Nitric Acid Extraction into a TODGA Solvent Modified with Octanol

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Summary

Distribution data for the partition of nitric acid between nitric acid solution and a solvent phase comprising various combinations of TODGA, octanol and inert kerosene diluent have been generated, covering a range of conditions from 0–9 mol/L HNO_3(aq), 0–100% octanol, 0–0.4 mol/L TODGA over a temperature range from 10–50 °C. The data have been used to derive a model describing the nitric acid equilibrium between the phases suitable for incorporation in process models of e.g. the innovative SANEX process. For the nitric acid / octanol / diluent system it was found that an accurate prediction of nitric acid distribution could be achieved using a model allowing 1:1, 1:2 and 1:3 nitric acid / octanol adducts. For the nitric acid / TODGA / diluent system the best models were found to be those allowing 4:1, 3:1, 2:1, 1:1 and 2:2 nitric acid / TODGA adducts. Superimposing the models for nitric acid distribution into the individual extractants and comparing with experimental results for the nitric acid / octanol / TODGA system showed systematic differences indicative of antagonistic and synergistic effects applying in the ranges 0.5–1.5 mol/L HNO_3 and > 1.5 mol/L HNO_3 respectively. These effects were modelled by the inclusion of 0:1:2, 1:1:1, 2:1:3 and 3:1:2 nitric acid / TODGA / octanol adducts. The effect of temperature on nitric acid extraction was well described by an Arrhenius type expression with an activation energy of −25.7 kJ/mol. No diluent dependence was found for nitric acid extraction.

Introduction

In order to reduce the burden of radioactive waste for geological disposal it is desirable to be able to separate the minor actinides (Np, Am, Cm) from the reprocessing waste stream. Removal of neptunium can be achieved by modification of the PUREX (Plutonium Uranium Reduction Extraction) process such that neptunium is initially routed with the uranium and plutonium [1-2]. The separation of americium and curium from fission products in general and lanthanides in particular is more challenging. TODGA *(N,N,N',N'*-tetra-*n*-octyl

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diglycolamide, Figure 1) has been identified as a promising extractant for the co-extraction of minor actinides and lanthanides from nitric acid based solution [3-4], allowing these to be separated from other fission products. In a subsequent process, americium and curium are separated from lanthanides [5]. This is achieved either by selectively stripping the former from the loaded TODGA solvent, employing an aqueous phase complexing agent such as polyaminocarboxylates [6-12], sulphonated bis-triazinyl-pyridines [13-15] or bis-triazolyl-pyridine [16-17], or by selective extraction from the TODGA product solution, obtained after backwashing the actinides and lanthanides, using nitrogen- or sulphur donor extracting agents [5, 18-21].
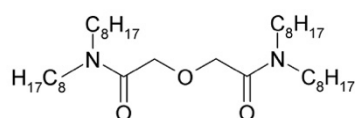

Figure 1: *N,N,N',N'*-tetra-*n*-octyl diglycolamide (TODGA).

A known disadvantage of TODGA-diluent mixtures is the tendency to form a third phase with only moderate loadings of nitric acid and / or metal ions, the extent of this tendency being dependent on the exact choice of diluent [4, 22]. In order to satisfactorily suppress third phase formation it is necessary to include a phase modifier in the formulation [4]. Various modifiers have been tried (e.g. tri-butyl phosphate [23-24], lipophilic alcohols [25-26], monoamides [27-29], DMDOHEMA (*N,N'*-dimethyl-*N,N'*-dioctyl-2-(2-hexyloxy-ethyl)-malonamide) [30-31]). A solvent comprising 0.2 mol/L TODGA with 5 v/v% octanol in an inert diluent such as odourless kerosene or hydrogenated tetra propylene (TPH) has been developed [32] and used [14] in recent European research programmes. This system has the advantage of employing only CHON species in the solvent, whilst keeping the amount of modifier at a small fraction of the overall solvent mix. However, both TODGA and octanol will extract nitric acid. In order to develop flowsheets using this solvent mix it is necessary to have a good understanding of nitric acid extraction as the distribution of nitric acid through a flow-sheet will be the prime determinant of solvent extraction behaviour within the plant. From a modelling perspective the development of good nitric acid extraction algorithms is a prerequisite for development of algorithms describing the extraction of other species present in the flow-sheet because all such algorithms must be designed to operate in the context of significant competition from nitric acid for the available extractant.

Nitric acid extraction into TODGA and similar diglycolamides is often described by assuming the formation of a 1:1 adduct, $HNO_3 \cdot TODGA$ [28]. This approximation is only sufficient to calculate nitric acid extraction at rather low aqueous nitric acid concentrations, see below. The formation of a 2:1 adduct, $2HNO_3 \cdot TODGA$ at nitric acid concentrations exceeding 2 mol/L is inferred from slope analysis [33].

Nitric acid extraction from 0.1–3 mol/L nitric acid into 0.01–0.2 mol/L T2EHDGA *(N,N,N',N'*-tetra(2-ethylhexyl) diglycolamide) dissolved in *n*-dodecane was modelled accounting for the formation of $HNO_3 \cdot T2EHDGA$ and $2HNO_3 \cdot T2EHDGA$ adducts [34]. Due to the absence of the modifier this model is not applicable to the TODGA + 5 v/v% octanol

solvent. Furthermore, we wished to extend the range of valid concentrations to 5 mol/L nitric acid and 0.3 mol/L TODGA.

The overall aim of this work was to establish reliable process models for calculating the distribution of nitric acid between a solvent containing TODGA with 5 v/v% octanol in kerosene diluents. As such, aggregation phenomena which are described in the literature [35-36] are not taken into account, work described herein finding that no improvement in model accuracy can be obtained by the inclusion of TODGA aggregates.

General Approach to Modelling

In order to model the extraction of nitric acid into TODGA-octanol mixtures, the approach taken is the following: nitric acid extraction into TODGA and into octanol are modelled separately. Then by comparing experimental results for extraction of nitric acid in TODGA-octanol mixtures with results obtained by superimposing the TODGA and octanol models an assessment of any antagonistic and/or synergistic effects is made.

In order to facilitate practical use of the models it is desirable to construct them such that they have the widest possible range of validity. For most applications this is more important than attaining very high levels of accuracy over a narrow range of conditions. For reasons to do with ease of numerical solution it is also desirable to have the model behave in a physically plausible manner outside of the range of known validity. A model that allows physically implausible features such as negative stability constants, even if they would only occur outside the range of conditions being modelled, will tend to give rise to numerical problems as the software used to implement the model searches for a solution. It is also desirable to avoid discontinuities in models, particularly in the case of dynamic models in which changing conditions through the course of a run can result in such discontinuities being encountered many times through a run. Although modern process modelling software, such as gPROMS and Aspen Custom Modeler, supports the implementation of discontinuities most notably through the inclusion of "*if ... then ... else*" constructs, the use of these features will typically incur a heavy penalty in terms of reliability of the model and required run time. A common problem in poorly designed dynamic models is that they "chatter", continually switching between two states making no useful progress. For this reason, features such as conditional stability constants should be avoided wherever feasible.

The above considerations will tend to lead to a modelling approach which is semi-empirical, employing theory where possible, but utilising empirical approaches to cover gaps in the theoretical understanding. A theoretical underpinning will normally give rise to a model that is continuous and behaves in a physically plausible manner over a wide range of conditions. Empirical add-ons allow features such as solvent phase activities, which are typically incompletely understood, to be taken into consideration in the model.

Experimental

The modelling approach followed requires experimental data for the extraction of nitric acid into octanol, TODGA and TODGA + octanol, each dissolved in kerosene. Furthermore, data with varying temperature are required for a complete description.

A dataset for the extraction of nitric acid into octanol-kerosene mixtures covering a range of acid (0–5 mol/L) and octanol (5–100 v/v%) concentrations at 20 °C is available [37], see Figure 2 and supporting information Table SI 1. It was verified that the kerosene used did not have a significant effect on nitric acid extraction. This is of importance since different kerosenes (Exxsol D80 and TPH) were used in further experiments.

Extraction data for nitric acid into TODGA or TODGA + mainly 5 v/v% (0.32 mol/L) octanol were determined in three different laboratories to produce a robust dataset (see Tables SI 2 and SI 3). The procedures involved were as follows:

Aqueous phase was nitric acid (0.1–9 mol/L). Organic phase was TODGA (0.05–0.4 mol/L) in Exxsol D80 or TODGA (0.05–0.3 mol/L) + octanol (5 v/v%) in TPH or Exxsol D80. Additional experiments with aqueous phase $\approx$ 2.8 mol/L HNO_3, organic phase TODGA (0.1 – 0.3 mol/L) + octanol (5–50 v/v%) were undertaken. Equal volumes of aqueous and organic phase were contacted on an orbital shaker (2500/min) for 15 minutes (it was previously verified that equilibrium had been attained within several minutes) at 20 ± 0.5 °C, 22 ± 1 °C or ambient ($\approx$ 20–25 °C), depending on which of the labs involved performed the experiments. Following centrifugation, organic phase aliquots were stripped into water *(A/O = 1–4)*. Nitric acid concentrations were determined by duplicate potentiometric titration with NaOH (0.02–0.1 mol/L).

To quantify the temperature effect on nitric acid extraction, experiments were performed with TODGA (0.1–0.2 mol/L) + octanol (5 v/v%) in TPH and HNO_3 (0.1–3 mol/L) at various temperatures (controlled to ± 0.5 °C at 10–50 °C) (see Table SI 4). To avoid changing temperature during centrifugation and phase separation, a different experimental approach was followed: Samples were shaken in a temperature-controlled water bath. The samples were kept in the water bath over night for phase disengagement.

TODGA was synthesised according to reference [38] or bought from Technocomm, UK. Exxsol D80 ("odourless kerosene", ExxonMobil), TPH (hydrogenated tetrapropylene, Prochrom, France) and octanol (puriss.) were used as received. Nitric acid 65% (Merck, p.a.) was diluted to the desired concentration, which was determined by potentiometric titration with 0.1 mol/L NaOH.

**Extraction of Nitric Acid into Octanol**

Various attempts have previously been made to model the data reported in reference [37]. A model based on Specific Ion Interaction Theory (SIT) [39] gave good predictions of organic phase acid concentrations, assuming that the acid was extracted as $HNO_3 \cdot 2Octanol$ only [37]. This model was, however, limited in that different equilibrium constants for each octanol

concentration considered had to be used. By taking only one starting octanol concentration at a time, the range of free octanol concentrations considered in fitting each of the equilibrium constants was very limited with the consequence that the dependence of acid extraction on the free octanol (and by implication the determination of the solvent phase acid adduct(s)) will be subject to significant uncertainty. From a practical perspective the inclusion of conditional stability constants is highly undesirable and a model that is not dependent on these is to be preferred.

Preliminary work on the modelling of these data considered a system with possible adducts 2HNO$_3$·Octanol, HNO$_3$·Octanol and HNO$_3$·2Octanol, similar to what was found for HNO$_3$ extraction into TBP [40]. When considering only one starting octanol concentration at a time it was found that $\beta_{12} \gg \beta_{11}$, β_{21} suggesting, in line with reference,[37] that only the HNO$_3$·2Octanol adduct is significant. However, when the dataset as a whole was considered it was found that the best fit was obtained with $\beta_{11} > \beta_{12} \gg \beta_{21}$, so that the significant adducts are HNO$_3$·Octanol and HNO$_3$·2Octanol, the former being more prevalent under most conditions. The resultant model gave acceptable results over most of the range covered by the data but predictions tended to lose accuracy near the ends of the acidity range, notably overstating extraction by $\approx 25\%$ for [HNO$_3$]$_{aq} > 4$ mol/L. The inclusion of a 3HNO$_3$·Octanol adduct was also considered, but this was found to offer no benefit. The dataset as a whole has thus been revisited with results as reported below.

