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Modelling of Acid Extraction into TODGA / Octanol Mixtures

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David Woodhead

Introduction

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- i-SANEX Solvent
  - 0.2M TODGA
  - 5v/v% Octanol
  - Inert diluent (e.g. OK or TPH)

  - Main Extractant (TODGA) extracts Actinides / Lanthanides
    - Also extracts acid (HNO_3)
    - Does not extract most fission products
  - Phase Modifier (Octanol) supresses 3rd Phase formation
    - Extracts Acid – but little else

Aims of Modelling

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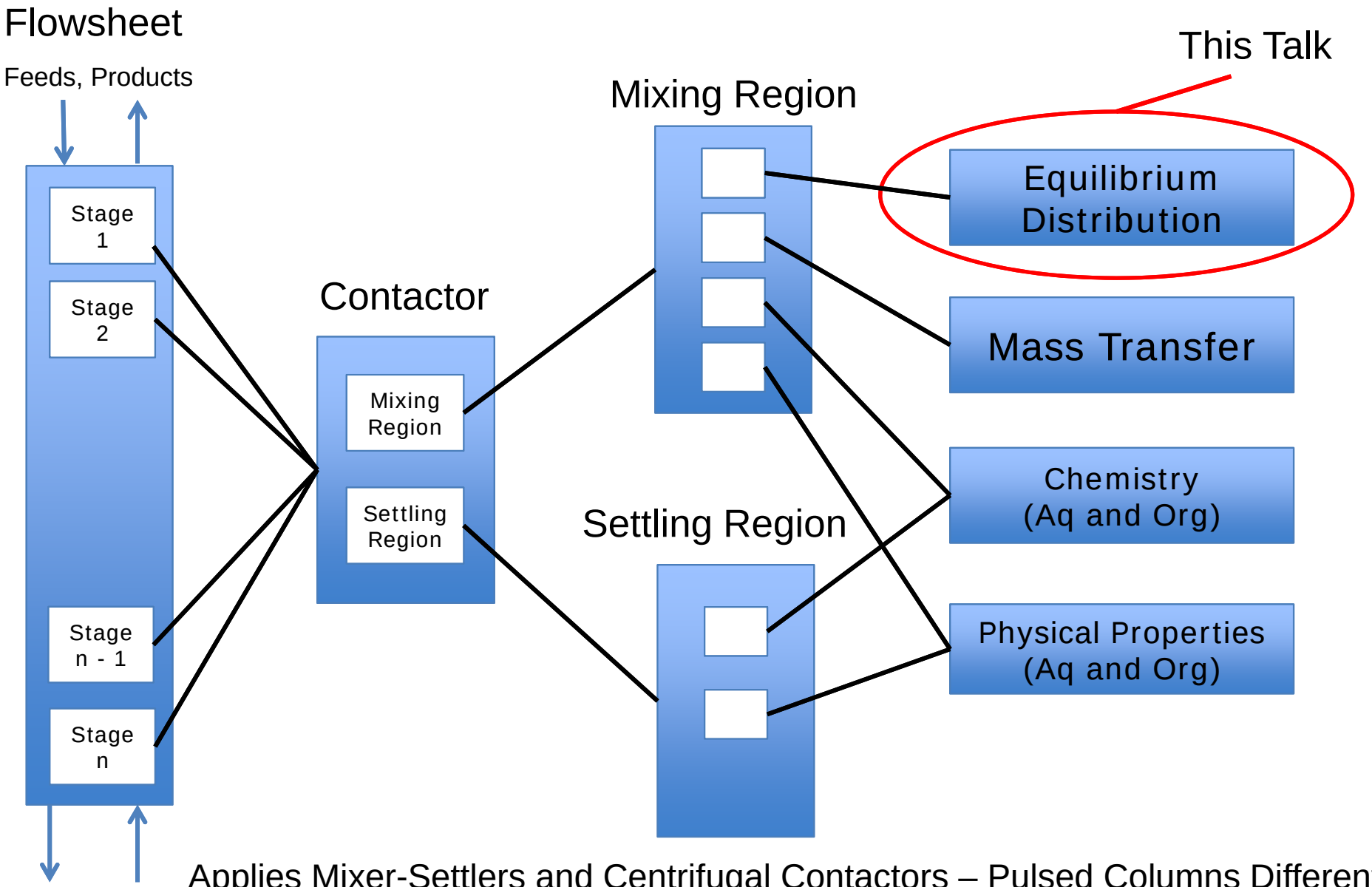
- Production of dynamic process model of proposed flowsheets for:

