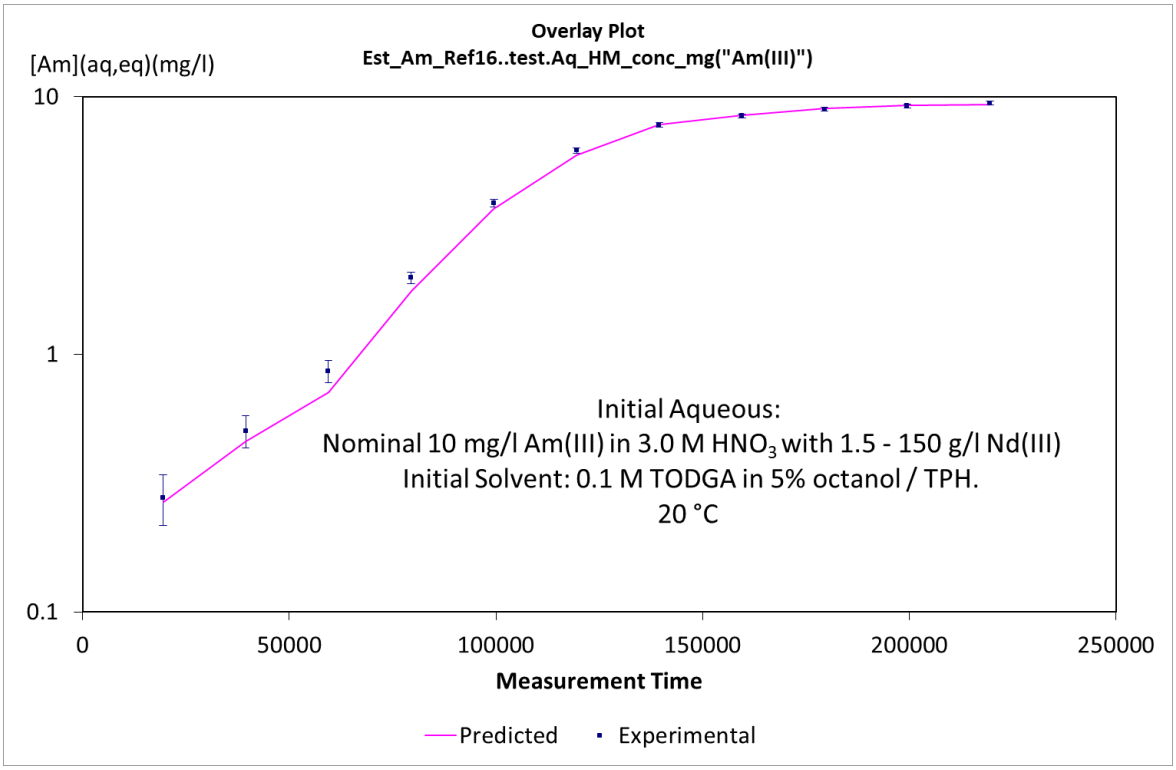

Figure 67: Fit of Am distribution model to experimental data (Aq Am data series 6).

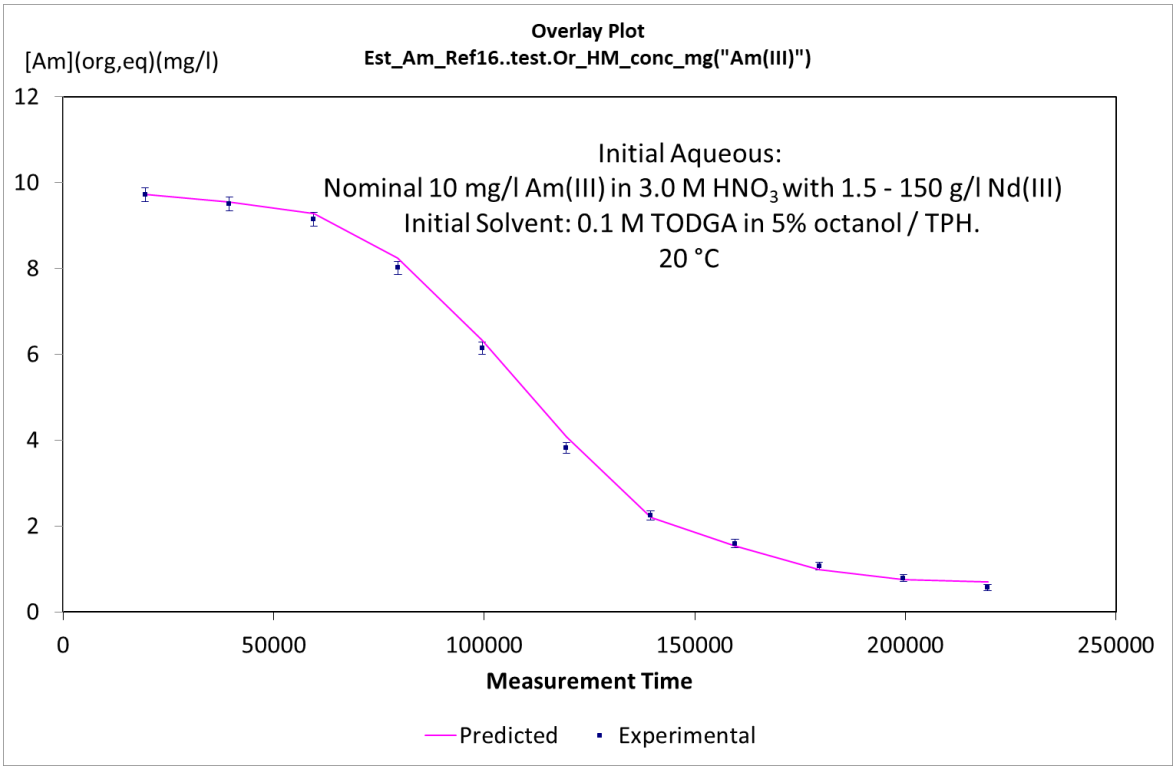

Figure 68: Fit of Am distribution model to experimental data (Or Am data series 6).

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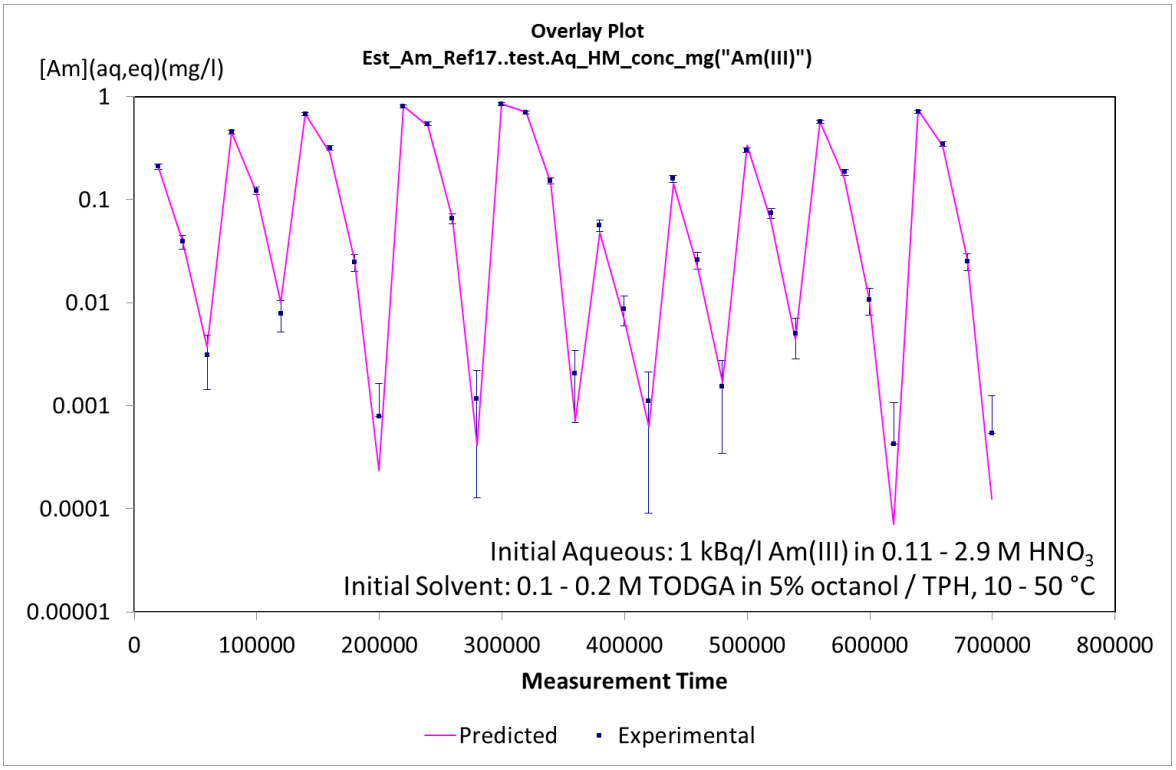

Figure 69: Fit of Am distribution model to experimental data (Aq Am data series 7).