Theory

The extraction of nitric acid into octanol is assumed to be governed by a number of equilibria of the form:

$$n\text{H}^+ + n\text{NO}_3^- + m\text{Octanol} \rightleftharpoons n\text{HNO}_3 \cdot m\text{Octanol} \qquad (\text{ Equation 1 })$$
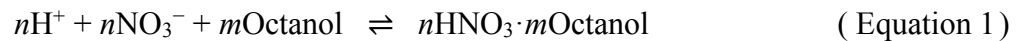
With equilibrium constants defined as below

$$\beta_{nm} = \frac{\gamma_{nHNO_3.mOctanol}[nHNO_3.mOctanol]}{\gamma_{H^+}^n[H^+]^n\gamma_{NO_3^-}^n[NO_3^-]^n\gamma_{Octanol}^m[Octanol]} \qquad (\text{ Equation 2 })$$

The concentration of octanol is the concentration of unbound (free) octanol. As the concentrations are expressed as molarities, the activity coefficients will be molar activity coefficients.

A number of simplifications are then made. In light of the lack of availability of data, the organic phase activity coefficients are taken to be unity and, in the aqueous phase, the mean stoichiometric activity coefficient for nitric acid (γ_s) is used instead of the activity coefficients of the individual ions. γ_s is related to the individual activity coefficients as in below in which α is the degree of dissociation of nitric acid:

$$\gamma_s^2 = \alpha^2 \gamma_{H^+} \gamma_{NO_3^-} \qquad (\text{ Equation 3 })$$

Taking [HNO$_3$] to be the total of dissociated and molecular nitric acid, the organic phase acid concentration is then given by:

$$[HNO_3]_{(org)} = \sum_{i=1}^{n} \sum_{j=1}^{m} i\beta_{ij}\gamma_s^{2i}[HNO_3]_{(aq)}^{2i}[Octanol]^j \qquad (\text{ Equation } 4)$$

The final element of the model is a continuity equation for the extractant (octanol) which allows the amount of free extractant to be determined. This takes the form:

$$[Octanol]_{(total)} = [Octanol] + \sum_{i=1}^{n} \sum_{j=1}^{m} j\beta_{ij}\gamma_s^{2i}[HNO_3]_{(aq)}^{2i}[Octanol]^j \qquad (\text{ Equation } 5)$$

In this equation [Octanol]$_{(total)}$ is the molar concentration of octanol in the unloaded solvent, while [Octanol] is the molar concentration of unbound octanol in the loaded solvent. By using molar concentrations this equation neglects dilation effects which would have the effect of reducing [Octanol]$_{(total)}$ as acid is taken up by the solvent. The neglect of dilation in this manner is a further simplification for which compensation is introduced in the empirical fitting process.

The modelling problem is then to find values for β_{ij} and an expression for γ_s such that a good fit is obtained to the experimentally determined data.

Fitting of Correlation for Nitric Acid Distribution into Octanol

Plotting (log[HNO$_3$]$_{org}$ − 2log[HNO$_3$]$_{aq}$) against log([Octanol]) where [Octanol] is an estimate of the free octanol (rather than total octanol) yields a gradient of ≈ 1.4, suggesting that the solvent contains a mix of HNO$_3$·Octanol and HNO$_3$·2Octanol adducts. Scoping work indicated that there are benefits in terms of a fit if a HNO$_3$·3Octanol adduct is also considered, but no other candidate adducts were identified as potentially useful. In principle the expression for γ_s could be either derived from a fit to literature activity data or calculated using a technique such as SIT [39] or Pitzer [41] equations, but in practice the expression for γ_s is not a true activity coefficient as it takes account of a number of other unknowns such as solvent phase activities and to that extent it can be considered to be an empirically derived correlation. It is, however, useful to consider the available literature data as a starting point. Data from Gazith [42] (original source [43]) for nitric acid activity coefficients were obtained and it was found that a good fit to these data could be obtained using an equation of the form:

$$\gamma_s = \frac{A}{([HNO_3] + B)^n} + C + D[HNO_3] + E[HNO_3]^2 + F[HNO_3]^3 \\ + G[HNO_3]^4 \qquad (\text{ Equation } 6)$$

Preliminary work suggested that setting $n = 2$, $F = 0$ and $G = 0$ gives acceptable fits and the fitting procedure thereafter took these as constant.

Fitting was undertaken using gPROMS 5.1.1 parameter estimation [44]. As well as fitting the β_{ij} and constants in equation 6, gPROMS was also set up to estimate the variance of the

experimental data. This was assumed to have a heteroscedastic distribution as described in Equation **7** below.

$$\sigma = \omega|x|^\gamma \qquad \text{(Equation 7)}$$

where σ is the standard deviation, x is the measured value and ω and γ are fitted constants, $\gamma = 0$ corresponding to constant variance across the dataset, while $\gamma = 1$ corresponds to constant relative variance. gPROMS performs the fitting by minimising the below objective function.

$$\Phi = \frac{N}{2}\ln(2\pi) + \frac{1}{2}\min_\theta \left\{ \sum_{i=1}^{NE} \sum_{j=1}^{NV_i} \sum_{k=1}^{NM_{ij}} \left[\ln(\sigma_{ijk}^2) + \frac{(\tilde{z}_{ijk} - z_{ijk})^2}{\sigma_{ijk}^2} \right] \right\} \qquad \text{(Equation 8)}$$

where N is the total number of measurements taken in all experiments, NE is the number of experiments performed, NV_i is the number of variables measured in the ith experiment, NM_{ij} is the number of measurements of the jth variable in the ith experiment, θ is the set of physical and variance model parameters to be determined, σ_{ijk}^2 is the variance of the kth measurement of the jth variable in the ith experiment, $\tilde{z}_{ijk}$ is the kth measured value of the jth variable in the ith experiment, z_{ijk} is the kth model predicted value of the jth variable in the ith experiment. For the fitting undertaken here the data series was considered as a single dynamic experiment in which equilibrium conditions (aqueous acidity and organic octanol concentration) were changed through time ($NE = 1$), the measured variable was the organic acid concentration ($NV_1 = 1$) and the number of measurements was taken to be the number of datapoints included in fitting ($NM_{11} = 53$).

An initial estimation run was undertaken to establish a suitable expression for the activity coefficient. This gave values for constants A through E as shown in Table 1 giving the expression for activity shown in Equation 10 which was used for all subsequent fitting. The expression for activity was then fixed and the estimation rerun, yielding the stability constants given in Table 1.

Table 1: Fitted coefficients for correlation (equations 4 and 6) to calculate nitric acid distribution into kerosene-octanol mixtures.

A	B	C	D	E	β_{11}	β_{12}	β_{13}
0.1080	0.5962	0.6100	0.1131	−0.002716	0.006101	0.001585	0.0003546

From this it is found that the expression for nitric acid distribution is given by Equation 9 where [Oct] is the free octanol concentration, [HNO₃] is the total (stoichiometric) nitric acid concentration and γ_s is given by Equation 10.

$$D_{HNO_3} = \gamma_s^2 [HNO_3](0.006101[Oct] + 0.001585[Oct]^2 + 0.0003546[Oct]^3) \qquad \text{(Equation 9)}$$

$$\gamma_s = \left[\frac{0.108}{(0.5962 + [HNO_3])^2} + 0.61 + 0.1131[HNO_3] - 0.002716[HNO_3]^2 \right] \qquad \text{(Equation 10)}$$

Statistical measures of the fit are given in Table 2 below.

Table 2: Quality of fit for model of HNO₃ extraction into octanol / TPH.

Variance model (see Equation 7)		χ^2-test	
ω	γ	χ^2	χ^2-critical
0.00744	0.724	53.00	65.17

The value of gamma indicates that errors are predominantly related to the magnitude of the measurement being made whilst the χ^2 value being less than the χ^2-critical value indicates that the null hypothesis (that the difference between the weighted residual and the and expected weighted residual is zero) cannot be rejected at the 95% confidence level, thereby indicating a good fit.

Plots of model predictions vs. experimental results (from reference [37]) are shown in Figure 2. Percentage errors across the range of the experiments are rather small. For aqueous phase nitric acid concentrations in excess of 1.5 mol/L, the model gives predictions with root mean square (rms) error of 1.5% whilst at acidities below 1.5 mol/L the rms error is 5.1%. This model shows slightly improved accuracy over the one reported in reference [37], most notably at aqueous nitric acid concentrations beyond 1 mol/L.
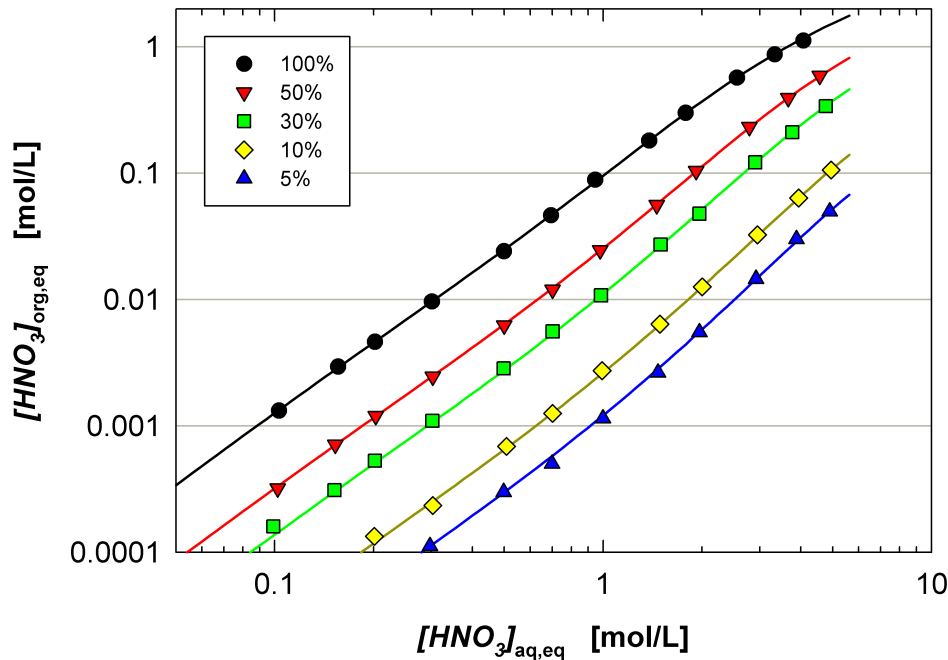

Figure 2: Extraction of nitric acid into octanol-TPH mixtures (octanol volume fraction as indicated); model predictions (lines) vs. experimental data (symbols). $A/O = 1$, $T = (20 \pm 0.5)$ °C. Experimental data from reference [37]. See Table SI 1 for experimental data.

Extraction of Nitric Acid into TODGA

The extraction of nitric acid into TODGA solvents was determined for the following experimental conditions, 0.05–0.4 mol/L TODGA, 0.1–8.7 mol/L HNO_3, diluent was Exxsol D80. Temperature was 20 ± 0.5 °C, 22 ± 1 °C or ambient ($\approx$ 20–25 °C), depending on which of the labs involved performed the experiments.

Experimental data for the extraction of nitric acid into TODGA in Exxsol D80 are compared to calculated values (see below) in Figure 3. A number of points are apparent from initial inspection of the experimental data:

- A series of datapoints at a TODGA concentration of 0.2 mol/L is somewhat inconsistent with the remaining data, generally showing around 0.05 mol/L more nitric acid being extracted into the solvent than the other data sets give for similar conditions.

- Organic phase acidity up to 2.5 times the TODGA concentration is observed at the highest nitric acid concentrations considered. This implies that adducts with at least a 3:1 nitric acid:TODGA ratio must be present.

- Distribution ratios show a roughly linear dependence on TODGA concentration for a given acidity. This suggests that the solvent phase adducts of the form $n HNO_3 \cdot$ TODGA are dominating.