- Process Optimisation
  - Sensitivity studies allow many permutations to be analysed
  - Identify most useful experiments to run.

- Support Safety Analysis
  - Maloperation Studies – What if?
  - Stability studies – flowsheet might look good but how wide is operating envelope?

- Requirement for above is model that is valid over a wide range of operating conditions

Elements of a Process Model



Applies Mixer-Settlers and Centrifugal Contactors – Pulsed Columns Different

D-Value Calculations (1)

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- Various Solvent phase complexes formed.
- Each solvent phase complex considered separately.
- e.g. acid extracting into octanol includes

$$HNO_3.2Oct$$

- Associated equilibrium:-

$$K = \frac{[HNO_3.2Oct]_{(org)}}{\gamma_{H^+}[H^+]_{(aq)}\gamma_{NO_3^-}[NO_3^-]_{(aq)}[Oct_{Free}]^2_{(org)}}$$

- Need to fit expressions for γ's and value for K

D-Value Calculations (2)

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- Data does not allow us to distinguish $\gamma_{H^+}, \gamma_{NO_3^-}$
- Can use $\gamma_{\pm}$ where $\gamma_{\pm}^2 = \gamma_{H^+}\gamma_{NO_3^-}$
- $\gamma_{\pm}$ available from literature – but as used here includes allowance for solvent phase activity effects.
- Expression for $\gamma_{\pm}$ is therefore ultimately empirical
- Aim to same expression for $\gamma_{\pm}$ in all equilibria
- In general *K*'s and $\gamma_{\pm}$ dependent on T – current data all insufficient to determine T dependence

The i-SANEX Solvent

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- Composition
  - 0.2M TODGA
  - 5 v/v% Octanol
  - Inert Diluent
- Approach
  1. Assume the diluent is genuinely inert
  2. Derive separate expressions for acid extraction into TODGA and Octanol
  3. Investigate synergistic and antagonistic effects

Acid Extraction into Octanol (1)

- Data from KIT-INE, 5 – 100% Octanol, 0 – 5M HNO_3
- Previous modelling used HNO_3.2Oct complex only [1]. Good fit but required conditional equilibrium constants – difficult to use in model.
- New model assumes additional HNO_3.Oct ,HNO_3.3Oct complexes.