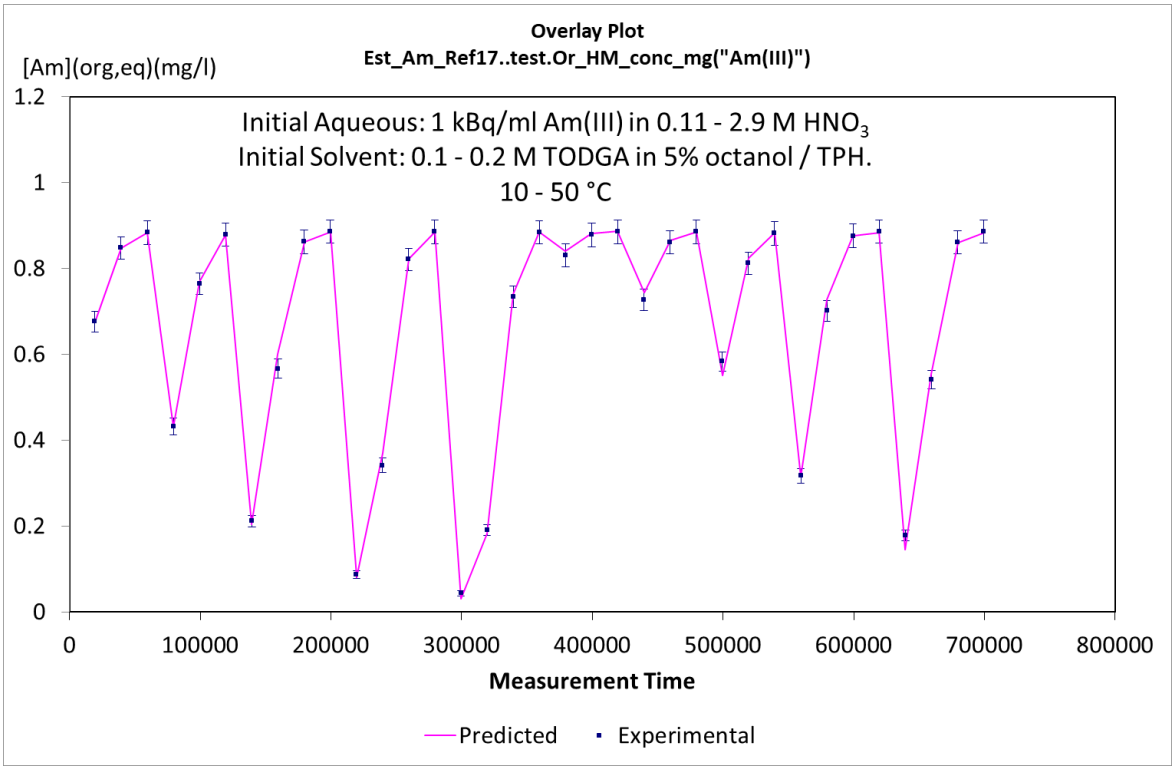

Figure 70: Fit of Am distribution model to experimental data (Or Am data series 7).

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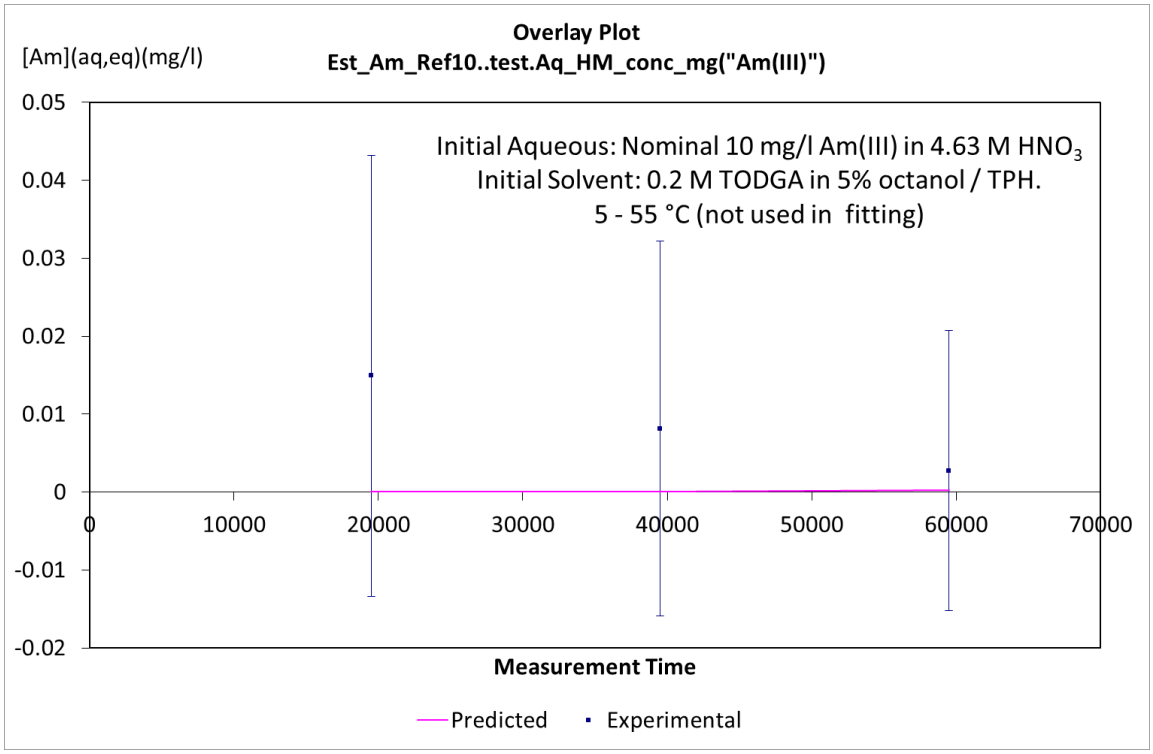

Figure 71: Fit of Am distribution model to experimental data (Aq Am Unused data series 1).

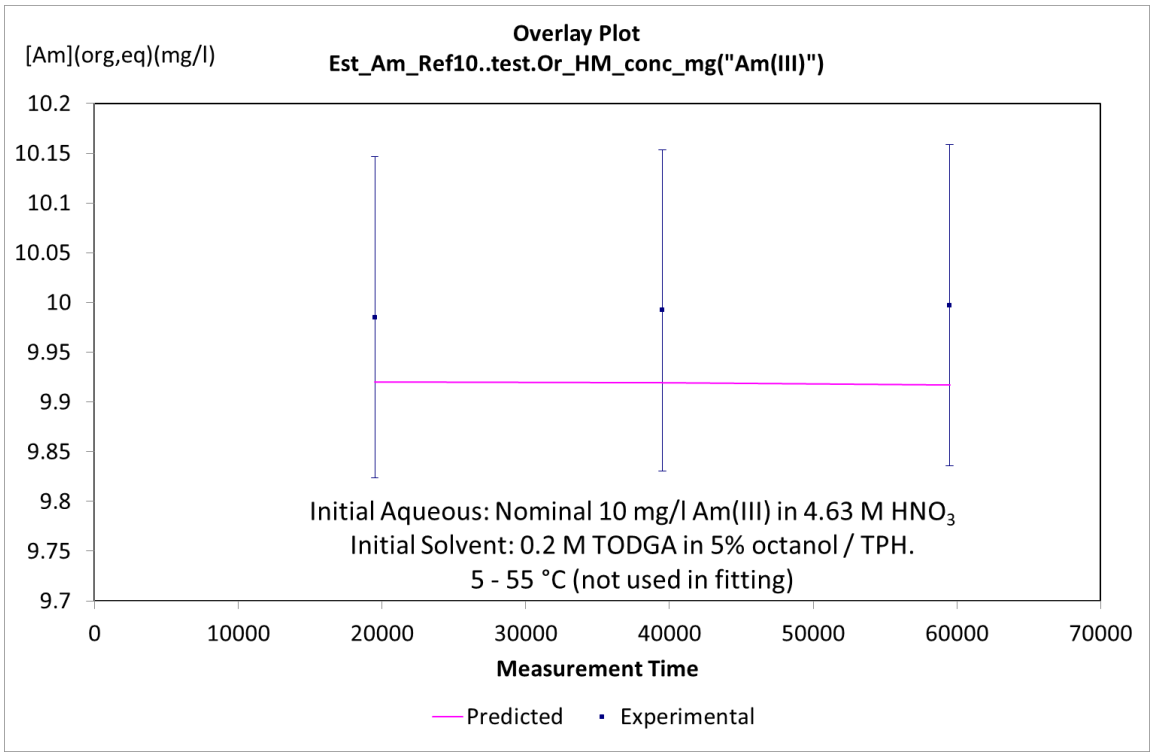

Figure 72: Fit of Am distribution model to experimental data (Or Am Unused data series 1).