- Distribution ratios for nitric acid show little dependence on acidity at moderate and high acidities. For 0.1 mol/L TODGA, $D(HNO_3)$ is around 0.033 for greater than 2 mol/L nitric acid. With 0.2 mol/L TODGA, $D(HNO_3)$ is around 0.06 to 0.07 for $[HNO_3] > 0.5$ mol/L and with 0.3 mol/L TODGA, $D(HNO_3)$ is around 0.1 to 0.12 for $[HNO_3] > 1$ mol/L. This behaviour is slightly unexpected as typical extraction behaviour would have distribution ratios initially increasing with acidity then decreasing at higher acidity as solvent saturation effects cut in.
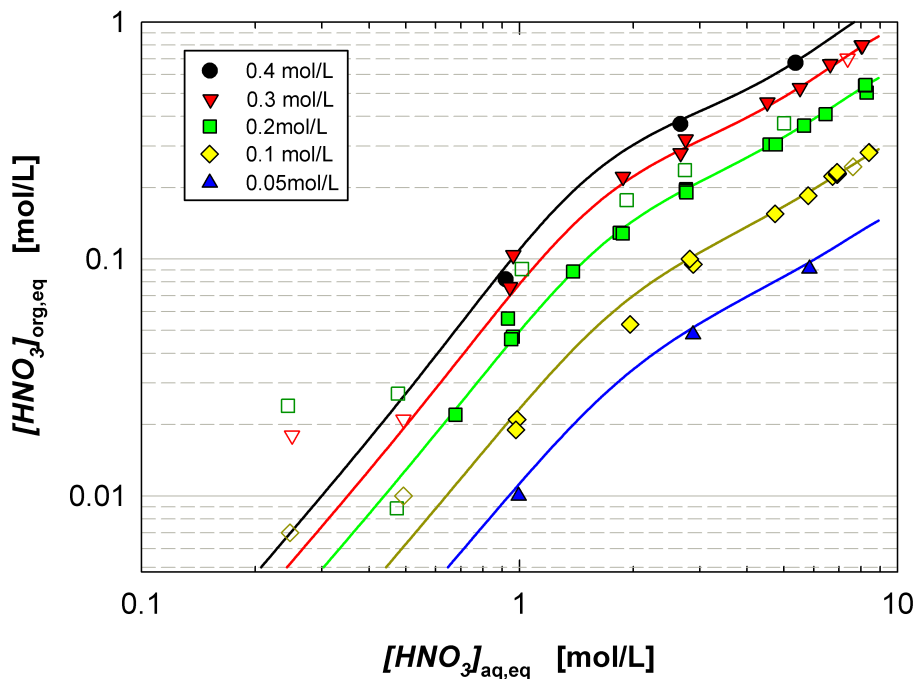
Figure 3: Nitric acid extraction into TODGA (concentration as indicated) in Exxsol D80. Model predictions (lines) vs. experimental data (symbols; open symbols excluded from fitting). *A/O* = 1. See Table SI 2 for experimental data.

Fitting of the experimental data has been undertaken in the same ways as for the extraction of nitric acid into octanol, assuming that the solvent phase contains adducts of the form iHNO$_3 \cdot j$TODGA so that the nitric acid concentration is described by Equation 11.

$$[HNO_3]_{(org)} = \sum_{i=1}^{n} \sum_{j=1}^{m} i\beta_{ij}\, \gamma_s^{2i}\, [HNO_3]_{(aq)}^{2i}\, [TODGA]^j \qquad \text{(Equation 11)}$$

In this equation [TODGA] is the free TODGA which is determined by use of a continuity equation analogous to that used for octanol (Equation 5). The fitting allowed adducts ranging from 4HNO$_3 \cdot$TODGA through to HNO$_3 \cdot$TODGA and HNO$_3 \cdot$2TODGA through to HNO$_3 \cdot$4TODGA. Additionally, the 2HNO$_3 \cdot$2TODGA adduct was allowed as were the TODGA oligomers 2TODGA, through to 4TODGA. Only the stability constants were fitted, the expression for γ_s derived in the fitting of octanol extraction being used here as well. Again, fitting was achieved by minimising the objective function given in Equation 8. Data at less than 0.5 mol/L aqueous acidity was omitted from the fitting in light of the scatter observed in the data in this region and the low amounts of extracted acid involved that will normally result in flow-sheet model predictions having a low sensitivity to relative errors in acid distribution values at low acidity. The outlying data (series 3, open triangles in Figure 3) was excluded from the fitting process due to the offset observed between it and the other data sets. Of the adducts allowed, initial fitting set stability constants for HNO$_3 \cdot$3TODGA, HNO$_3 \cdot$4TODGA, 2TODGA, and 3TODGA to zero. Although the best fit was obtained when HNO$_3 \cdot$2TODGA and 4TODGA species had non-zero stability constants, the 95% confidence limits for the predicted values took in zero and it was found that there was very little loss in

model accuracy if these species were omitted. For the remaining adducts the fitting process resulted in stability constants as in Table 3 below:

Table 3: Fitted constants for nitric acid distribution into TODGA (0.1–0.3 mol/L) in Exxsol D80.

β_{41}	β_{31}	β_{21}	β_{11}	β_{22}
9.056E−7	9.009E-5	0.02193	0.4482	0.4987

These constants differ from those reported in a previous study [24]. The differences are explained by the use of different activity models and the use of the $2HNO_3 \cdot 2TODGA$ adduct instead of the $HNO_3 \cdot 2TODGA$ adduct.

Statistical measures of the fit are given in Table 4 below.

Table 4: Quality of fit for model of HNO_3 distribution into TODGA in Exxsol D80.

Variance model (see Equation 7)		χ^2-test	
ω	γ	χ^2	χ^2-critical
0.01609	0.2701	58.00	68.67

Figure 3 shows a comparison of the model results against the available experimental data. Root mean square error for the fitted data is 9.9% overall (17% for $[HNO_3]_{(aq)} < 1.5$ mol/L, 5.6% for $[HNO_3]_{(aq)} > 1.5$ mol/L) The wide scatter of data at low acidity is apparent, making a close fit to data in this region impossible. Despite potentially high relative errors in the calculation of organic phase nitric acid concentration under conditions of low aqueous phase nitric acid concentrations, absolute errors remain small so that models of typical flow-sheets should not be greatly affected by sensitivity to nitric acid distribution at low acidity

Extraction of Nitric Acid into TODGA-Octanol Solvents

Data sets for the extraction of acid into combined TODGA/octanol solvents have been generated for varied experimental conditions, 0.05–0.3 mol/L TODGA, 5 v/v% octanol, 0.1–6 mol/L HNO_3 and 0.1–0.3 mol/L TODGA, 5–50% v/v% octanol, ≈ 2.8 mol/L HNO_3. Diluent was Exxsol D80 or TPH (it was verified that the diluent does not have any effect on the quantity of nitric acid extracted, see Supporting Information, "diluent effect on nitric acid extraction"). Temperature was 20 ± 0.5 °C, 22 ± 1 °C or ambient (≈ 20–25 °C), depending on which of the labs involved performed the experiments. However, the temperature effect on nitric acid extraction is moderate (see below).

Following exclusion of obvious outliers, experimental data from different laboratories typically agreed well. Results are shown in Figure 4.

Performance of Correlations Neglecting Synergistic Effects

Initial calculations were undertaken in which the solvent phase nitric acid concentration was modelled as the sum of the predicted nitric acid extraction into TODGA plus that resulting from nitric acid extraction into octanol. Figure 4 shows predicted vs. measured organic nitric acid concentrations for experimental series at 0.05, 0.1, 0.2 and 0.3 mol/L TODGA, respectively.

General trends are apparent. For nitric acid concentrations above about 1.5 mol/L HNO_3, the superposition of the TODGA and octanol models results in under prediction of extracted nitric acid, typically by approximately 10%. In the region 0.5–1.5 mol/L nitric acid, the model over predicts nitric acid extraction by up to 40%, the over prediction being largest at lower acidity. For acidities less than 0.6 mol/L, the data are too scattered to allow any general trends to be discerned.

The antagonistic behaviour observed at low acidity could be caused by association of TODGA with octanol resulting in a reduction in the availability of both TODGA and octanol for extraction of nitric acid. Synergistic behaviour observed at higher acidities is potentially a consequence of the formation of adducts containing nitric acid, TODGA and octanol in some ratio.

Figure 4: Nitric acid extraction into TODGA (concentration as indicated) + 5 v/v% octanol in Exxsol D80 or TPH. Symbols, experiments (open symbols excluded from fitting). Lines, calculated by superposition of models for nitric acid extraction into octanol and nitric acid extraction into TODGA. $A/O = 1$. See Table SI 3 for experimental data.

Inclusion of Synergistic Extraction of Acid by TODGA-Octanol Mixtures.

In light of the results above, the additive model for extraction of acid into TODGA-octanol mixtures was extended by the inclusion of a range of adducts containing both TODGA and octanol. Initial runs allowed a range of adducts of the form iHNO$_3$·jTODGA·kOctanol ((i, j, k) = (0, 1, 1), (0, 1, 2), (0, 1, 3), (0, 1, 4), (0, 2, 1), (0, 3, 1), (0, 4, 1), (1, 1, 1), (1, 1, 2), (1, 1, 3), (1, 1, 4), (2, 1, 1), (2, 1, 2), (2, 1, 3) (3, 1, 1), (3, 1, 2), (4, 1, 1)). gPROMS parameter estimation was used to estimate the stability constants of these species, only data corresponding to greater than 0.6 mol/L HNO$_3$(aq) being used due to scatter of data measured at lower acidity. Of these adducts only nine ((i, j, k) = (0, 1, 2), (0, 1, 4), (1, 1, 1), (1, 1, 2), (2, 1, 1), (2, 1, 2), (2, 1, 3), (3, 1, 2), (4, 1, 1)) were predicted to have non-zero stability constants. Of these nine potential adducts five could be eliminated with minimal effect on the observed residuals leaving ((i, j, k) = (0, 1, 2), (1, 1, 1), (2, 1, 3), (3, 1, 2)). Adducts were chosen for elimination based on the 95% confidence limits for the stability constants calculated by gPROMS taking in zero. Root mean square errors for the model with all adducts considered was 5.66% compared to 6.02% with only 4 TODGA octanol cross adducts being considered. The fitted stability constants are presented in Table 5 below.

Table 5: Fitted equilibrium constants for HNO$_3$-TODGA-octanol adducts.

TODGA·2Oct β_{012}	HNO$_3$·TODGA·Oct β_{111}	2HNO$_3$·TODGA·3Oct β_{213}	3HNO$_3$·TODGA·2Oct β_{312}
27.47	2.419	0.7328	0.06431

Statistical measures of the fit are given in Table 6 below.

Table 6: Quality of fit for model of HNO$_3$ distribution into TODGA / octanol / diluent.

Variance model (see Equation 7)		χ^2-test	
ω	γ	χ^2	χ^2-critical
0.0556	0.959	83.02	98.48

The organic phase nitric acid in the improved model is calculated by Equation 12 below where the TODGA and octanol concentrations are the concentration of free TODGA and octanol.

$$[HNO_3]_{(org)} = \sum_{i=1}^{n} \sum_{j=0}^{m} \sum_{k=0}^{p} i\beta_{ijk}\gamma_s^{2i}[HNO_3]_{(aq)}^{2i}[TODGA]^j[Octanol]^k \qquad \text{(Equation 12)}$$