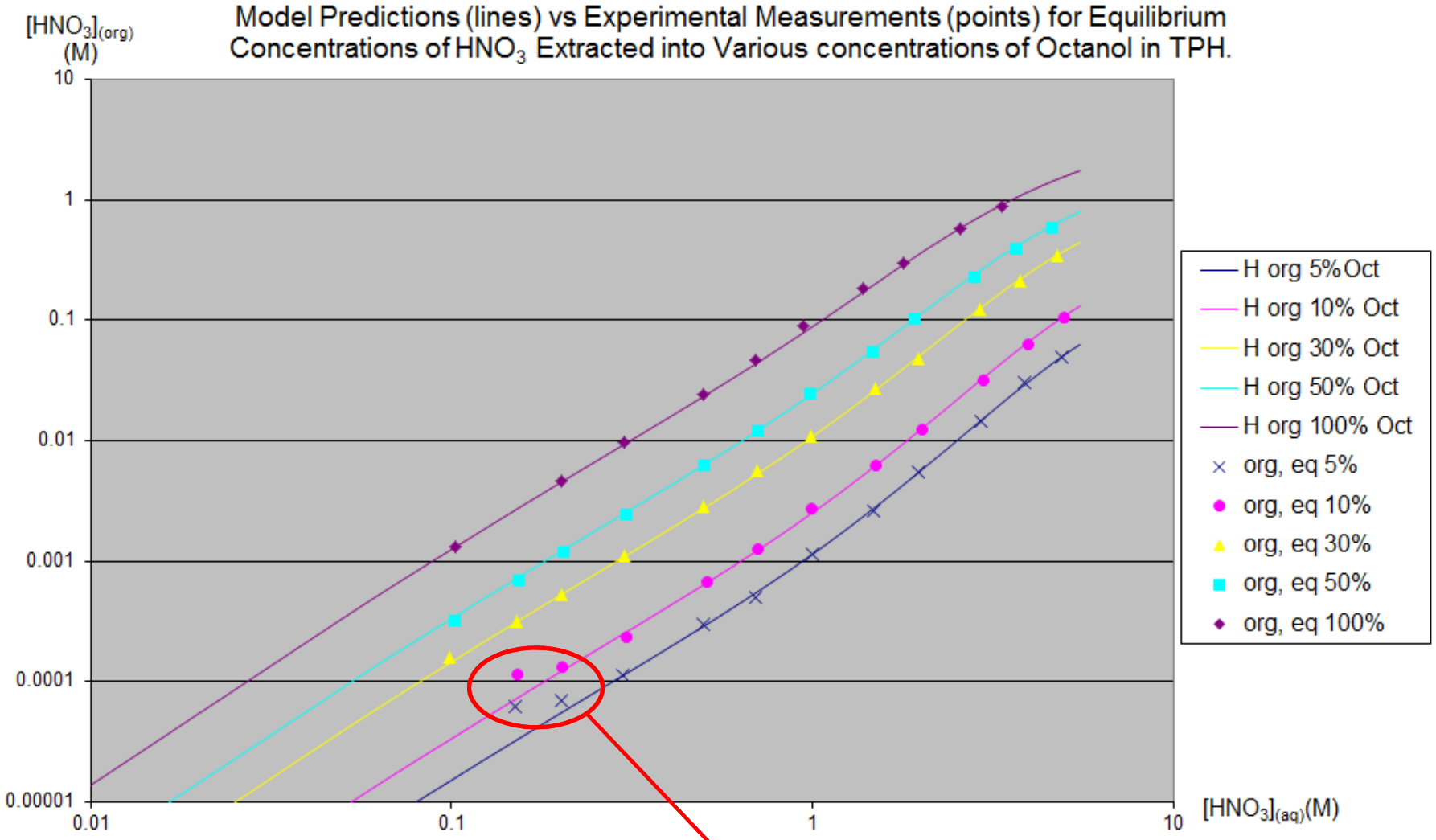
$$[HNO_3]_{org} = \sum_{i=1}^{i=3} \beta_i \gamma_{\pm}^2 [H^+][NO_3^-][Oct_{free}]^i$$

$$\gamma_{\pm} = \frac{A}{([NO_3^-]+B)^2} + C + D[NO_3^-] + E[NO_3^-]^2$$

- β_i's and A through E fitted constants. Form of 2nd equation gives good fit to published activity coefficient data.
- No additional benefit found from adding $2HNO_3$.Oct or HNO_3.4Oct complexes