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With regard to the quality of the fit, it is clear that this is dependent on the on the concentrations involved. In general for higher concentrations there is a good fit but for very low concentrations in the aqueous phase the predicted aqueous concentrations are much less than the observed aqueous concentrations (see Figure 51). In general, these very low aqueous concentrations are associated with high distribution values so the indications are that the model is overpredicting distribution values when the experimental distribution values are already very high. There are known issues with the measurement of extremely low concentrations, partly to do with the limits of detection of the measurement techniques themselves but probably at least as significantly to do with difficulty achieving the required quality of separation. With a distribution value of 10000 (not unlikely for americium being extracted into TODGA from a moderate to high acidity aqueous) it only takes one part in 10^4 of the solvent to be entrained in the aqueous as some sort of haze to double the measured concentration in the aqueous. For this reason it is thought to be at least plausible that under such conditions the model may be more representative of the true equilibrium than experimental results. In most applications there will be little sensitivity to errors in distribution values when they are extremely high. The practical difference between a distribution value of 10^3 and a value of 10^5 is typically small; in both cases the species in question almost entirely extracts.

7.4. ORGANIC AMERICIUM SPECIATION

To give some idea of the relative importance of the different complexes being proposed by this model, the model was run for extraction of trace (0.01 mg/l in equilibrium aqueous) Am into 0.2M TODGA in 5% octanol / TPH at 20 °C for a range of aqueous acid and Nd concentrations. The percentage of the extracted Am accounted from by each complex predicted by these runs are shown in Figure 73 through Figure 79 below. Predicted Am distribution values and the Am/Nd separation factor are presented in Figure 80 and Figure 81 respectively.

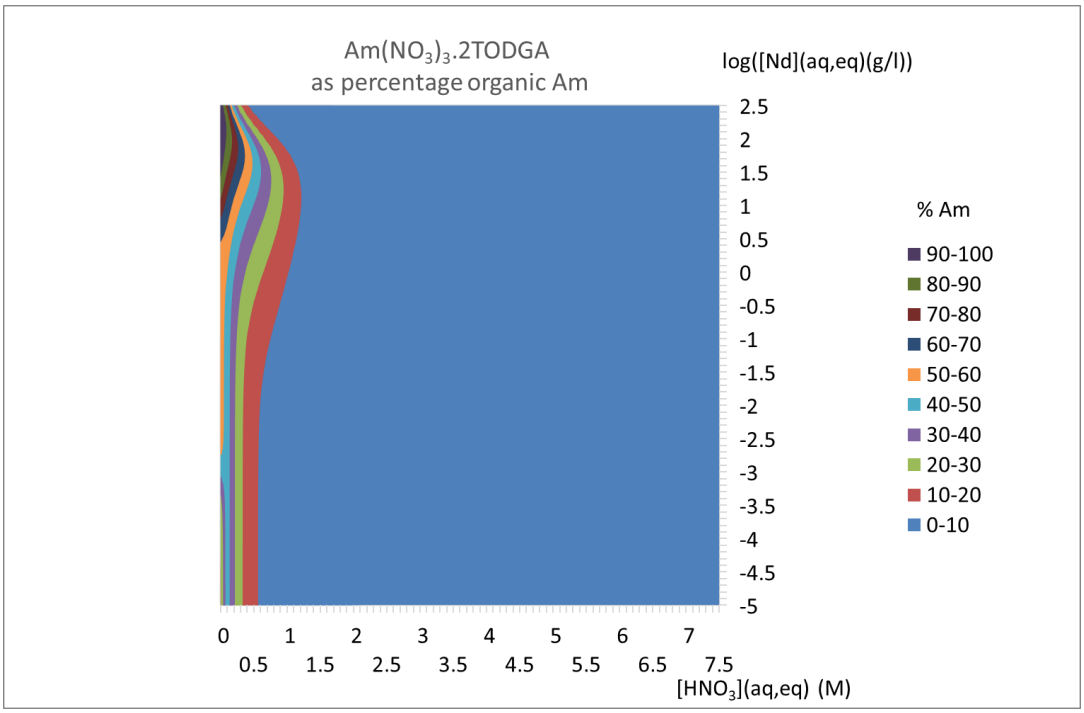

Figure 73: Predicted %Am$(NO_3)_3$.2TODGA in 0.2M TODGA in 5% octanol / TPH at 20 °C (Trace Am).

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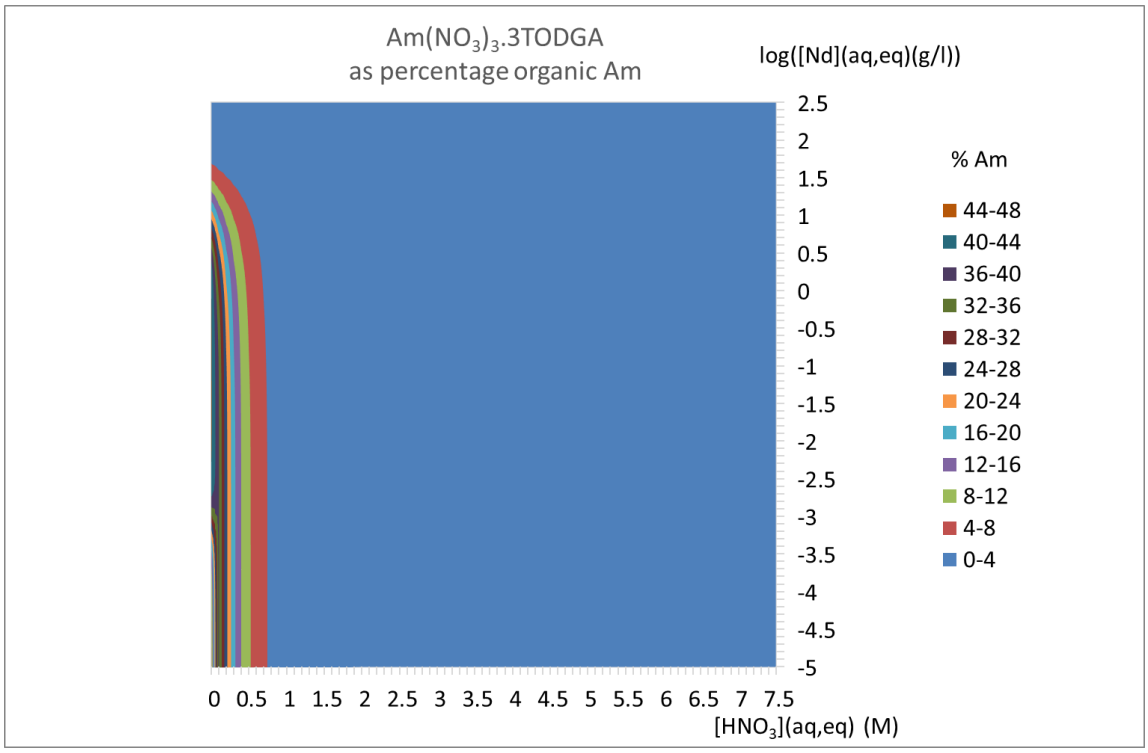

Figure 74: Predicted %Am(NO₃)₃.3TODGA in 0.2M TODGA in 5% octanol / TPH at 20 °C (Trace Am).