The continuity equations for TODGA and octanol are updated in the obvious manner to take account of the cross adducts. Results for the updated model are shown in Figure 5. Comparison to Figure 4 (i.e. the system not including the cross adducts) shows that the over prediction in acidity range 0.5–1.5 mol/L and the tendency to under predict at higher acidity are both largely eliminated.
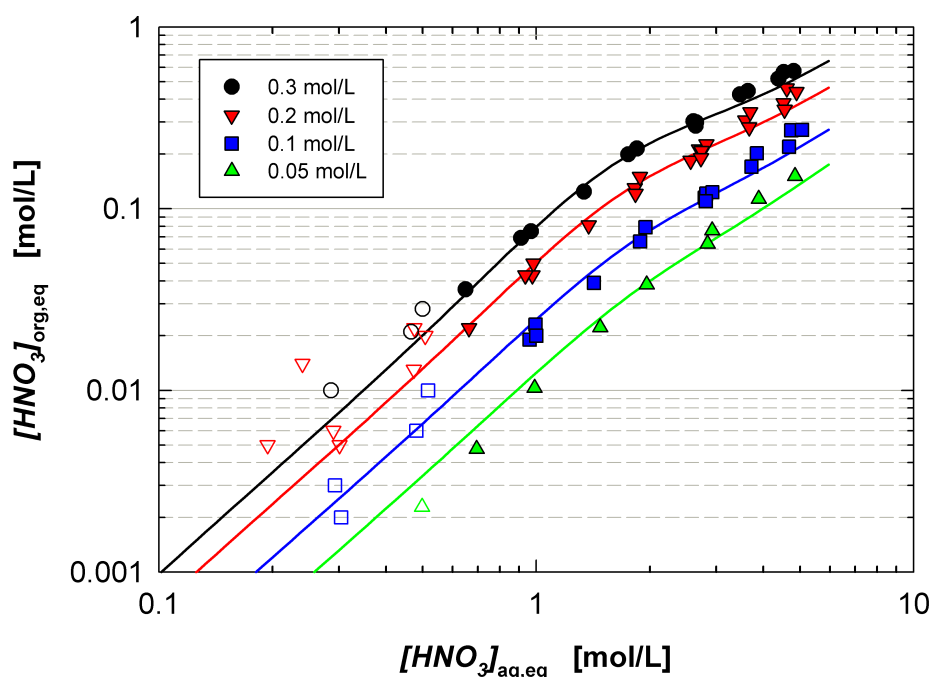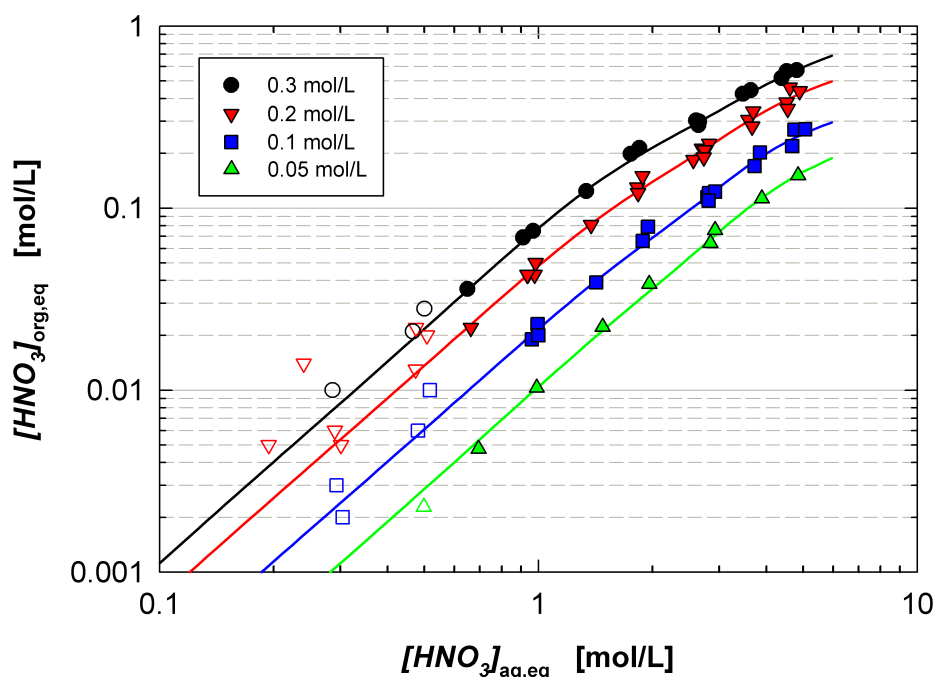
Figure 5: Nitric acid extraction into TODGA (concentration as indicated) + 5 v/v% octanol in Exxsol D80 or TPH. Symbols, experiments (open symbols excluded from fitting). Lines, calculated by the **improved model accounting for synergistic adducts.** *A/O* = 1. See Table SI 3 for experimental data.

The range of adducts considered allows a good fit to the available data to be achieved, with Figure 5 showing no clear trends in residual errors that would suggest the possibility of a significantly better model being found. The situation at the lowest acidities remains uncertain due to scatter in the data. However, the absolute deviations are on the order of few mmol/L.

The work reported here has considered a wide but not comprehensive range of cross adducts and narrowed down the list to those required to give a good fit to the available data. However, there is no guarantee that these adducts are present in reality or that there are no other adducts present. Further refinement of the correlations is, however, unlikely to be feasible without substantial expansion of the dataset.

Predicted Prevalence of Different Adducts in Extracted Nitric Acid

In order to give an indication of the relative importance of the different adducts, the concentrations of individual species expressed as a percentage of the extracted nitric acid were calculated for a number of representative cases. These are shown in Tables SI 5–7 (see Supporting Information) which present predicted solvent phase composition given by the model with inclusion of cross adducts. For the particular case of 0.2 mol/L TODGA + 5 v/v% octanol in an inert diluent, i.e. the solvent used in the i-SANEX flowsheet [14], the predicted speciation diagrams for solvent phase nitric acid, octanol and TODGA as a function of aqueous phase acidity are shown in Figure 6, Figure 7 and Figure 8, respectively. A number of points are apparent from these tables and figures:

- A large fraction of the octanol remains unbound in all cases.

- Extraction of nitric acid into TODGA is generally greater than into octanol, except when high octanol concentrations are used. Even in this case much of the nitric acid is extracted as a cross adduct rather than as a pure TODGA or octanol adduct.

- The $4HNO_3 \cdot TODGA$ adduct is significant only at the highest acidity considered.

- The $HNO_3 \cdot 2Octanol$ and $HNO_3 \cdot 3Octanol$ adducts are only significant when the octanol concentration is well above the 5 v/v% expected to be used in practice.
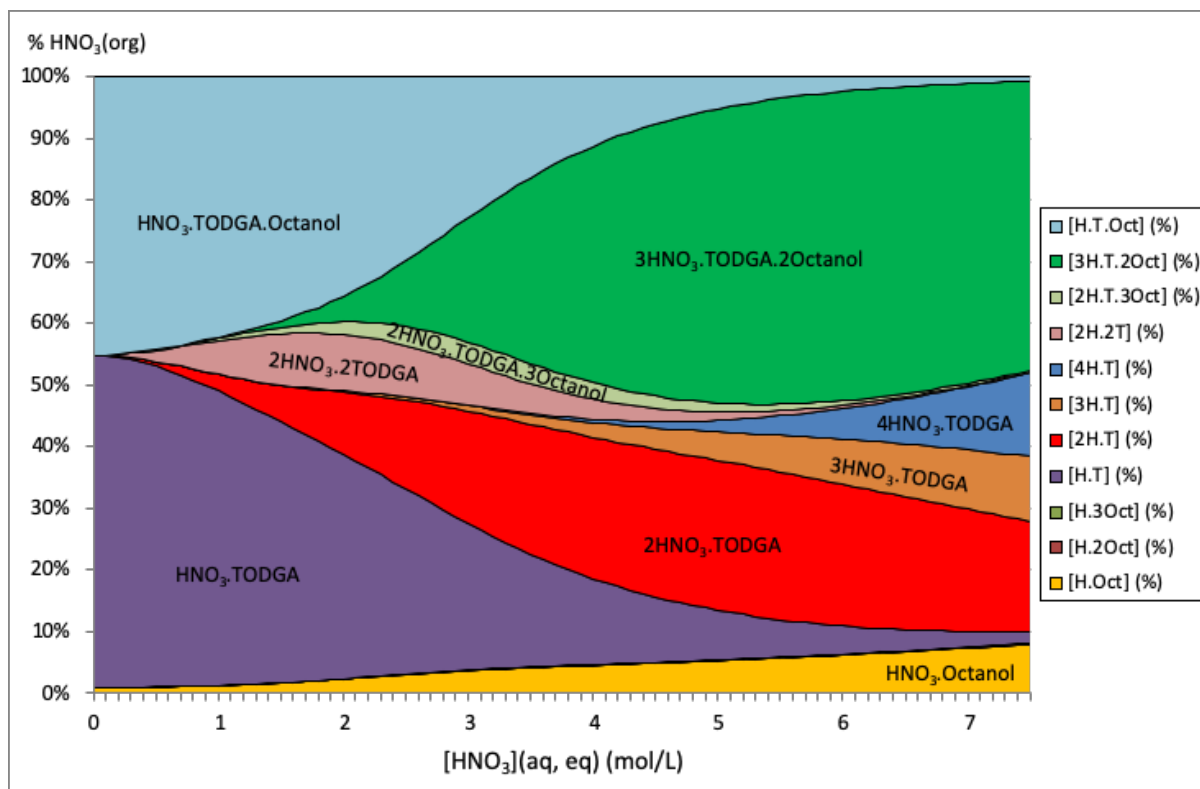
Figure 6: Predicted organic nitric acid speciation in a 0.2 mol/L TODGA + 5 v/v% octanol system.
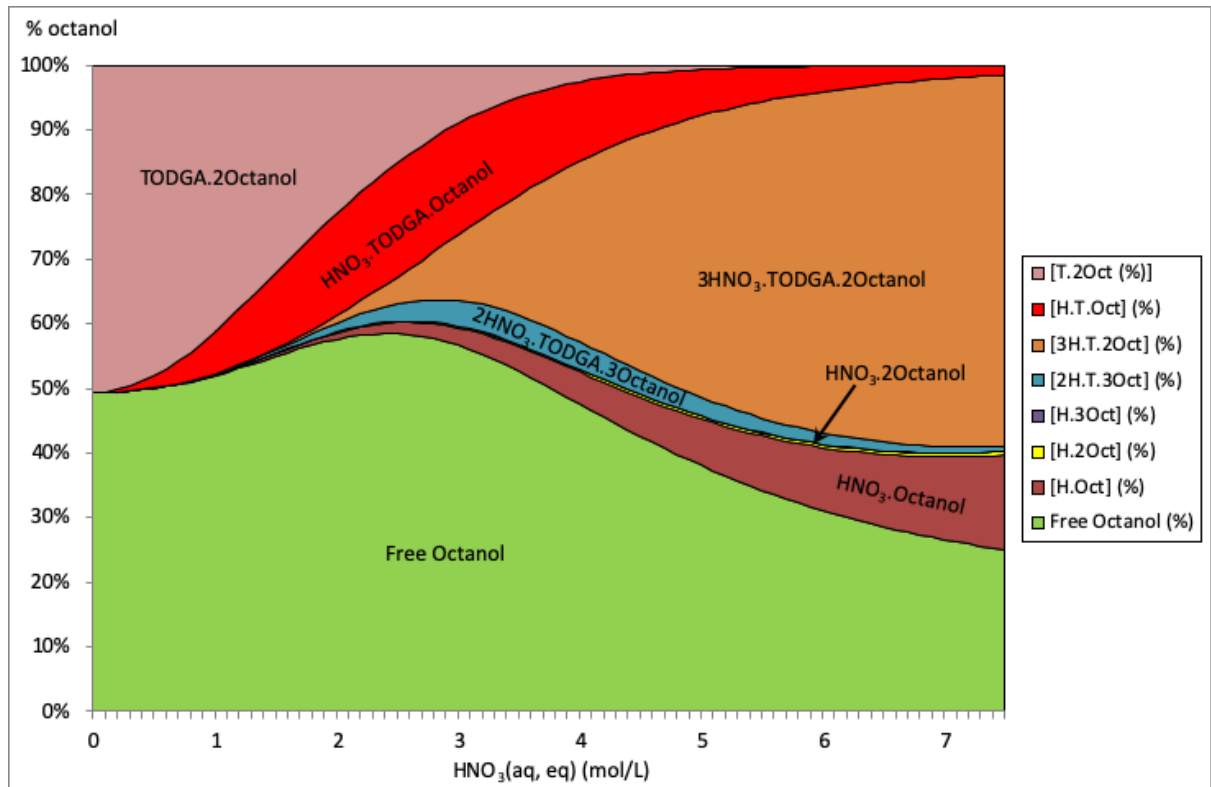
Figure 7: Predicted octanol speciation in a 0.2 mol/L TODGA + 5 v/v% octanol system.
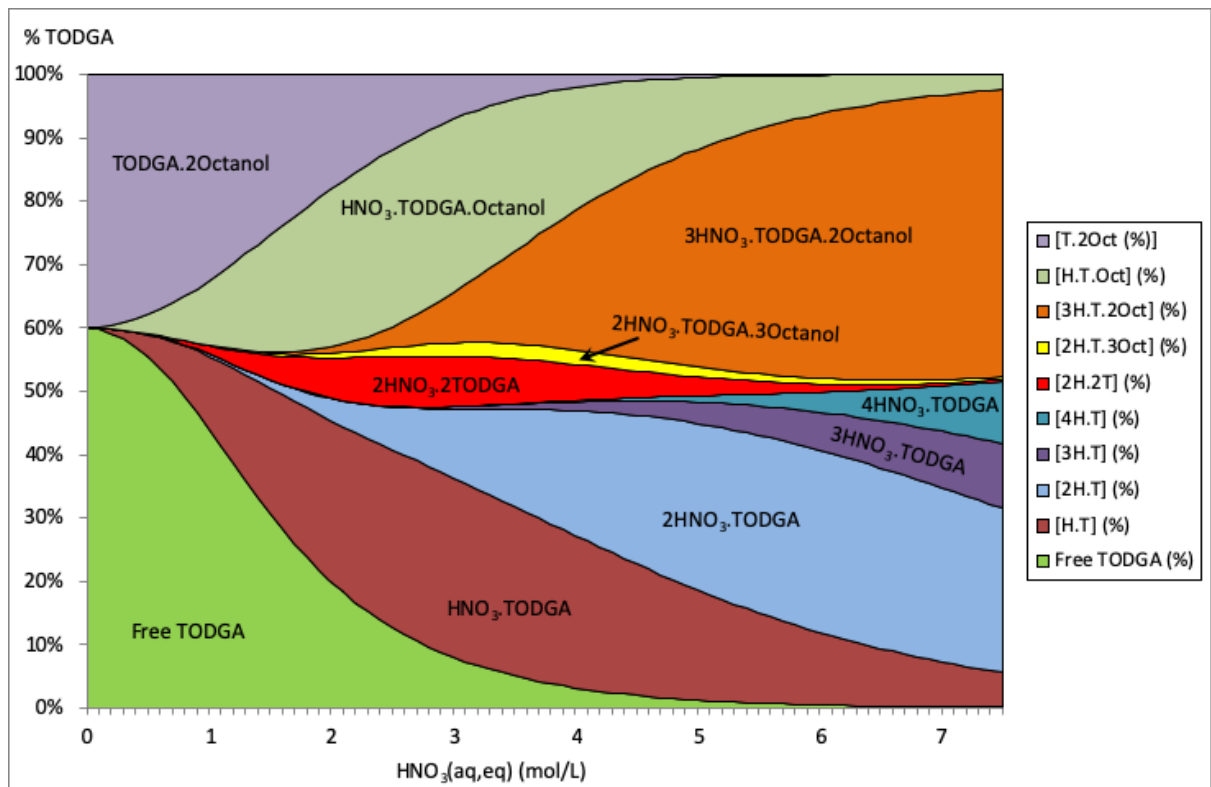
Figure 8: Predicted TODGA speciation in a 0.2 mol/L TODGA + 5 v/v% octanol system.