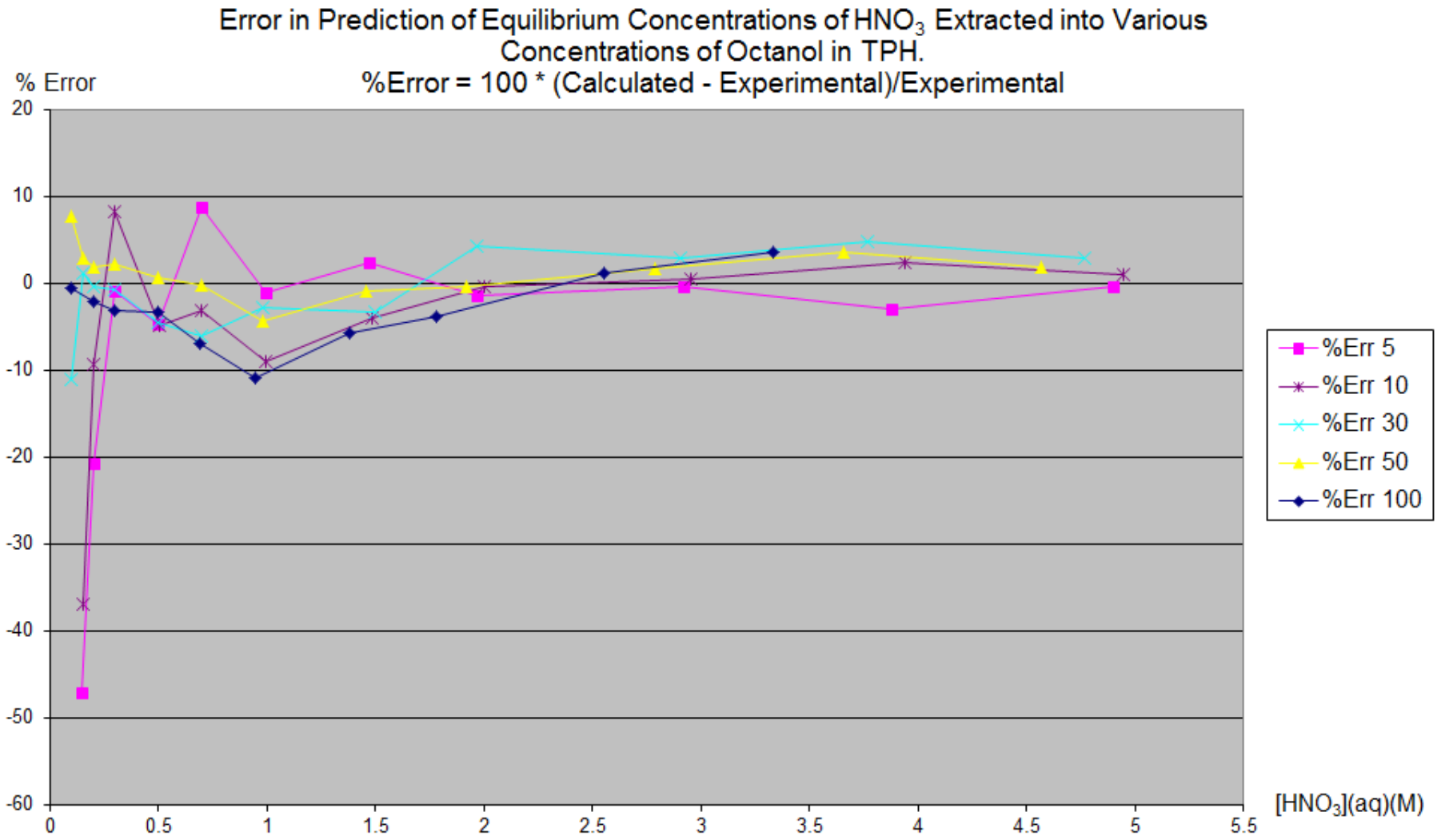
[1] Geist, A., Extraction of Nitric Acid into Alcohol: Kerosene Mixtures, J. SXIX, 28, pp 596-607, 2010

Acid Extraction into Octanol (2)