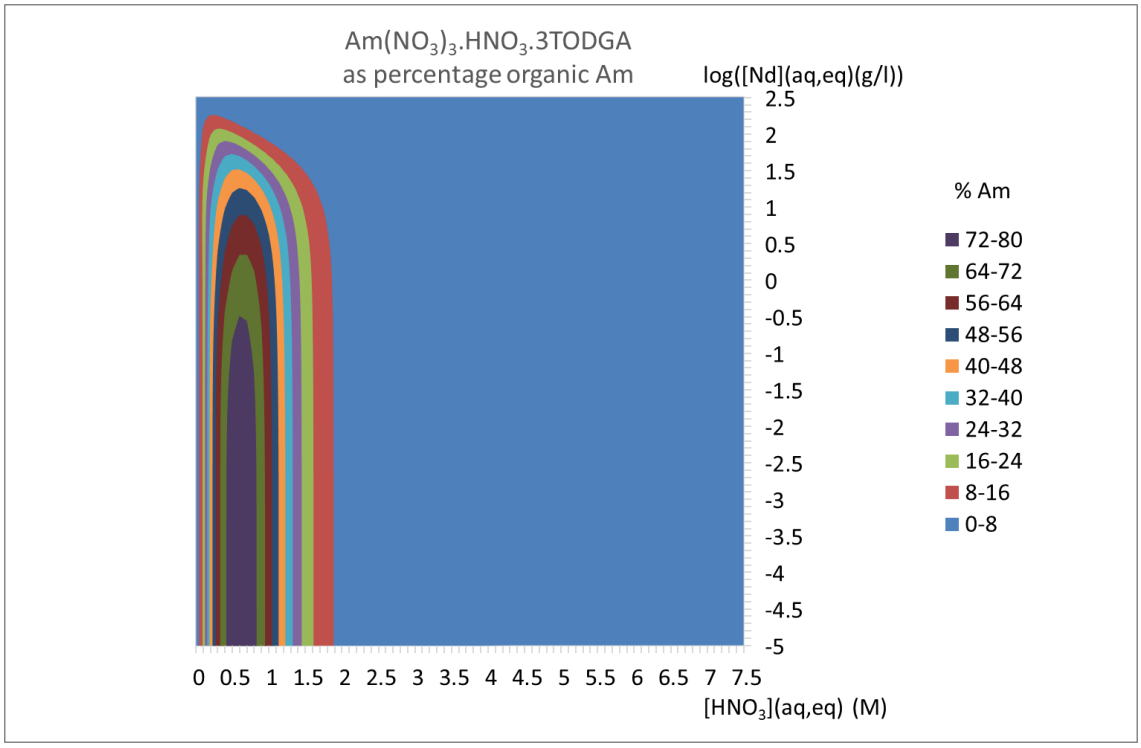

Figure 75: Predicted %Am(NO₃)₃.HNO₃.3TODGA in 0.2M TODGA in 5% octanol / TPH at 20 °C (Trace Am).

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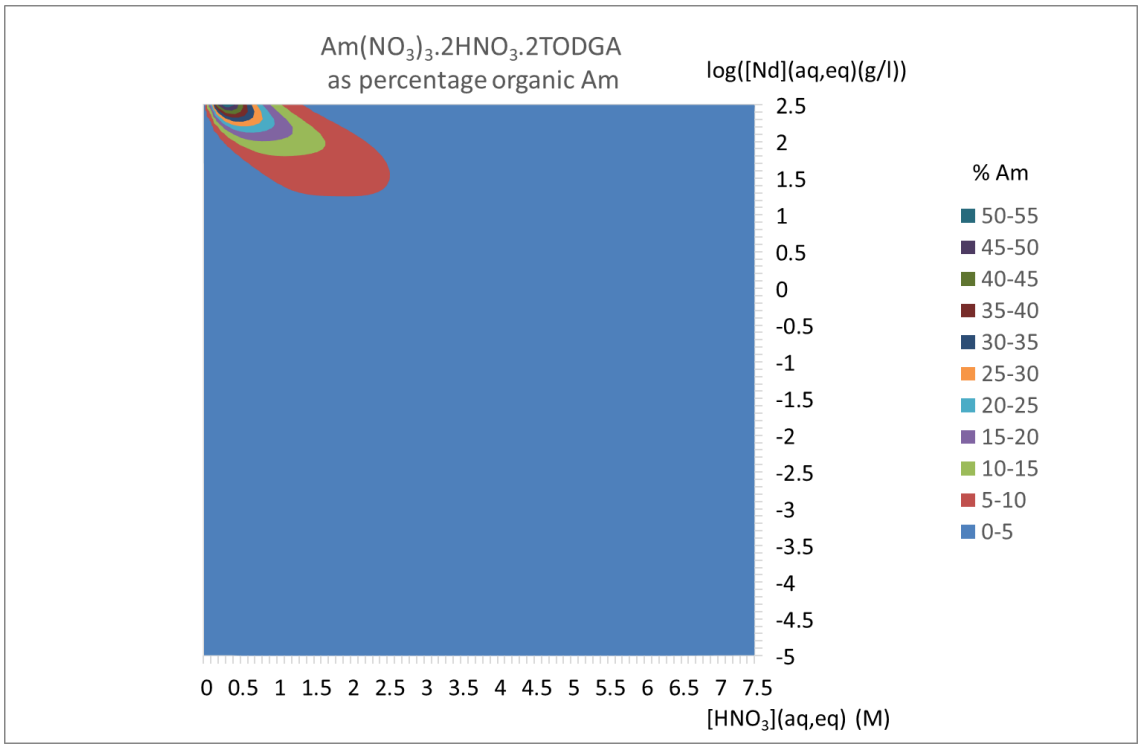

Figure 76: Predicted %$Am(NO_3)_3.2HNO_3.2TODGA$ in 0.2M TODGA in 5% octanol / TPH at 20 °C (Trace Am).

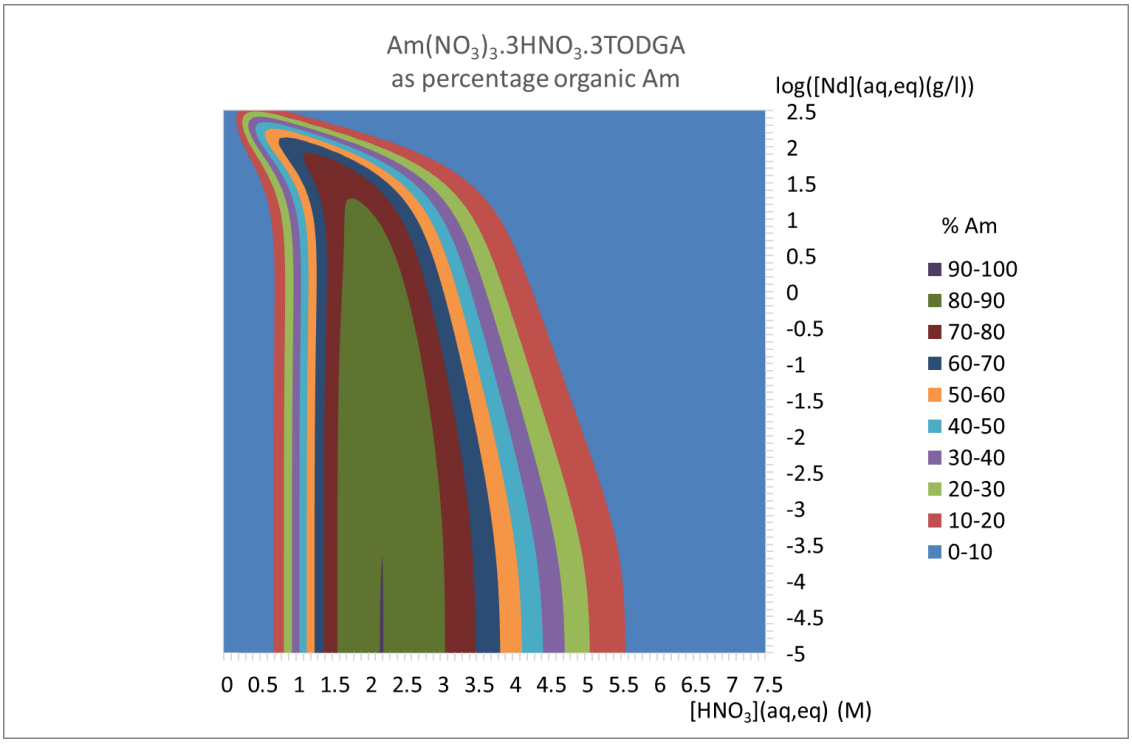

Figure 77: Predicted %$Am(NO_3)_3.3HNO_3.3TODGA$ in 0.2M TODGA in 5% octanol / TPH at 20 °C (Trace Am).