Temperature Effects

Data for the extraction of nitric acid into mixtures of TODGA and octanol as a function of temperature were determined for the following experimental conditions, 0.1– 0.2 mol/L TODGA, 5% v/v octanol, 0.31–3.1 mol/L HNO_3, 10–50 °C.

In order to incorporate temperature effects into the model it is assumed that the stability constants for the solvent phase adducts have an Arrhenius type dependence on temperature resulting in calculation of organic phase acid by Equation 13 below.

$$[HNO_3]_{(org)} = \sum_{i=1}^{n} \sum_{j=0}^{m} \sum_{k=0}^{p} iA_{ijk} e^{\left(-\frac{E_{ijk}}{RT}\right)} \beta_{ijk} \gamma_s^{2i} [HNO_3]_{(aq)}^{2i} [TODGA]^j [Octanol]^k \quad \text{(Equation 13)}$$

In the above equation T is the temperature in Kelvin and R is the universal gas constant. A_{ijk} and E_{ijk} are fitted constants with the E_{ijk} taking a role analogous to the Gibbs free energies (ΔG^0) for the adducts $(HNO_3)_i \cdot TODGA_j \cdot Octanol_k$. They cannot be considered to be true ΔG^0 for the adducts because the actual adducts are likely to contain water as well as the modelled solvent phase species. The above general form is impractical for use in models due to the requirement to provide fitted constants for each of the postulated solvent phase adducts, the available data being too limited to allow the necessary deconvolution. The more practical approach is then to assume that a single value of E applies for all the adducts so that Equation 14 below applies.

$$[HNO_3]_{(org)} = \sum_{i=1}^{n} \sum_{j=0}^{m} \sum_{k=0}^{p} iA_{ijk} e^{\left(-\frac{E}{RT}\right)} \beta_{ijk} \gamma_s^{2i} [HNO_3]_{(aq)}^{2i} [TODGA]^j [Octanol]^k \quad \text{(Equation 14)}$$

In effect, a temperature correction factor, K, is applied to the existing model, this being given by:

$$K = Ae^{\left(-\frac{E}{RT}\right)} \quad \text{(Equation 15)}$$

Fitting is further constrained by the requirement for consistency with the model (and hence underpinning data) obtained at ambient temperature. For this reason a constraint was applied to the fitting such that K takes a value of 1 at 20 °C. As with fitting of other data for extraction of acid into TODGA containing solvents, the fit did not include points where the aqueous acidity was less than 0.6 mol/L. When this is done we obtain $E = -25.7$ kJ/mol, $A = 2.580E{-}5$.

Statistical measures of the fit are given in Table 7 below.

Table 7 : Quality of fit for model of HNO_3 distribution into TODGA / octanol / diluent with temperature dependence.

Variance model (see Equation 7)		χ^2-test	
ω	γ	χ^2	χ^2-critical
0.0293	0.8435	24.00	32.67

Fits of the data in Table SI 4 (see Supporting Information) against the model with the temperature correction are shown in Figure 9 below.
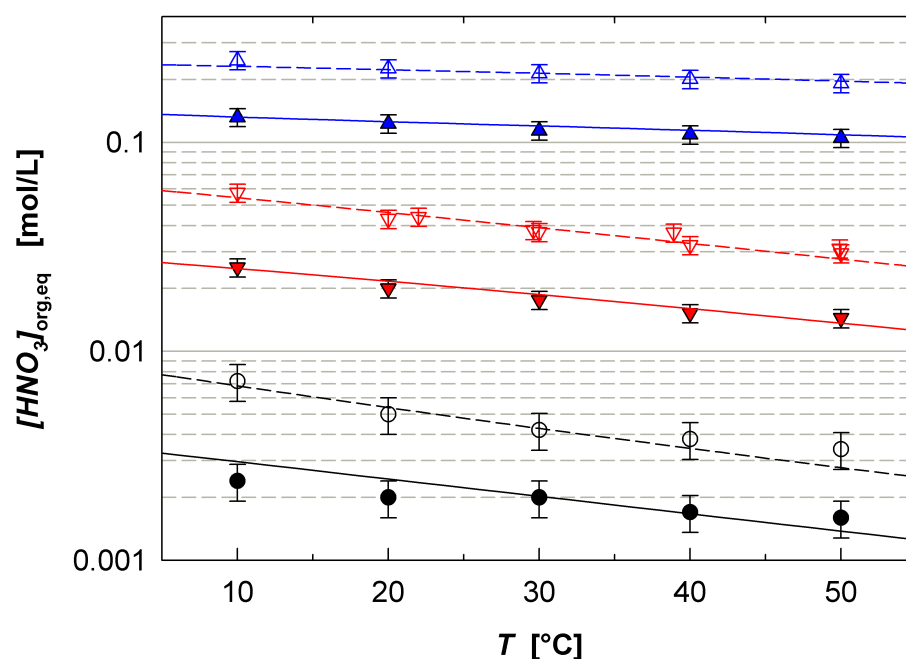
Figure 9: Temperature dependent nitric acid extraction. Organic phase, 0.1 mol/L (solid symbols and lines) or 0.2 mol/L (open symbols, dashed lines) TODGA + 5 v/v% octanol in TPH. Aqueous phase, initial HNO₃ (**0.306 – 1.02 – 3.05** mol/L). *A/O* = 1. Lines, model: *E* = −25.7 kJ/mol, *A* = 2.580E−5. Experimental uncertainty estimated to 5% *([HNO₃]*org,eq ≥ 10 mmol/L) and 20% *([HNO₃]*org,eq < 10 mmol/L)*

Figure 9 shows a good model fit to data at nitric acid concentrations of 1.0 and 3.1 mol/L with a less good fit at lower acidity, particularly at the lower TODGA concentration. This once again reflects the wider scatter of the data at low acidity. Absolute organic acid concentrations are always very low in this region and although relative errors are substantial, absolute model errors are less than 1 mmol/L which is of little concern in most practical modelling applications.

Model Applicability and Limitations

The work reported in this paper has resulted in the production of a model of nitric acid extraction into mixtures of TODGA and octanol with an essentially inert kerosene diluent. The model has an underlying framework rooted in the theory of solvent extraction, but includes a significant element of empirical modification to take account of the unknown parameters in the system. The empirical component will limit the extent to which the model can be reliably applied to conditions beyond those used to fit the model. In general, these give coverage for 0.05–0.3 mol/L TODGA, 5–50 v/v% octanol, 0–5 mol/L HNO₃ and 10–50 °C, although a few data points outside of these ranges have also been used in fitting of the models. Not all combinations of data within these ranges have considered, with the largest

amounts of data relating to extraction into 0.2 mol/L TODGA with 5 v/v% octanol at ambient temperature. Notably temperature dependent data relates only to systems containing 5 v/v% octanol, leaving the possibility that high octanol systems may exhibit a different temperature response. It will also be noted that although the datasets include a significant amount of low acidity data, there is considerable scatter of the data in this region reducing confidence in model predictions in this region. The approach adopted was to exclude the highly scattered data at low acidity from the fitting process and confirm that the resultant model gives results within the range of the scatter at low acidity. Although relative errors in this region may be large, absolute errors will be small and for most practical applications of modelling flowsheets it will be absolute errors that are of concern.

When using the distribution algorithms described above, there is a requirement to bear in mind the limitations of the algorithms. These relate to the range of conditions covered by the data used in the fitting. The main limitations are summarised below:

Extrapolation to very high acidity

The organic phase speciation models underlying the distribution correlations described herein have been empirically derived such that the available data can be adequately explained. It is probable that the actual speciation of the organic phase is significantly more complex than that incorporated in the models. In particular it has been suggested that various organic phase aggregates may occur including tetramers and larger micelles.[45-46] Although TODGA tetramers were considered in the fitting (as was the $HNO_3 \cdot 4TODGA$ species), their addition to the model was not found to confer any benefit in the fitting of the available data. The use of an incomplete organic phase speciation model has the potential to curtail the reliability of the model beyond the range of the data used to derive it. Similarly, the aqueous phase activity effects are built into the empirical correlations and it cannot be assumed that these will extrapolate successfully. Such activity effects will become more important at higher acidity.

Use with species other than nitric acid in the aqueous phase

The derivation of the distribution correlations in this paper has employed mean stoichiometric activity coefficients. This approach is adequate provided that $[H^+] \approx [NO_3^-]$. With appreciable quantities of e.g. metal nitrates in the aqueous phase this approximation will no longer be valid and it is likely that nitric acid distribution will vary from prediction, even if none of the additional aqueous phase species are extractable.

Use with a metal loaded solvent phase

When modelling solvent extraction systems it is normal to extend the continuity equation for the extractant to include terms for all organic phase species. In this way the effect of competition for the extractant from other species can be taken into account. In the case of TODGA based systems, the situation becomes more complicated as there is evidence that nitric acid co-extracts to a significant extent with actinide and lanthanide species.[47] The nitric

acid / metal cross complexes would need to be included in any model of nitric acid extraction in the presence of such metals if under-prediction of nitric acid extraction is to be avoided.

Conclusions

Sophisticated models for the extraction of nitric acid into octanol, TODGA, or TODGA + 5 v/v% octanol were established, covering a range of nitric acid and TODGA concentrations and temperatures relevant to process modelling. While the octanol model is based on published experimental data, previously unavailable data on nitric acid extraction into TODGA and TODGA + (mostly) 5 v/v% octanol were collected. An additive model for TODGA/octanol solvents, predicting nitric acid extraction into TODGA plus that resulting from nitric acid extraction into octanol, yields reasonable agreement with experimental data. However, nitric acid extraction is systematically under predicted for aqueous nitric acid concentrations above about 1.5 mol/L HNO_3, while it is over predicted for lower nitric acid concentrations. Adding cross adducts, $i HNO_3 \cdot j TODGA \cdot k Octanol$ *(i,j,k* = (0, 1, 2), (1, 1, 1), (2, 1, 3), (3, 1, 2), results in a significantly improved accuracy. Fitting of temperature series data (10–50 °C) showed a temperature dependence dictated by the relationship

$$H_{orgT} = 2.58 \times 10^{-5} H_{org293} e^{\frac{25700}{RT}}$$

where H_{orgT} and H_{org293} are the organic acid concentrations at temperature T and 293 K respectively. No diluent dependence was found for nitric acid extraction.