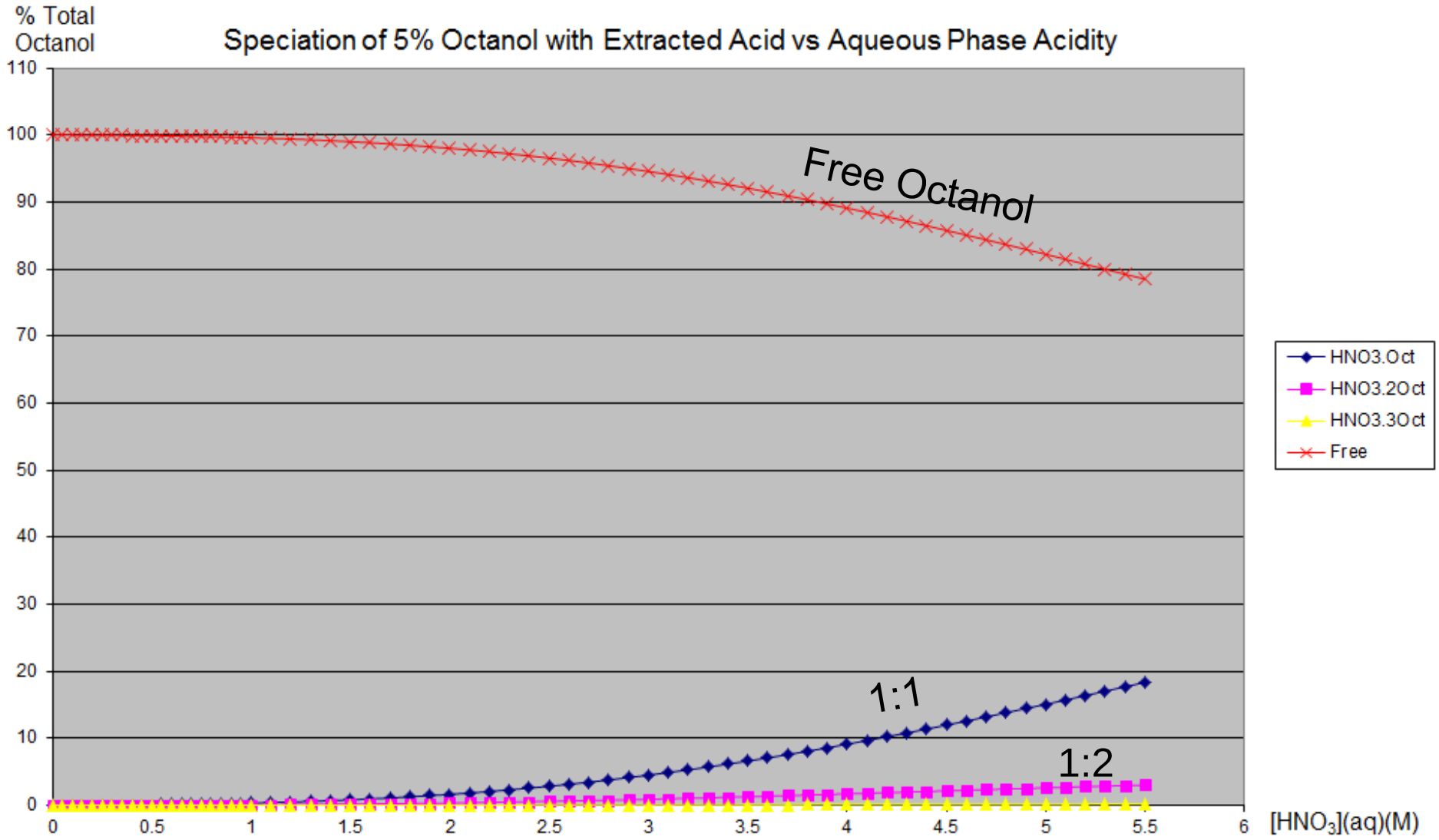


Very good fit except at lowest acidity

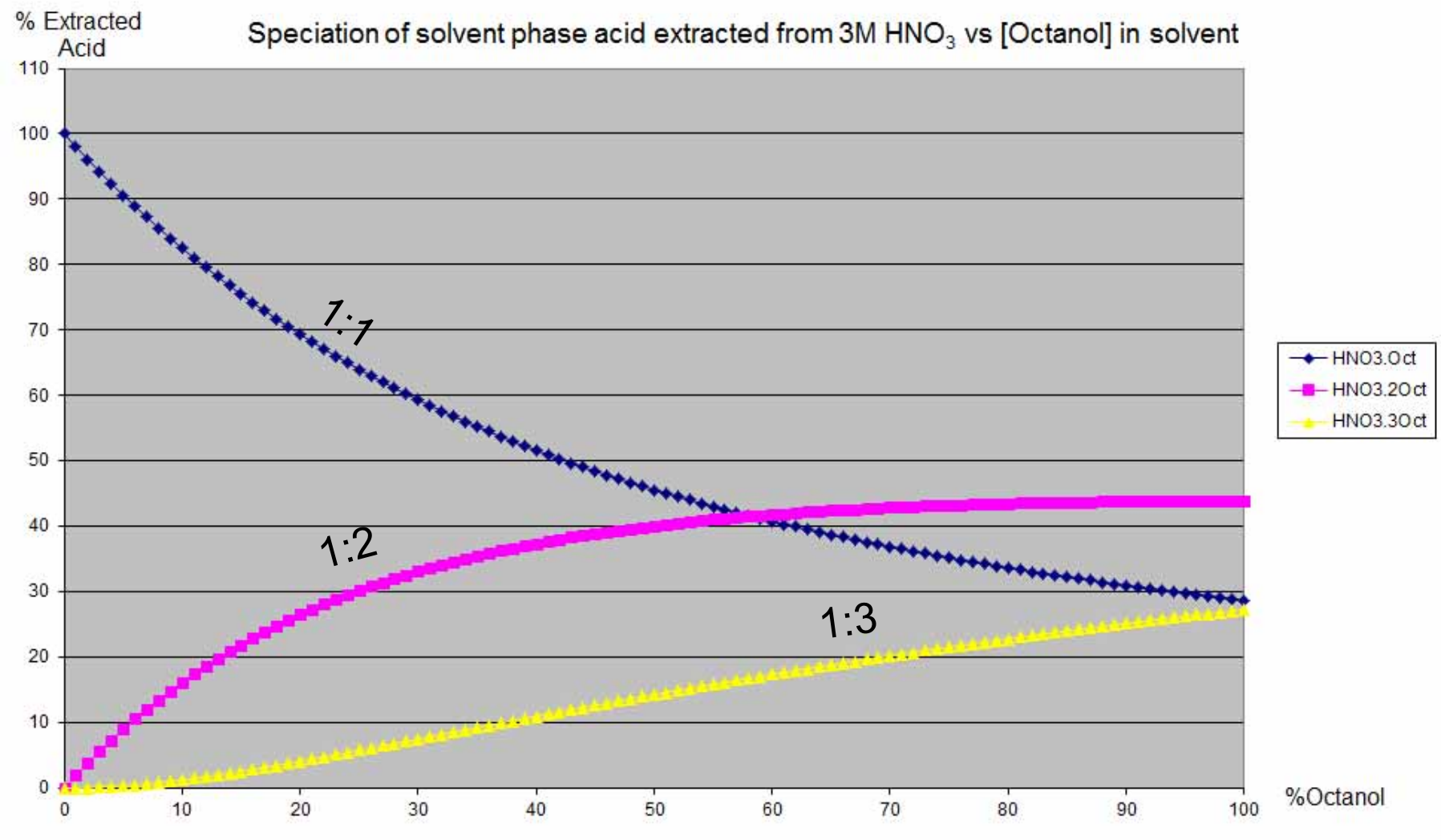
Acid Extraction into Octanol (3)



Acid Extraction into Octanol (4)



Acid Extraction into Octanol (5)



Octanol : Acid ratio in complexes increases with increasing [octanol]

Acid Extraction into TODGA (1)