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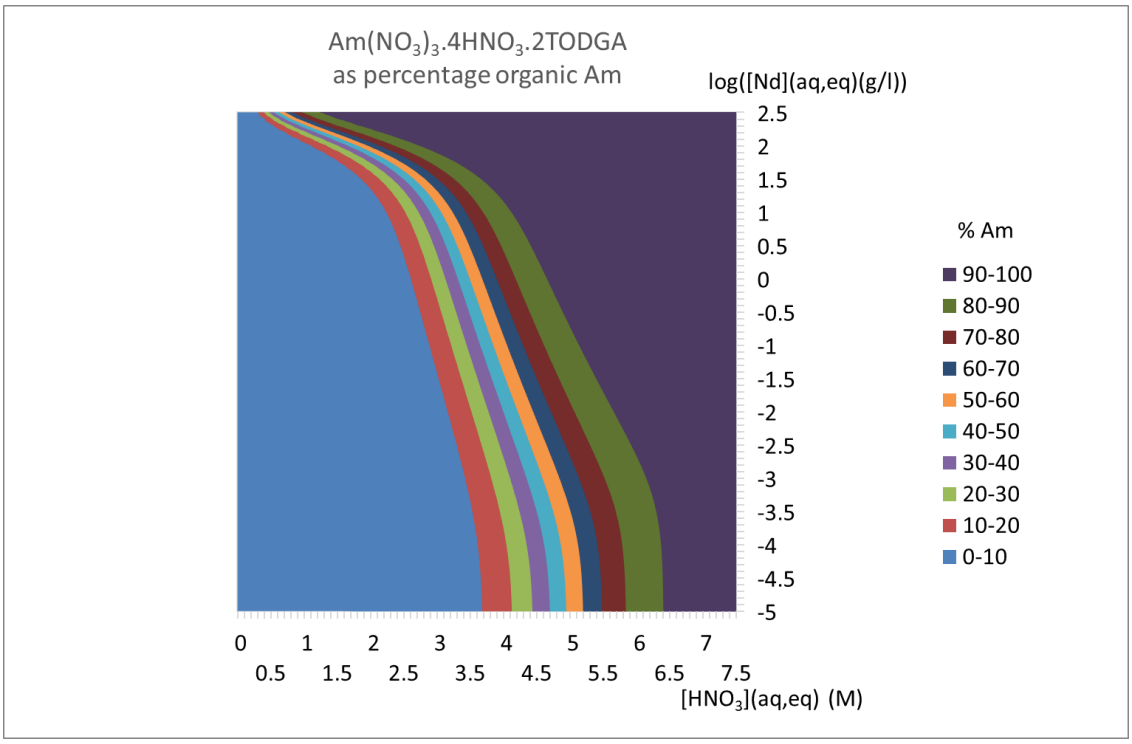

Figure 78: Predicted %Am(NO$_3$)$_3$.4HNO$_3$.2TODGA in 0.2M TODGA in 5% octanol / TPH at 20 °C (Trace Am).

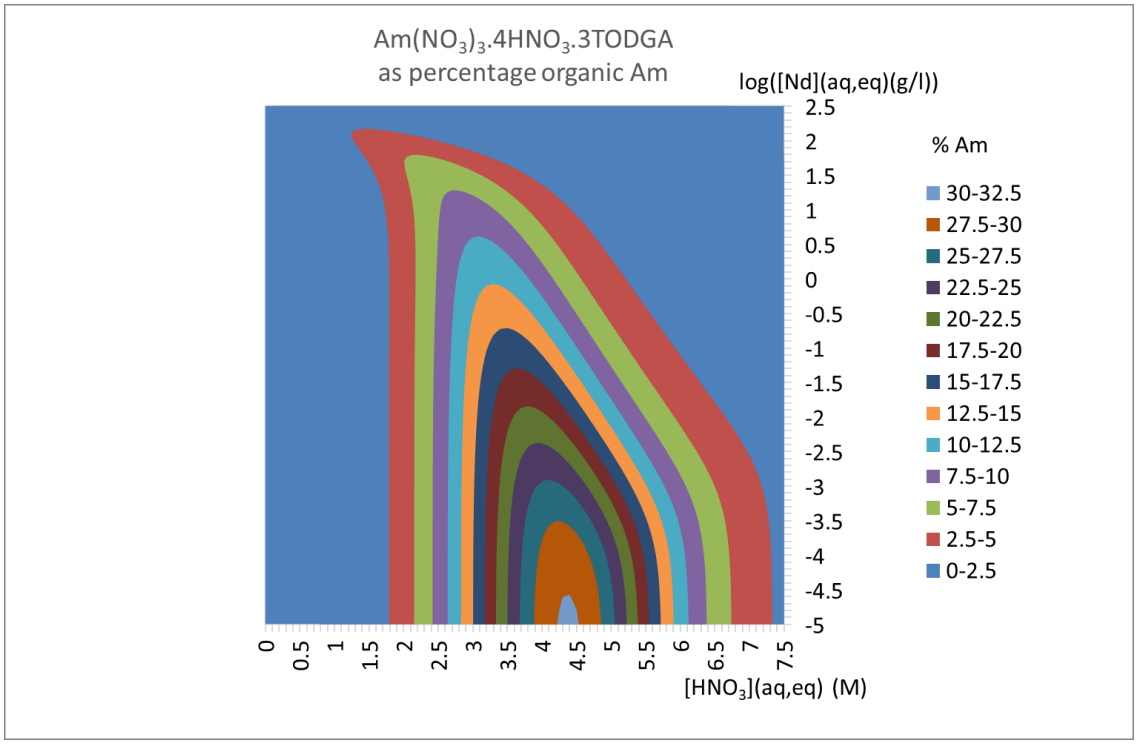

Figure 79: Predicted %Am(NO$_3$)$_3$.4HNO$_3$.3TODGA in 0.2M TODGA in 5% octanol / TPH at 20 °C (Trace Am).

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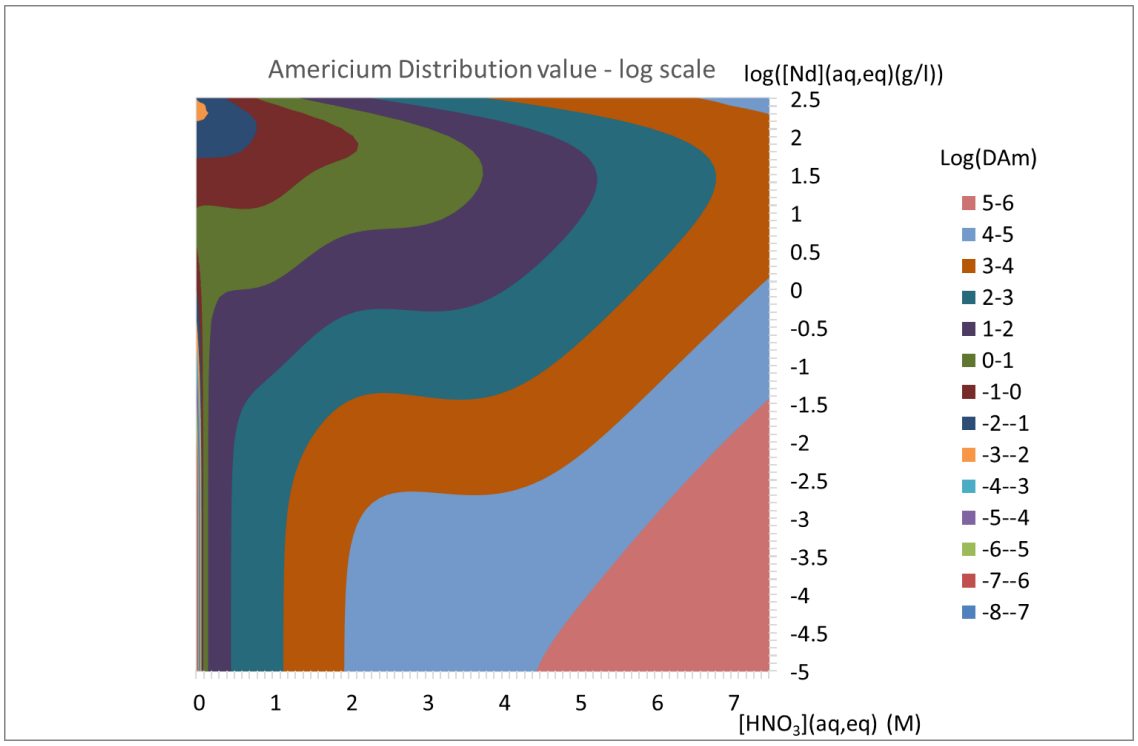

Figure 80: Predicted distribution of trace Am into 0.2M TODGA in 5% octanol / TPH at 20 °C (Trace Am).