Acknowledgements

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Nitric Acid Extraction into a TODGA Solvent Modified with Octanol

— Supporting Information —

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Nitric Acid Extraction into Octanol / TPH Mixtures

Extraction of 0.1 – 5.0 mol/L nitric acid into 5 – 100 v/v% octanol in TPH was measured at a temperature of 20 ± 0.5 °C. Data as published in [Geist, A., *Solvent Extr. Ion Exch.* **2010,** *28* (5), 596–607] are presented in Table SI 1 below.

Table SI 1: Extraction of Nitric Acid into Octanol / TPH

[octanol] (v/v%)	[HNO$_3$] (aq, ini) (mol/L)	[HNO$_3$] (aq, eq) (mol/L)	[HNO$_3$] (org, eq) (mol/L)	Mass Balance (%)	D	Used in Fit?	Estimated Error
5	0.151	0.151	0.0000613	99.78	0.000407	No[a]	
5	0.201	0.201	0.0000693	100.03	0.000345	No[a]	
5	0.3	0.297	0.000112	98.84	0.000377	Yes	9.2 %
5	0.498	0.498	0.0003	100.06	0.000602	Yes	7.0 %
5	0.697	0.699	0.000504	100.36	0.000721	Yes	6.1 %
5	0.998	0.998	0.00115	100.12	0.00115	Yes	4.8 %
5	1.487	1.47	0.00264	99.04	0.0018	Yes	3.8 %
5	1.991	1.966	0.00552	99.02	0.00281	Yes	3.1 %
5	2.968	2.919	0.0146	98.83	0.00502	Yes	2.4 %
5	3.964	3.88	0.0302	98.64	0.00779	Yes	2.0 %
5	5	4.901	0.0499	99.03	0.0102	Yes	1.7 %
10	0.151	0.152	0.000115	100.47	0.000758	No[a]	
10	0.201	0.201	0.000134	100.04	0.000666	Yes	8.8 %
10	0.3	0.303	0.000235	100.88	0.000776	Yes	7.5 %
10	0.495	0.508	0.00069	102.89	0.00136	Yes	5.6 %
10	0.697	0.702	0.00126	100.9	0.00179	Yes	4.7 %
10	0.998	0.994	0.00274	99.96	0.00276	Yes	3.8 %
10	1.487	1.489	0.0064	100.6	0.0043	Yes	3.0 %
10	1.991	2.005	0.0126	101.34	0.00627	Yes	2.5 %
10	2.968	2.953	0.0325	100.59	0.011	Yes	1.9 %

[octanol] (v/v%)	[HNO$_3$] (aq, ini) (mol/L)	[HNO$_3$] (aq, eq) (mol/L)	[HNO$_3$] (org, eq) (mol/L)	Mass Balance (%)	D	Used in Fit?	Estimated Error
10	3.964	3.941	0.0636	101.02	0.0161	Yes	1.6 %
10	5	4.947	0.106	101.05	0.0213	Yes	1.4 %
30	0.101	0.099	0.00016	98.18	0.00162	Yes	8.3 %
30	0.152	0.152	0.000311	100.2	0.00205	Yes	6.9 %
30	0.201	0.202	0.000531	100.76	0.00263	Yes	6.0 %
30	0.302	0.302	0.0011	100.36	0.00365	Yes	4.9 %
30	0.498	0.498	0.00286	100.57	0.00574	Yes	3.8 %
30	0.702	0.702	0.0056	100.87	0.00798	Yes	3.1 %
30	1.01	0.985	0.0108	98.63	0.011	Yes	2.6 %
30	1.5	1.497	0.0273	101.62	0.0182	Yes	2.0 %
30	2.04	1.965	0.0478	98.67	0.0243	Yes	1.7 %
30	3.06	2.908	0.122	99.01	0.0418	Yes	1.3 %
30	3.964	3.769	0.211	100.4	0.0559	Yes	1.1 %
30	5	4.77	0.339	102.17	0.071	Yes	1.0 %
50	0.102	0.102	0.00032	99.92	0.00314	Yes	6.9 %
50	0.152	0.153	0.00071	101.13	0.00464	Yes	5.5 %
50	0.203	0.203	0.0012	100.39	0.00591	Yes	4.8 %
50	0.299	0.303	0.00246	101.99	0.00813	Yes	3.9 %
50	0.502	0.5	0.00625	100.91	0.0125	Yes	3.0 %
50	0.702	0.701	0.012	101.64	0.0171	Yes	2.5 %
50	1.004	0.98	0.0246	100.06	0.0251	Yes	2.1 %
50	1.5	1.457	0.056	100.87	0.0384	Yes	1.7 %
50	1.984	1.918	0.104	101.89	0.054	Yes	1.4 %
50	2.977	2.789	0.233	101.49	0.0834	Yes	1.1 %
50	3.98	3.661	0.394	101.88	0.108	Yes	0.96 %
50	4.984	4.566	0.59	103.45	0.129	Yes	0.86 %
100	0.1	0.103	0.00132	103.76	0.0128	Yes	4.7 %
100	0.152	0.156	0.00295	104.6	0.0189	No[b]	
100	0.201	0.202	0.00464	102.68	0.023	Yes	3.3 %
100	0.304	0.301	0.00964	102.25	0.032	Yes	2.7 %
100	0.508	0.499	0.0241	102.96	0.0483	Yes	2.1 %
100	0.719	0.694	0.0464	102.97	0.0668	Yes	1.7 %
100	1.016	0.946	0.0888	101.85	0.0938	Yes	1.5 %
100	1.511	1.381	0.181	103.41	0.131	Yes	1.2 %
100	2.017	1.785	0.3	103.35	0.168	Yes	1.0 %
100	3.028	2.556	0.57	103.22	0.223	Yes	0.87 %
100	4.045	3.334	0.871	103.95	0.261	Yes	0.77 %
100	5	4.074	1.121	103.9	0.275	No[b]	

a   Outlier excluded from fitting
b   Data received after fitting undertaken

Errors quoted are one standard deviation as reported by gPROMS. The absolute measurement errors are calculated by $\sigma = \omega |x|^\gamma$ where σ is the standard deviation, ω and γ are constants fitted in gPROMS (giving values 0.007437 and 0.7325 respectively) and x is the measured value (in this

case organic acidity). Errors at very low acidity, not included in the gPROMS fitting are likely to be larger than given by this formula.

Nitric Acid Extraction into TODGA / Exxsol D80 Mixtures

Extraction of 0.1 – 8.7 mol/L nitric acid into 0.05 – 0.4 mol/L TODGA in Exxsol D80 was measured with results as presented in Table SI 2 below.

Table SI 2: Extraction of Nitric Acid into TODGA / Exxsol D80

Series	[TODGA] (mol/L)	[HNO$_3$] (aq, ini) (mol/L)	[HNO$_3$] (aq, eq) (mol/L)	[HNO$_3$] (org, eq) (mol/L)	Mass Balance (%)	D	Used in Fitting?	Estimated Error
1	0.1	0.096	0.097	0.001	102.08	0.0103	No[a]	
1	0.1	0.242	0.247	0.007	104.96	0.0283	No[a]	
1	0.1	0.490	0.493	0.010	102.65	0.0203	No[a]	
1	0.1	0.969	0.985	0.021	103.82	0.0213	Yes	27 %
1	0.1	1.935	1.962	0.053	104.13	0.0270	Yes	14 %
1	0.1	2.858	2.881	0.095	104.13	0.0330	Yes	9 %
1	0.1	4.797	4.746	0.155	102.17	0.0327	Yes	6.3 %
1	0.1	6.739	6.736	0.223	103.26	0.0331	Yes	4.8 %
1	0.1	7.099	6.923	0.227	100.72	0.0328	Yes	4.7 %
1	0.1	7.099	6.940	0.229	100.99	0.0330	Yes	4.7 %
1	0.1	7.099	6.919	0.232	100.73	0.0335	Yes	4.7 %
1	0.1	8.661	7.626	0.245	90.88	0.0321	No[b]	
1	0.2	0.096	0.096	0.017	117.71	0.1771	No[ab]	
1	0.2	0.242	0.244	0.024	110.74	0.0984	No[ab]	
1	0.2	0.490	0.477	0.027	102.86	0.0566	No[a]	
1	0.2	0.969	0.932	0.056	101.96	0.0601	Yes	13 %
1	0.2	1.935	1.841	0.129	101.81	0.0701	Yes	7.2 %
1	0.2	2.858	2.758	0.197	103.39	0.0714	Yes	5.3 %
1	0.2	4.797	4.586	0.304	101.94	0.0663	Yes	3.8 %
1	0.2	6.739	6.451	0.408	101.78	0.0632	Yes	3.1 %
1	0.2	8.661	8.291	0.503	101.54	0.0607	Yes	2.7 %
1	0.3	0.096	0.099	0.001	104.17	0.0101	No[a]	
1	0.3	0.242	0.250	0.018	110.74	0.0720	No[ab]	
1	0.3	0.490	0.493	0.021	104.90	0.0426	No[a]	
1	0.3	1.020	0.962	0.104	104.51	0.1081	Yes	8.4 %
1	0.3	2.056	1.878	0.222	102.14	0.1182	Yes	4.8 %
1	0.3	3.025	2.750	0.320	101.49	0.1164	Yes	3.7 %
1	0.3	4.797	4.523	0.458	103.84	0.1013	Yes	2.8 %
1	0.3	7.099	6.632	0.663	102.76	0.1000	Yes	2.2 %
1	0.3	8.661	7.373	0.702	93.23	0.0952	No[b]	
4	0.05	0.969	0.994	0.010	103.61	0.0101	Yes	46 %
4	0.075	0.969	0.986	0.016	103.41	0.0162	Yes	33 %
4	0.1	0.969	0.979	0.019	102.99	0.0194	Yes	29 %
4	0.15	0.969	0.972	0.024	102.79	0.0247	Yes	24 %

Series	[TODGA] (mol/L)	[HNO₃] (aq, ini) (mol/L)	[HNO₃] (aq, eq) (mol/L)	[HNO₃] (org, eq) (mol/L)	Mass Balance (%)	D	Used in Fitting?	Estimated Error
4	0.2	0.969	0.961	0.047	104.02	0.0489	Yes	15 %
4	0.25	0.969	0.954	0.060	104.64	0.0629	Yes	13 %
4	0.3	0.969	0.943	0.076	105.16	0.0806	Yes	11 %
4	0.35	0.969	0.930	0.069	103.10	0.0742	Yes	11 %
4	0.4	0.969	0.919	0.082	103.30	0.0892	Yes	10 %
4	0.05	2.858	2.876	0.048	102.31	0.0167	Yes	15 %
4	0.075	2.858	2.825	0.078	101.57	0.0276	Yes	10 %
4	0.1	2.858	2.823	0.100	102.27	0.0354	Yes	8.6 %
4	0.15	2.858	2.786	0.154	102.87	0.0553	Yes	6.3 %
4	0.2	2.858	2.756	0.194	103.22	0.0704	Yes	5.3 %
4	0.25	2.858	2.707	0.255	103.64	0.0942	Yes	4.4 %
4	0.3	2.858	2.667	0.280	103.11	0.1050	Yes	4.1 %
4	0.35	2.858	2.652	0.344	104.83	0.1297	Yes	3.5 %
4	0.4	2.858	2.662	0.371	106.12	0.1394	Yes	3.3 %
4	0.05	5.872	5.846	0.091	101.11	0.0156	Yes	9.3 %
4	0.075	5.872	5.821	0.142	101.55	0.0244	Yes	6.7 %
4	0.1	5.872	5.805	0.185	102.01	0.0319	Yes	5.5 %
4	0.15	5.872	5.708	0.281	101.99	0.0492	Yes	4.1 %
4	0.2	5.872	5.659	0.365	102.59	0.0645	Yes	3.4 %
4	0.25	5.872	5.577	0.449	102.62	0.0805	Yes	2.9 %
4	0.3	5.872	5.519	0.527	102.96	0.0955	Yes	2.6 %
4	0.35	5.872	5.442	0.609	103.05	0.1119	Yes	2.3 %
4	0.4	5.872	5.369	0.672	102.88	0.1252	Yes	2.2 %
2	0.2	0.5	0.474	0.00886	96.47	0.0187	No[a]	
2	0.2	0.7	0.677	0.022	99.86	0.0325	Yes	26 %
2	0.2	1	0.951	0.0458	99.68	0.0482	Yes	15 %
2	0.2	1.5	1.385	0.0885	98.23	0.0639	Yes	9.4 %
2	0.2	2	1.875	0.128	100.15	0.0683	Yes	7.2 %
2	0.2	3	2.763	0.191	98.47	0.0691	Yes	5.4 %
2	0.2	5	4.765	0.304	101.38	0.0638	Yes	3.8 %
2	0.1	8.568	8.41	0.282	101.45	0.0336	Yes	4.1 %
2	0.1	8.568	8.402	0.281	101.34	0.0335	Yes	4.1 %
2	0.2	8.568	8.202	0.540	102.02	0.0658	Yes	2.5 %
2	0.2	8.568	8.225	0.542	102.32	0.0659	Yes	2.5 %
2	0.3	8.568	8.027	0.796	102.96	0.0991	Yes	1.9 %
2	0.3	8.568	8.06	0.799	103.39	0.0991	Yes	1.9 %
3	0.2	1.031	1.015	0.091	107.26	0.0893	No[c]	
3	0.2	2.033	1.922	0.177	103.23	0.0922	No[c]	
3	0.2	2.954	2.741	0.237	100.84	0.0865	No[c]	
3	0.2	5.265	5.008	0.373	102.21	0.0745	No[c]	