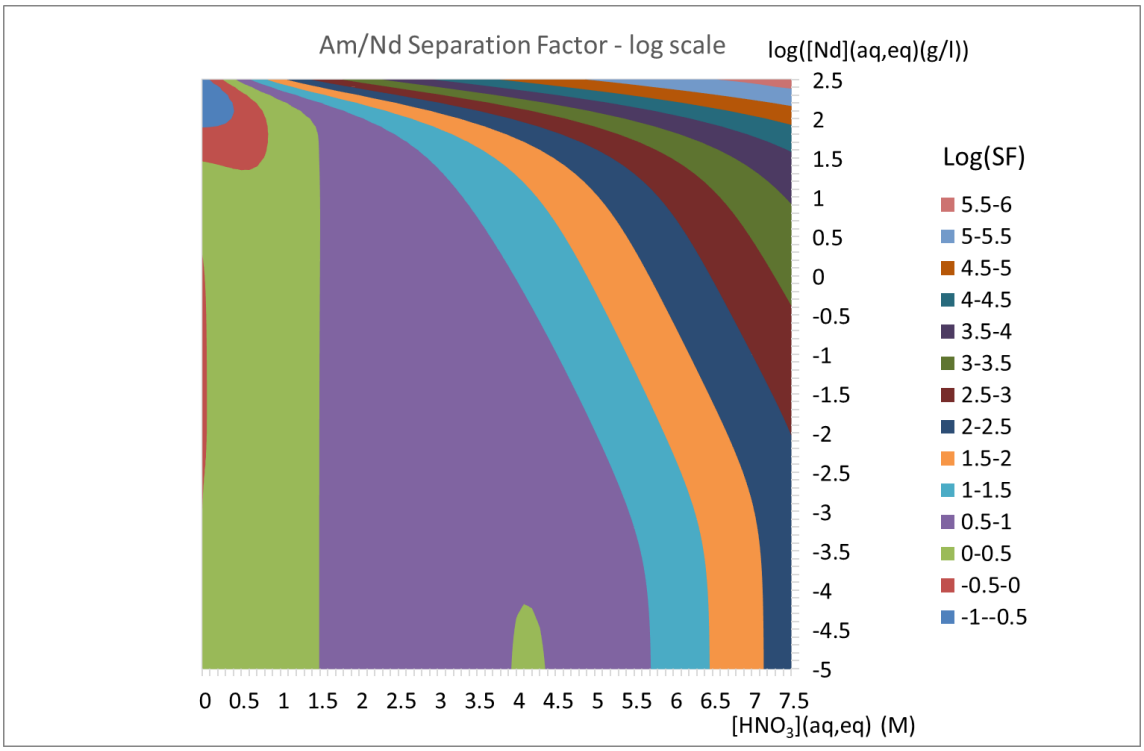

Figure 81: Predicted Am/Nd separation factor for extraction into 0.2M TODGA in 5% octanol / TPH at 20 °C (Trace Am).

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Figure 81 above shows that at low to moderate acidity the separation factor relative to neodymium has little dependence on Nd loading except at the very highest loadings. This is in line with experimental data (albeit the experimental data are at 1 M HNO_3). The figure suggests that under conditions of high neodymium loading and high acidity the extraction of Am is preferred to extraction of Nd. This is probably due to the presence of a Metal.4HNO_3.2TODGA complex in the Am model which is not present in the Nd model. Formation of such complexes will be favoured over complexes containing 3 TODGA ligands under high loading conditions and complexes containing a lot of acid will be favoured under high acidity conditions. There are no experimental data available under such conditions and use of the model in this region is dependent on considerable extrapolation from the extant experimental data.

The correct prediction of separation factors is a requirement for successful models whether applied under normal or maloperation conditions.

7.5. SCOPE FOR AMERICIUM MODEL IMPROVEMENT

All available data for the extraction of americium in the TODGA / octanol system are essentially for trace americium concentration in the sense that [Am] << [TODGA]. Practical experimental considerations dictate that this is likely to remain the case going forward although it is conceivable that loading trials with low TODGA concentrations could be undertaken in the future. Such trials could offer improved understanding of the balance between complexes containing 2 TODGA vs those containing 3 TODGA. The lack of existing or potential future data relating to extraction of macroscopic amounts of Am has a second consequence in that there is little prospect of obtaining direct measurements of solvent phase acidity that would be of value in determining the amount of acid coextracted with americium. Either the amount of acid directly extracted into the solvent would be very much greater than the amount coextracted with americium or, if very low TODGA concentrations were used, the quantity of coextracted acid would still be very low, possibly too low for accurate measurement of the acidity. If attempts to measure solvent acidity in an Am loaded low TODGA system were to be undertaken it would be best to work with a solvent containing only TODGA and inert diluent so that the data are not complicated by the extraction of acid by any other component of the solvent phase (octanol in the case of the i-SANEX system).

A further issue relating to data for americium extraction is the very high distribution values that apply under many conditions. With experiments limited to very low americium concentrations this can give rise to measurement problems. These may relate to the actual measurement, although counting techniques allow extremely low concentrations to be measured. The more likely problem, however, arises from difficulty of obtaining perfect phase separation, without which measured aqueous concentrations may be more a reflection of residual entrained solvent haze than true aqueous concentration of the analyte.

Regarding the model itself there are a couple of concerns which might be resolved with the addition of further experimental data.

The expression fitted for the activity coefficient of americium appears somewhat suspect. The acidity needs to be increased to very high levels before the activity coefficient exceeds that at near zero nitrate concentration (Figure 50). It is not certain that this is wrong but it is not well aligned with the way that the activity of nitric acid behaves or the fitted expressions for the other metal activities considered in this report. It is not necessarily a problem if it is wrong, provided that distribution values calculated using it are in agreement with

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experiment, but typically use of such incorrect intermediate quantities (which are essentially empirical) in a model will result in the model extrapolating poorly.

The model uses a total of seven different complexes of which the evidence for two is rather weak (the 95% t-value is less than the reference t-value). It would be desirable to reduce the number of complexes required by the model. Experimental work focussed on regions in which these two complexes are predicted to be most prevalent could provide evidence with regard to the existence or otherwise of these complexes.

7.6. EXPERIMENT DESIGN FOR AMERICIUM EXTRACTION

The process described in the previous sections for Nd, La and Yb was repeated for Am and run through 10 iterations. There were a number of major differences compared to the experiment design used to support development of the distribution algorithms for other species:

- It was assumed that trace (10 mg/l) initial Am would be used in all experiments. This is in recognition of the fact that use of bulk americium was unlikely to be feasible. Although a concentration of 10 mg/l has been used in the modelling, the exact amount used in experiments is unimportant as the analysis is only dependent on having [Am] << [TODGA]
- In the absence of loading with Am the experiment design allowed up to 150 g/l of Nd to give loading of the solvent.
- It was assumed that the measured variables in experiments were the aqueous and organic concentrations of Am. It was assumed that no acidity measurements would be undertaken as solvent phase acidity would comprise mainly directly extracted acid and acid coextracted with the Nd, if present, so that measurement of solvent phase acidity would not give a useful indication of acid coextracted with Am.
- The experiment design was constrained to give only experiments where the distribution value of Am was predicted to lie in the range 0.001 to 1000. This limits the potential for suggested experiments to be compromised by imperfect phase separation.

The initial parameter estimation suggested that there was reasonable confidence in the values of the stability constants for the $Am(NO_3)_3.2TODGA$, $Am(NO_3)_3.4HNO_3.2TODGA$, and $Am(NO_3)_3.HNO_3.3TODGA$ complexes (95% t-value > 10), with lesser but still usable confidence in the stability constants of $Am(NO_3)_3.3TODGA$ and $Am(NO_3)_3.3HNO_3.3TODGA$ complexes (95% t-value in range 4 – 10) but stability constants for the $Am(NO_3)_3.2HNO_3.2TODGA$ and $Am(NO_3)_3.4HNO_3.3TODGA$ complexes are less well defined as evidenced by low 95% t-values (<2). An aim of any further experimental work would be to confirm or refute the existence of these complexes.

The limits placed on the experimental conditions were as for the Nd experiment design except in that lower TODGA concentrations were allowed i.e. 0.001 – 0.3 M [TODGA], 0.01 – 7.0 M initial [HNO_3], 0.01 – 150 g/l initial [Nd] and 10 – 50 °C.

Table 23 below presents the initial conditions for the optimised experiment and the rounded version of these carried forward into subsequent calculations. Table 24 presents the predicted values of the measured variables for the optimised and rounded experiments. Table 25 and Table 26 then present the standard deviations and 95% t-values resulting from parameter estimation as each of the proposed experiments is added to the set of experiments used for the estimation.

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Table 23: Control Variables for Beaker Trials from Experiment design.

Expt No	Initial values from Optimisation				Rounded Values carried forward			
	[TODGA] (M)	[HNO_3] (aq)(M)	[Nd](aq) (g/l)[16]	T (°C)	[TODGA] (M)	[HNO_3] (aq)(M)	[Nd](aq) (g/l)	T (°C)
1	0.004907	0.58156	150	10	0.005	0.6	150	10
2	0.05315	4.35883	0.00001	50	0.05	4.5	0	50
3	0.3	0.42967	0.00001	10	0.3	0.43	0	10
4	0.048938	4.21331	0.00001	42.3421	0.05	4	0	40
5	0.005253	1.09009	66.0141	49.6695	0.005	1.1	70	50
6	0.3	0.01	0.00001	23.9511	0.3	0.01	0	25
7	0.051779	4.42665	0.00001	50	0.05	4.5	0	50
8	0.051409	4.44482	0.00001	50	0.05	4.5	0	50
9	0.041625	7	150	50	0.04	7	150	50
10	0.050146	4.50615	0.00001	50	0.05	4.5	0	50

The suggested experiments have mostly been designed to give distribution values near the lower end of the allowed range (experiments 1, 5 and 6) or the upper end of the allowed range (the rest). Five of the proposed experiments are under broadly similar conditions (0.05 M TODGA, 4 – 4.5 M HNO_3, no Nd, 40 – 50 °C). These are the conditions most favourable for formation of the $Am(NO_3)_3.4HNO_3.3TODGA$ complex within the scope of the experiment design parameters (see Figure 79). The experiments can therefore be considered to be focussed on pinning down the value of the stability constant for this complex.

[16] In line with normal nuclear industry practice concentrations of heavy metals have been expressed in g/L. To convert to neodymium molarity divide by 144.242. It is assumed that experiments will use natural neodymium. Fission derived neodymium will have a slightly greater atomic weight.

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Table 24: Predicted Values for Measured Variables from Experiment design.

Expt No	Experiment as first optimised			Experiment with rounded control variables		
	[Am](aq) (mg/l)	[Am] (org)(mg/l)	D_{Am} (derived)	[Am](aq) (mg/l)	[Am] (org)(mg/l)	D_{Am} (derived)
1	9.993	0.009993	0.001	9.992	0.01078	0.001078
2	0.009965	9.965	1000	0.0101	9.965	986.2
3	0.01338	9.982	745.9	0.01336	9.982	747
4	0.009968	9.968	1000	0.01032	9.968	965.6
5	9.961	0.04101	0.004117	9.963	0.03881	0.003896
6	9.779	0.2221	0.02271	9.804	0.197	0.0201
7	0.009965	9.965	1000	0.0101	9.965	986.2
8	0.009965	9.965	1000	0.0101	9.965	986.2
9	0.02355	9.946	422.4	0.02413	9.946	412.2
10	0.009965	9.965	1000	0.0101	9.965	986.2

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Table 25: Predicted standard deviations of parameters obtainable from parameter estimation after running of designed experiments.

	Stability Constant							ΔG
Complex	$Am(NO_3)_3$ .2TODGA	$Am(NO_3)_3$ .3TODGA	$Am(NO_3)_3$. HNO_3 .3TODGA	$Am(NO_3)_3$.$2HNO_3$ .2TODGA	$Am(NO_3)_3$.$3HNO_3$ .3TODGA	$Am(NO_3)_3$.$4HNO_3$ .2TODGA	$Am(NO_3)_3$.$4HNO_3$ .3TODGA	J/mol
Initial Value	495.28	2250	146217	159.043	284607	9.78337	2196.04	-92088
Initial SD	24.53	253.7	5763	65.02	19120	0.3083	1809	951.6
Initial SD/value	4.95%	11.28%	3.94%	40.88%	6.72%	3.15%	82.38%	-1.03%
SD after Expt 1	24.51	253.5	5641	17.47	13650	0.2969	1783	950.1
" " " 2	24.43	250.1	5571	17.38	10940	0.2575	549.3	938.9
" " " 3	22.79	240.4	4753	17.38	10750	0.2573	525.3	835.4
" " " 4	22.79	240.3	4753	17.37	10740	0.2549	434.8	833.2
" " " 5	22.69	238.9	4641	17.14	10250	0.2548	400.3	706.6
" " " 6	21.22	188.2	4576	17.12	10160	0.2548	400.3	702
" " " 7	21.21	188.1	4575	17.11	10070	0.2545	354.9	699.9
" " " 8	21.21	188	4574	17.1	10020	0.2544	331.1	699
" " " 9	21.14	186.5	4561	17.1	10000	0.2282	305.8	623.8
" " " 10	21.14	186.4	4560	17.1	9975	0.2281	289.4	623.3
Final SD/Value	4.27%	8.28%	3.12%	10.75%	3.50%	2.33%	13.18%	-0.68%

It will be noted that standard deviations reduce with the addition of each experiment.

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Table 26: Predicted 95% t-values of parameters obtainable from parameter estimation after running of designed experiments.

	Stability Constant							ΔG
Complex	$Am(NO_3)_3$ .2TODGA	$Am(NO_3)_3$ .3TODGA	$Am(NO_3)_3$. HNO_3 .3TODGA	$Am(NO_3)_3$.$2HNO_3$ .2TODGA	$Am(NO_3)_3$.$3HNO_3$ .3TODGA	$Am(NO_3)_3$.$4HNO_3$ .2TODGA	$Am(NO_3)_3$.$4HNO_3$ .3TODGA	J/mol
Initial 95% t-Value	10.24	4.5	12.87	1.241	7.551	16.1	0.616	49.09
95% t-value after Expt 1	10.26	4.504	13.16	4.62	10.58	16.73	0.6252	49.19
" " " 2	10.29	4.566	13.32	4.645	13.2	19.28	2.029	49.78
" " " 3	11.03	4.751	15.61	4.646	13.44	19.3	2.122	55.95
" " " 4	11.03	4.752	15.62	4.648	13.45	19.48	2.563	56.1
" " " 5	11.08	4.781	15.99	4.709	14.09	19.49	2.784	66.15
" " " 6	11.85	6.069	16.22	4.716	14.21	19.49	2.784	66.58
" " " 7	11.85	6.073	16.22	4.719	14.35	19.51	3.141	66.78
" " " 8	11.85	6.074	16.23	4.72	14.42	19.52	3.367	66.87
" " " 9	11.89	6.125	16.27	4.72	14.44	21.76	3.645	74.92
" " " 10	11.89	6.126	16.27	4.721	14.48	21.77	3.852	74.99

95% t-values increase with each subsequent experiment.

As previously indicated much of the experimental effort suggested by the design process is focussed on the $Am(NO_3)_3.4HNO_3.3TODGA$ complex. This is one of the less important complexes, making up a maximum of 30% of the extracted Am under the most favourable conditions. This is seen in Figure 79 for 0.2 M TODGA although it is predicted to occur to some extent across a fairly wide range of conditions. The first suggested experiment appears to be directed at determination of the stability constant of the $Am(NO_3)_3.2HNO_3.2TODGA$ complex. This complex is only predicted to occur in significant quantities at high loading and fairly low acidity (~0.5M – see Figure 76). An experiment in this region would do a lot to determine whether this complex exists at all, something that has not been definitively determined by the experimental work to date.

Experiment 6 can be identified as being focussed primarily on the $Am(NO_3)_3.3TODGA$ complex (Figure 74), being under the low acidity, high TODGA conditions that will maximise the generation of this complex.