a   Data at below 0.6 M aq acidity excluded from fitting.

b   Data excluded from fitting due to poor mass balance.

c   Series 3 data not used in fitting due to systematic offset from remainder of data

Errors quoted are one standard deviation as reported by gPROMS. The absolute measurement errors are calculated by $\sigma = \omega |x|^{\gamma}$ where σ is the standard deviation, ω and γ are constants fitted in gPROMS (giving values 0.01609 and 0.2701 respectively) and x is the measured value (in this case organic acidity). Errors at very low acidity, not included in the gPROMS fitting are likely to be larger than given by this formula.

Series 1 and 4, Exxsol D80 diluent, ambient temperature ($\approx$ 20 – 25 °C), *A/O* = 1. Series 2, Exxsol D80 diluent, 20 ± 0.5 °C, *A/O* = 1. Series 3, Exxsol D80 diluent 22 ± 1 °C, *A/O* = 1.

Diluent Effect on Nitric Acid Extraction

The extraction of 3 mol/L nitric acid into 0.1 mol/L TODGA + 5 v/v% octanol in TPH, Exxsol D80, Fluka kerosene or *n*-dodecane was measured. Duplicate experiments with duplicate titrations each were performed at a temperature of 20°C and an *A/O* phase ratio of 1. The equilibrium nitric acid concentrations as determined by potentiometric titration after stripping into water *(A/O* = 2) in the organic phases are as follows:

TPH,   (132 ± 1) mmol/L

Exxsol D80,   (127 ± 8) mmol/L

Fluka kerosene,   (128 ± 3) mmol/L

n-dodecane,   (131 ± 3) mmol/L

The results imply that the kind of "kerosene" used does not have a significant effect on HNO_3 extraction.

Nitric Acid Extraction into TODGA / Octanol / Diluent Mixtures at 20 – 25°C

Extraction of 0.1 – 5.4 mol/L nitric acid into 0.05 – 0.4 mol/L TODGA, 5 – 50 v/v% octanol in Exxsol D80 or TPH diluent was measured with results as presented in Table SI 3 below.

Table SI 3: Ambient Temperature Data for Nitric Acid Extraction into TODGA/Octanol/Diluent Mixtures

Series	[Octanol] (mol/L)	[TODGA] (mol/L)	[HNO$_3$] (aq, ini) (mol/L)	[HNO$_3$] (aq, eq) (mol/L)	[HNO$_3$] (org, eq) (mol/L)	Mass Balance (%)	D	Used in Fitting	Estimated Error
1	0.316	0.2	0.096	0.096	1E-6	100.00	1E-05	No[a]	
1	0.316	0.2	0.242	0.24	0.014	104.96	0.0583	No[a]	
1	0.316	0.2	0.490	0.475	0.022	101.43	0.0463	No[a]	
1	0.316	0.2	0.969	0.935	0.043	100.93	0.0460	Yes	6.3 %
1	0.316	0.2	1.935	1.832	0.121	100.93	0.0660	Yes	6.1 %
1	0.316	0.2	2.858	2.743	0.208	103.25	0.0758	Yes	5.9 %
1	0.316	0.2	3.887	3.667	0.281	101.57	0.0766	Yes	5.9 %
1	0.316	0.2	4.797	4.55	0.351	102.17	0.0771	Yes	5.8 %
1	0.316	0.2	2.794	2.564	0.184	98.35	0.0718	Yes	6 %
1	0.631	0.2	2.794	2.586	0.203	99.82	0.0785	Yes	5.9 %
1	1.251	0.2	2.794	2.510	0.245	98.60	0.0976	Yes	5.9 %

Series	[Octanol] (mol/L)	[TODGA] (mol/L)	[HNO$_3$] (aq, ini) (mol/L)	[HNO$_3$] (aq, eq) (mol/L)	[HNO$_3$] (org, eq) (mol/L)	Mass Balance (%)	D	Used in Fitting	Estimated Error
1	1.880	0.2	2.794	2.452	0.292	98.21	0.1191	Yes	5.8 %
1	2.493	0.2	2.794	2.510	0.325	101.47	0.1295	Yes	5.8 %
1	3.110	0.2	2.794	2.428	0.337	98.96	0.1388	Yes	5.8 %
1	0.316	0.3	2.858	2.655	0.299	103.36	0.1126	Yes	5.8 %
1	0.631	0.3	2.858	2.638	0.317	103.39	0.1202	Yes	5.8 %
1	0.941	0.3	2.858	2.628	0.331	103.53	0.1260	Yes	5.8 %
1	1.251	0.3	2.858	2.608	0.355	103.67	0.1361	Yes	5.8 %
1	1.562	0.3	2.858	2.527	0.377	101.61	0.1492	Yes	5.8 %
1	1.880	0.3	2.858	2.507	0.396	101.57	0.1580	Yes	5.8 %
1	2.493	0.3	2.858	2.424	0.440	100.21	0.1815	Yes	5.8 %
1	2.804	0.3	2.858	2.38	0.465	99.55	0.1954	Yes	5.7 %
1	3.110	0.3	2.858	2.417	0.470	101.01	0.1945	Yes	5.7 %
1	0.316	0.1	2.858	2.821	0.121	102.94	0.0429	Yes	6.1 %
1	0.631	0.1	2.858	2.782	0.144	102.38	0.0518	Yes	6 %
1	0.941	0.1	2.858	2.711	0.162	100.52	0.0598	Yes	6 %
1	1.251	0.1	2.858	2.695	0.180	100.59	0.0668	Yes	6 %
1	1.562	0.1	2.858	2.655	0.200	99.90	0.0753	Yes	5.9 %
1	1.880	0.1	2.858	2.639	0.221	100.07	0.0837	Yes	5.9 %
1	2.493	0.1	2.858	2.601	0.264	100.24	0.1015	Yes	5.9 %
1	2.804	0.1	2.858	2.561	0.291	99.79	0.1136	Yes	5.9 %
1	0.316	0.05	2.858	2.845	0.064	101.78	0.0225	Yes	6.2 %
1	0.316	0.075	2.858	2.814	0.088	101.54	0.0313	Yes	6.1 %
1	0.316	0.1	2.858	2.815	0.110	102.34	0.0391	Yes	6.1 %
1	0.316	0.15	2.858	2.755	0.155	101.82	0.0563	Yes	6 %
1	0.316	0.2	2.858	2.732	0.190	102.24	0.0695	Yes	6 %
1	0.316	0.25	2.858	2.652	0.250	101.54	0.0943	Yes	5.9 %
1	0.316	0.3	2.858	2.645	0.286	102.55	0.1081	Yes	5.9 %
1	0.316	0.35	2.858	2.615	0.336	103.25	0.1285	Yes	5.8 %
1	0.316	0.4	2.858	2.581	0.356	102.76	0.1379	Yes	5.8 %
2	0.316	0.05	0.5	0.498	2.28E-3		0.0046[c]	No[a]	
2	0.316	0.05	0.7	0.695	4.75E-3		0.0068[c]	Yes	6.9 %
2	0.316	0.05	1	0.990	0.0103		0.0104[c]	Yes	6.7 %
2	0.316	0.05	1.5	1.478	0.0222		0.0150[c]	Yes	6.5 %
2	0.316	0.05	2	1.962	0.0382		0.0195[c]	Yes	6.4 %
2	0.316	0.05	3	2.924	0.0758		0.0259[c]	Yes	6.2 %
2	0.316	0.05	4	3.887	0.113		0.0291[c]	Yes	6.1 %
2	0.316	0.05	5	4.849	0.1511		0.0312[c]	Yes	6 %
2	0.316	0.1	0.296	0.293	0.003		0.0119	No[a]	
2	0.316	0.1	0.487	0.481	0.006		0.0127	No[a]	
2	0.316	0.1	0.980	0.961	0.019		0.0195	Yes	6.5 %
2	0.316	0.1	1.460	1.422	0.039		0.0271	Yes	6.4 %
2	0.316	0.1	1.950	1.884	0.066		0.0349	Yes	6.2 %
2	0.316	0.1	2.910	2.795	0.115		0.0411	Yes	6.1 %
2	0.316	0.1	3.890	3.720	0.170		0.0458	Yes	6 %

Series	[Octanol] (mol/L)	[TODGA] (mol/L)	[HNO$_3$] (aq, ini) (mol/L)	[HNO$_3$] (aq, eq) (mol/L)	[HNO$_3$] (org, eq) (mol/L)	Mass Balance (%)	D	Used in Fitting	Estimated Error
2	0.316	0.1	4.900	4.681	0.219		0.0468	Yes	5.9 %
2	0.316	0.2	0.100	0.096	0.004		0.0412	No[a]	
2	0.316	0.2	0.199	0.194	0.005		0.0253	No[a]	
2	0.316	0.2	0.296	0.290	0.006		0.0209	No[a]	
2	0.316	0.2	0.487	0.474	0.013		0.0277	No[a]	
2	0.316	0.2	0.685	0.663	0.022		0.0332	Yes	6.5 %
2	0.316	0.2	0.980	0.937	0.043		0.0457	Yes	6.3 %
2	0.316	0.2	1.459	1.377	0.081		0.0591	Yes	6.2 %
2	0.316	0.2	1.953	1.823	0.130		0.0716	Yes	6 %
2	0.316	0.2	2.911	2.699	0.212		0.0786	Yes	5.9 %
2	0.316	0.2	3.887	3.581	0.306		0.0855	Yes	5.8 %
2	0.316	0.2	4.902	4.521	0.381		0.0843	Yes	5.8 %
2	0.316	0.3	0.296	0.286	0.010		0.0335	No[a]	
2	0.316	0.3	0.487	0.466	0.021		0.0451	No[a]	
2	0.316	0.3	0.685	0.649	0.036		0.0556	Yes	6.4 %
2	0.316	0.3	0.980	0.911	0.069		0.0761	Yes	6.2 %
2	0.316	0.3	1.460	1.336	0.124		0.0928	Yes	6.1 %
2	0.316	0.3	1.950	1.751	0.199		0.1136	Yes	5.9 %
2	0.316	0.3	2.910	2.607	0.303		0.1162	Yes	5.8 %
2	0.316	0.3	3.890	3.465	0.425		0.1227	Yes	5.8 %
2	0.316	0.3	4.900	4.381	0.519		0.1185	Yes	5.7 %
3	0.316	0.2	0.519	0.508	0.020	101.64	0.0394	No[a]	
3	0.316	0.2	1.020	0.982	0.050	101.18	0.0509	Yes	6.3 %
3	0.316	0.2	2.017	1.882	0.150	100.74	0.0797	Yes	6 %
3	0.316	0.2	4.025	3.690	0.340	100.11	0.0922	Yes	5.8 %
3	0.316	0.2	4.989	4.609	0.460	101.60	0.0998	Yes	5.7 %
3	0.316	0.2	5.354	4.894	0.440	99.62	0.0899	Yes	5.8 %
3	0.316	0.1	0.519	0.517	0.010	101.58	0.0201	No[a]	
3	0.316	0.1	1.020	0.995	0.023	99.84	0.0232	Yes	6.5 %
3	0.316	0.1	2.017	1.947	0.079	100.41	0.0405	Yes	6.2 %
3	0.316	0.1	4.025	3.845	0.202	100.55	0.0526	Yes	5.9 %
3	0.316	0.1	4.989	4.740	0.270	100.42	0.0571	Yes	5.9 %
3	0.316	0.1	5.354	5.062	0.271	99.61	0.0535	Yes	5.9 %
3	0.316	0.3	0.519	0.500	0.028	101.77	0.0560	No[a]	
3	0.316	0.3	1.020	0.968	0.075	102.25	0.0775	Yes	6.2 %
3	0.316	0.3	2.017	1.848	0.214	102.21	0.1158	Yes	5.9 %
3	0.316	0.3	4.025	3.634	0.445	101.33	0.1225	Yes	5.7 %
3	0.316	0.3	4.989	4.526	0.565	102.04	0.1248	Yes	5.7 %
3	0.316	0.3	5.354	4.809	0.573	100.51	0.1192	Yes	5.7 %