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8. DISCUSSION

Models have been developed that successfully describe the available distribution data for Nd, La, Yb and Am from nitric acid solution into solvents comprising TODGA in 5% octanol / TPH (hydrogenated tetrapropylene). In the cases of Nd and La the fits obtained are extremely good with very few outliers. In the case of Yb there is a tendency for the fitted model to underpredict aqueous concentrations in experiments that resulted in very low concentrations in the aqueous. These experiments correspond to those in which the distribution values are very high. The situation with regard to the Am model is similar with a tendency to underpredict aqueous concentrations and hence overpredict distribution value in cases where the latter are very large. It appears likely that the problems obtaining a good fit to very high distribution value data may be down to issues with the experiments themselves. The data in these cases show a wide scatter, which irrespective of any other considerations will limit the quality of the fit that can be obtained. A more serious problem is that the data may be systematically biased due to problems with measurement of very low concentrations in the aqueous. This could arise from imperfect separation of the phases prior to analysis, with very low levels of organic haze in the aqueous being sufficient to result in erroneously high measurements of the aqueous metal concentrations.

There are other possible reasons for aqueous measurements of metal concentration being too high. One is the possibility that very small amounts of the metal are complexing with trace levels of impurities such as solvent breakdown products resulting in complexes that are somewhat more hydrophilic than the TODGA / metal complexes. This would appear plausible but is speculative. Another possibility is that the TODGA / metal complexes themselves partition to some limited extent into the aqueous, as opposed to being exclusively solvent phase species as assumed by the models. In this case the effect on the data would have to be considered real and the models would have to be considered deficient in so far as they do not capture this phenomenon. Whilst this again would appear plausible, evidence to support it as a hypothesis is not available.

To a significant extent it is unimportant whether the model is accurate under conditions in which distribution values are extremely high so long as the qualitative behaviour is captured. The behaviour of a typical flowsheet will not, in general, be sensitive to the difference between say a distribution value of 10^3 and a value of 10^5. In both cases the species in question will quantitatively extract and in any practical flowsheet extraction efficiency will be less than 100% so that apparent distribution values will not approach 10^3 never mind 10^5.

Given the semi-empirical nature of the models the range of validity of the models will not extend greatly beyond the range of the data available to develop and test the models. This varies somewhat with the species in question. The data required for the construction of models can be divided into a number of different classes as below:

- Distribution of trace amounts of the species in question.
- Distribution of macroscopic amounts of the species in question. Macroscopic in this context is taken as referring to amounts of the extracting species that are sufficient to complex a significant fraction of the ligand.
- Distribution of acid in the presence of macroscopic amounts of the extracting metal. This can provide insights into the form of the solvent phase complexes which in many cases will include co-extracted acid.

In each of the above cases there is a requirement to cover a range of acidities, TODGA concentrations and temperatures.

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In the case of neodymium the coverage provided by the data is better than for any of the other species considered here in that there are both trace and bulk distribution data and a limited amount of acid coextraction data. However, additional data would be beneficial to cover a greater range of TODGA concentrations (existing data are just for 0.1 and 0.2 M), coextraction of acid under a wider range of conditions (current data all relates to 3M acidity, 0.1 M TODGA), highly loaded systems under a wider range of conditions (in particular different temperatures, and extremes of the acidity range).

For lanthanum the situation is broadly similar to that for neodymium except in that there are no data available for coextracted acid, and the extent of data is generally less than for neodymium.

For ytterbium the data are significantly more limited in that the available data for distribution of trace ytterbium cover only fairly low acidities. To a large extent this is a reflection of the difficulties associated with collecting reliable data for what is an extremely extractable species. The data at 3M acidity obtained under high loading conditions do however alleviate this situation to some extent.

Americium is the species for which the widest range of distribution data are available. These data are, however, all for trace levels of americium reflecting the practical difficulties of working with large quantities of a rare and highly alpha active species. The absence of loading data is to some extent alleviated by the availability of a certain amount of data for americium extraction in systems which are loaded with other species (Nd, La). The variety of different sources of americium distribution data is probably behind some of the scatter seen in the data, although the larger issue is probably the inclusion of a large amount of data for conditions under which the distribution value is very high which as discussed previously is subject to a number of experimental problems. Additional data to cover high loading with americium and coextraction of acid in systems with a high americium loading would be desirable for model construction, but it must be recognised that practical considerations likely mean that such data are very difficult to obtain.

For all species the addition of data relating to extraction in the presence of an inextractable nitrate (e.g $NaNO_3$) would be of value in sorting out or confirming the situation with regard to the coextraction of acid. Ideally such data would include points in which the acidity was as low as reasonably practicable.

An important test for models is the ability to predict separation factors between different species. There are relatively few data available with which to validate the models in this regard, although some americium / neodymium separation factor data are available and the models have been shown to predict these well. Separation factors matter because to a large extent it is these that will determine the performance of a flowsheet rather than the absolute magnitude of the distribution values. They are also very important in the modelling of maloperation scenarios where oversaturation can lead to competition between species for the available extractant. The success of models in such scenarios will be largely dependent on their ability to correctly predict separation factors.

There is a general uncertainty with regard to possible diluent effects. Some very limited data from KIT-INE indicates that for americium at least these may be significant. The vast majority of data for distribution of metals for the TODGA system have been obtained using TPH as a diluent, but this is not necessarily going to be the diluent of choice in the future and there is a requirement to understand whether alternative diluents act in a sufficiently similar manner to TPH to allow models derived using TPH to be more widely applied.

The species predicted by the models (those with non-zero stability constants) are summarised in Table 27 along with the calculated ΔG for each metal ion. All metal ions were found to have di- and tr- solvated complexes $M(NO_3)_3(TODGA)_2$ and $M(NO_3)_3(TODGA)_3$ as well as the adduct $M(NO_3)_3(HNO_3)_4(TODGA)_3$. Americium shows the

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most complicated behaviour. The magnitude of the ΔG values increases across the lanthanide series and americium is closer to Nd as might be expected.

Table 27: Coordination numbers for lanthanide and americium species in complexes of general formula $M(NO_3)_x(HNO_3)_y(TODGA)_z$ proposed from modelling (i.e. non-zero stability constants) and calculated ΔG.

NO_3^-	HNO_3	TODGA	La	Nd	Yb	Am
3	0	2	X	X	X	X
3	0	3	X	X	X	X
3	1	3			X	X
3	2	2				X
3	2	3		X		
3	3	3		X		X
3	4	3	X	X	X	X
3	4	2	X			X
ΔG (kJ/mol)			-80.6	-90.8	-96.2	-92.1
Ionic radius (+3) (Å)			1.061	0.995	0.838	0.982

The gPROMS experiment design facility has been applied to each of the species modelled in the course of this work with a view to identifying experiments that would best improve the models described herein. Specifically, the design has been undertaken with a view to improving confidence in the values of the stability constants associated with the solvent phase complexes of the extracted metals. This acts to highlight a significant limitation with experiment design in gPROMS; namely that it is set up to suggest experiments that will allow an existing model to be refined. It will not suggest experiments that could require a change in structure of the model such as the addition of an extra complex. Where there are large gaps in current data coverage it would be advisable to add experiments in these regions even if gPROMS experiment design has not suggested any experiments are required in these regions. Such experiments would provide confirmation (or otherwise) that the model structure is essentially correct.

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9. CONCLUSIONS

1. Models to predict the distribution of neodymium, lanthanum, ytterbium and americium between nitric acid and TODGA in 5% octanol / TPH have been developed that describe the available data within the expected accuracy of that data.
2. Discrepancies between experimental and modelled results are greatest when distribution values are very high. In these cases the models tend to overpredict distribution values. It is probable that in such cases the experimentally reported distribution values, although still very high, give an understatement of the true distribution values. This is due to potential experimental problems leading to measurements of very low concentrations in the aqueous being higher than would be the case if, for example, perfect as opposed to near perfect phase separation could be achieved.

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10. RECOMMENDATIONS

1. Consideration should be given to undertaking experimental work defined from the gPROMS experimental design studies with a view to extending and improving the metal extraction models.
2. Application of the models to the simulation of the extract-scrub section of the i-SANEX process should be tested.
3. Modelling of the stripping sections of the i-SANEX process should be considered once the stripping agent is confirmed and sufficient distribution data have been accumulated.

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