a   Points at less than 0.6 M HNO$_3$(aq)(eq) excluded from fitting

Errors quoted are one standard deviation as reported by gPROMS. The absolute measurement errors are calculated by $\sigma = \omega|x|^\gamma$ where σ is the standard deviation, ω and γ are constants fitted in

gPROMS (giving values 0.05561 and 0.9590 respectively) and x is the measured value (in this case organic acidity). Errors at very low acidity, not included in the gPROMS fitting are likely to be larger than given by this formula.

Four points from Table SI 4 (at 20 °C) were also used in fitting of TODGA / octanol cross complexes.

0.316 mol/L octanol equivalent to 5 v/v% octanol.

Series 1 experiments used ambient temperature ($\approx$ 20 – 25 °C) and Exxsol D80 diluent, A/O = 1. Series 2 experiments undertaken at 20 ± 0.5 °C with TPH diluent, A/O = 1. Equilibrium aqueous acidity was not measured in series 2 experiments and values in table above are from mass balance. Series 3 experiments undertaken at 22 ± 1 °C with TPH diluent, A/O = 1.

Temperature Effect on Nitric Acid Extraction

The extraction of nitric acid into 0.1 and 0.2 mol/L TODGA in diluent with 5% octanol was measured. Results are reported in Table SI 4 below. Series 1 experiments used Exxsol D80 as a diluent whilst series 2 experiments used a TPH diluent. Equilibrium aqueous acidity calculated by mass balance, A/O = 1 in all experiments.

Table SI 4: Experimental Data for Extraction of Nitric acid into TODGA /5% Octanol/Diluent: Effect of Temperature

Series	T (°C)	[TODGA] (mol/L)	[HNO$_3$] (aq, ini) (mol/L)	[HNO$_3$] (aq, eq) (mol/L)	[HNO$_3$] (org, eq) (Mol/L)	D	Used in Fitting?	Estimated error
1	22	0.2	1.021	0.977	0.0440	0.0450	Yes	4.8 %
1	29.6	0.2	1.028	0.990	0.0380	0.0384	Yes	4.9 %
1	38.9	0.2	1.057	1.020	0.0370	0.0363	Yes	4.9 %
1	49.9	0.2	1.061	1.030	0.0310	0.0301	Yes	5 %
2	10	0.1	0.306	0.303	0.0024	0.0099	No[a]	
2	20	0.1	0.306	0.304	0.0020	0.0066	No[a]	
2	30	0.1	0.306	0.304	0.0020	0.0079	No[a]	
2	40	0.1	0.306	0.304	0.0017	0.0066	No[a]	
2	50	0.1	0.306	0.304	0.0016	0.0053	No[a]	
2	10	0.1	1.020	0.995	0.0252	0.0253	Yes	5.2 %
2	20	0.1	1.020	1.000	0.0200	0.0200	Yes	5.4 % [b]
2	30	0.1	1.020	1.002	0.0176	0.0176	Yes	5.5 %
2	40	0.1	1.020	1.005	0.0152	0.0151	Yes	5.6 %
2	50	0.1	1.020	1.006	0.0144	0.0143	Yes	5.7 %
2	10	0.1	3.050	2.918	0.1320	0.0452	Yes	4 %
2	20	0.1	3.050	2.927	0.1230	0.0420	Yes	4.1 % [c]
2	30	0.1	3.050	2.936	0.1140	0.0388	Yes	4.1 %
2	40	0.1	3.050	2.941	0.1090	0.0371	Yes	4.1 %
2	50	0.1	3.050	2.945	0.1050	0.0357	Yes	4.2 %
2	10	0.2	0.306	0.299	0.0072	0.0241	No[a]	
2	20	0.2	0.306	0.301	0.0050	0.0166	No[a]	
2	30	0.2	0.306	0.302	0.0042	0.0139	No[a]	
2	40	0.2	0.306	0.302	0.0038	0.0126	No[a]	

Series	T (°C)	[TODGA] (mol/L)	[HNO₃] (aq, ini) (mol/L)	[HNO₃] (aq, eq) (mol/L)	[HNO₃] (org, eq) (Mol/L)	D	Used in Fitting?	Estimated error
2	50	0.2	0.306	0.303	0.0034	0.0112	No[a]	
2	10	0.2	1.020	0.963	0.0574	0.0596	Yes	4.6 %
2	20	0.2	1.020	0.977	0.0430	0.0440	Yes	4.8 % [d]
2	30	0.2	1.020	0.983	0.0372	0.0379	Yes	4.9 %
2	40	0.2	1.020	0.988	0.0322	0.0326	Yes	5 %
2	50	0.2	1.020	0.991	0.0294	0.0297	Yes	5.1 %
2	10	0.2	3.050	2.803	0.2470	0.0881	Yes	3.6 %
2	20	0.2	3.050	2.824	0.2260	0.0800	Yes	3.7 % [e]
2	30	0.2	3.050	2.836	0.2140	0.0755	Yes	3.7 %
2	40	0.2	3.050	2.849	0.2010	0.0706	Yes	3.8 %
2	50	0.2	3.050	2.858	0.1920	0.0672	Yes	3.8 %

a   Points at less than 0.6 M HNO₃(aq)(eq) excluded from fitting

bcde   Points also included with Table SI 3 data in fitting of TODGA / octanol cross complexes. In this context estimated errors were b: 6.5%, c: 6.1%, d: 6.3% e: 5.9%

Errors quoted above are one standard deviation as reported by gPROMS. The absolute measurement errors are calculated by $\sigma = \omega|x|^{\gamma}$ where σ is the standard deviation, ω and γ are constants fitted in gPROMS (giving values 0.02932 and 0.8435 respectively) and x is the measured value (in this case organic acidity). Errors at very low acidity, not included in the gPROMS fitting are likely to be larger than given by this formula.

Speciation Predictions for Nitric Acid, Octanol and TODGA

Table SI 5: Predicted speciation of extracted nitric acid for selected cases.

Conditions			Percentage of Extracted Acid in each Complex										
[TODGA] (M)	[Oct] (M)	[HNO₃] (aq)(eq) (M)	HNO₃. Oct	HNO₃. 2Oct	HNO₃. 3Oct	HNO₃. TODGA	2HNO₃. TODGA	3HNO₃. TODGA	4HNO₃. TODGA	2HNO₃. 2TODGA	2HNO₃. TODGA. 3Oct	3HNO₃. TODGA. 2Oct	HNO₃. TODGA. Oct
0.1	0.316	2.5	7.031	0.417	0.021	25.807	12.415	0.376	0.025	3.219	4.929	13.983	31.776
0.2	0.316	2.5	2.964	0.142	5.86E-3	30.038	14.451	0.438	0.029	8.363	3.032	10.637	29.901
0.3	0.316	2.5	1.704	0.070	2.47E-3	31.621	15.212	0.461	0.030	13.790	1.997	8.191	26.921
0.2	0.316	0.1	0.953	0.039	1.35E-3	53.701	0.037	1.64E-6	1.57E-10	0.102	4.74E-3	2.85E-5	45.162
0.2	0.316	2.0	2.251	0.106	4.33E-3	36.371	10.075	0.176	6.66E-3	9.159	2.023	4.147	35.680
0.2	0.316	5.0	5.235	0.164	4.40E-3	8.047	24.290	4.618	1.908	1.390	1.413	47.708	5.223
0.2	0.630	2.5	5.790	0.568	0.048	15.514	7.463	0.226	0.015	2.337	13.423	23.011	31.605
0.2	2.497	2.5	16.085	7.873	3.320	0.466	0.224	6.79E-3	4.47E-4	3.78E-3	50.084	17.203	4.734

Table SI 6: Predicted speciation of octanol for selected cases.

Conditions			Percentage of Octanol in each Complex							
[TODGA] (M)	[Oct] (M)	[HNO₃] (aq)(eq) (M)	Free Oct	HNO₃. Oct	HNO₃. 2Oct	HNO₃. 3Oct	2HNO₃. TODGA. 3Oct	3HNO₃. TODGA. 2Oct	HNO₃. TODGA. Oct	TODGA. 2Oct
0.1	0.316	2.5	72.274	2.168	0.257	0.020	2.280	2.874	9.797	10.330
0.2	0.316	2.5	58.430	1.753	0.168	0.010	2.689	4.194	17.683	15.073
0.3	0.316	2.5	49.974	1.499	0.123	6.51E-3	2.635	4.805	23.688	17.270
0.2	0.316	0.1	49.365	2.15E-3	1.74E-4	9.09E-6	1.60E-5	4.28E-8	0.102	50.531
0.2	0.316	2.0	57.584	0.995	0.094	5.73E-3	1.341	1.221	15.763	22.997
0.2	0.316	5.0	38.102	7.171	0.448	0.018	2.903	43.568	7.155	0.634
0.2	0.630	2.5	59.889	1.796	0.352	0.045	6.247	4.760	9.806	17.106
0.2	2.497	2.5	75.466	2.264	2.216	1.402	10.572	1.614	0.666	5.801

Table SI 7: Predicted speciation of TODGA for selected cases.

Conditions			Percentage of TODGA in each Complex									
[TODGA] (M)	[Oct] (M)	[HNO₃] (aq)(eq) (M)	Free TODGA	HNO₃. TODGA	2HNO₃. TODGA	3HNO₃. TODGA	4HNO₃. TODGA	2HNO₃. 2TODGA	2HNO₃. TODGA. 3Oct	3HNO₃. TODGA. 2Oct	HNO₃. TODGA. Oct	TODGA. 2Oct
0.1	0.316	2.5	11.399	25.122	6.043	0.122	6.03E-3	3.133	2.399	4.537	30.932	16.307
0.2	0.316	2.5	12.725	28.042	6.745	0.136	6.73E-3	7.808	1.415	3.310	27.914	11.897
0.3	0.316	2.5	13.287	29.281	7.043	0.142	7.02E-3	12.770	0.924	2.528	24.929	9.087
0.2	0.316	0.1	59.764	0.191	6.65E-5	1.95E-09	1.39E-13	3.62E-4	8.42E-6	3.38E-8	0.161	39.884
0.2	0.316	2.0	19.989	25.364	3.513	0.041	1.16E-3	6.388	0.705	0.964	24.883	18.152
0.2	0.316	5.0	1.258	17.400	26.263	3.329	1.031	3.006	1.528	34.389	11.295	0.500
0.2	0.630	2.5	6.884	15.171	3.649	0.074	3.64E-3	2.285	6.563	7.501	30.908	26.960
0.2	2.497	2.5	0.371	0.818	0.197	3.97E-03	1.96E-4	6.64E-03	43.999	10.075	8.317	36.211