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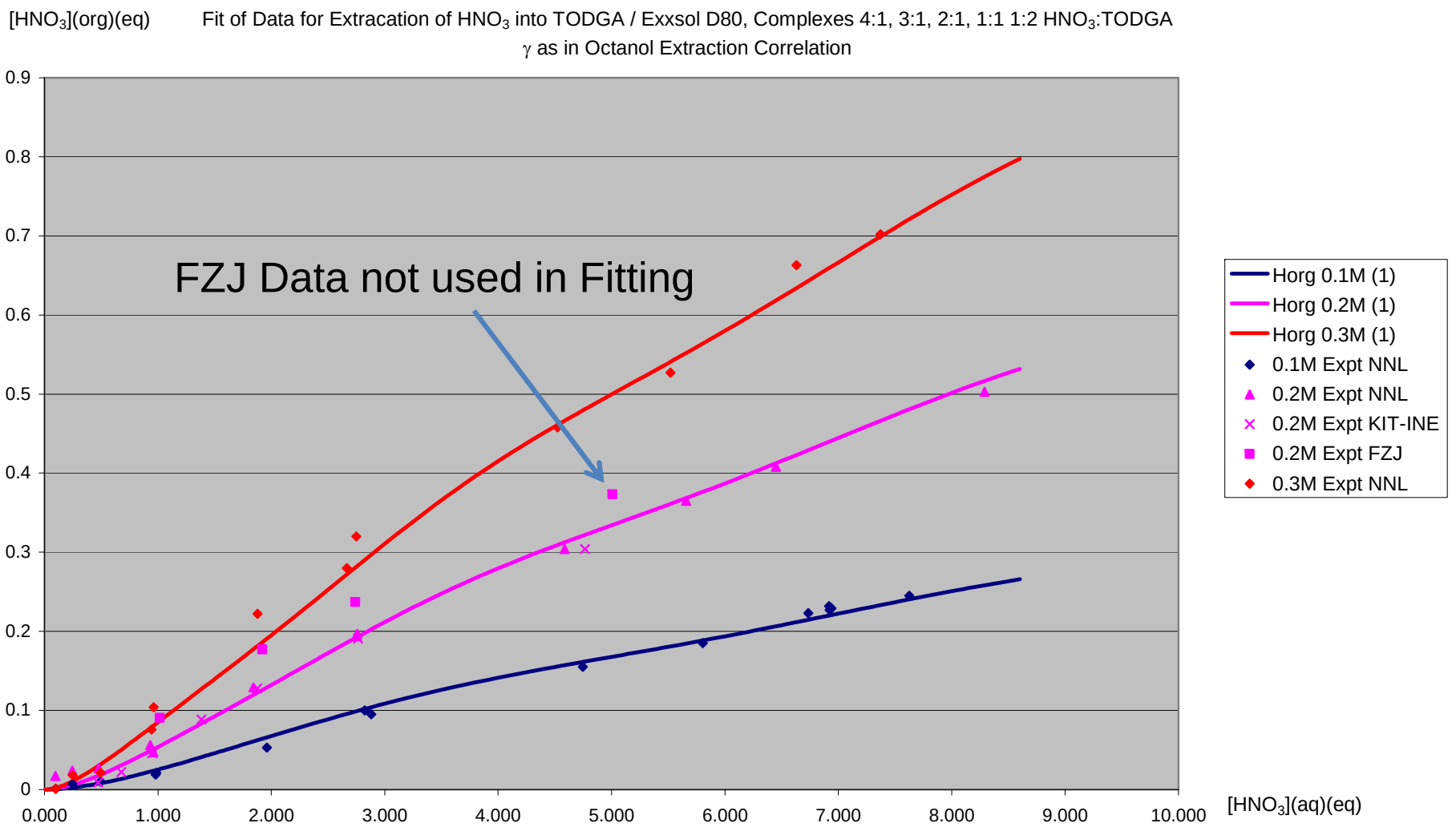
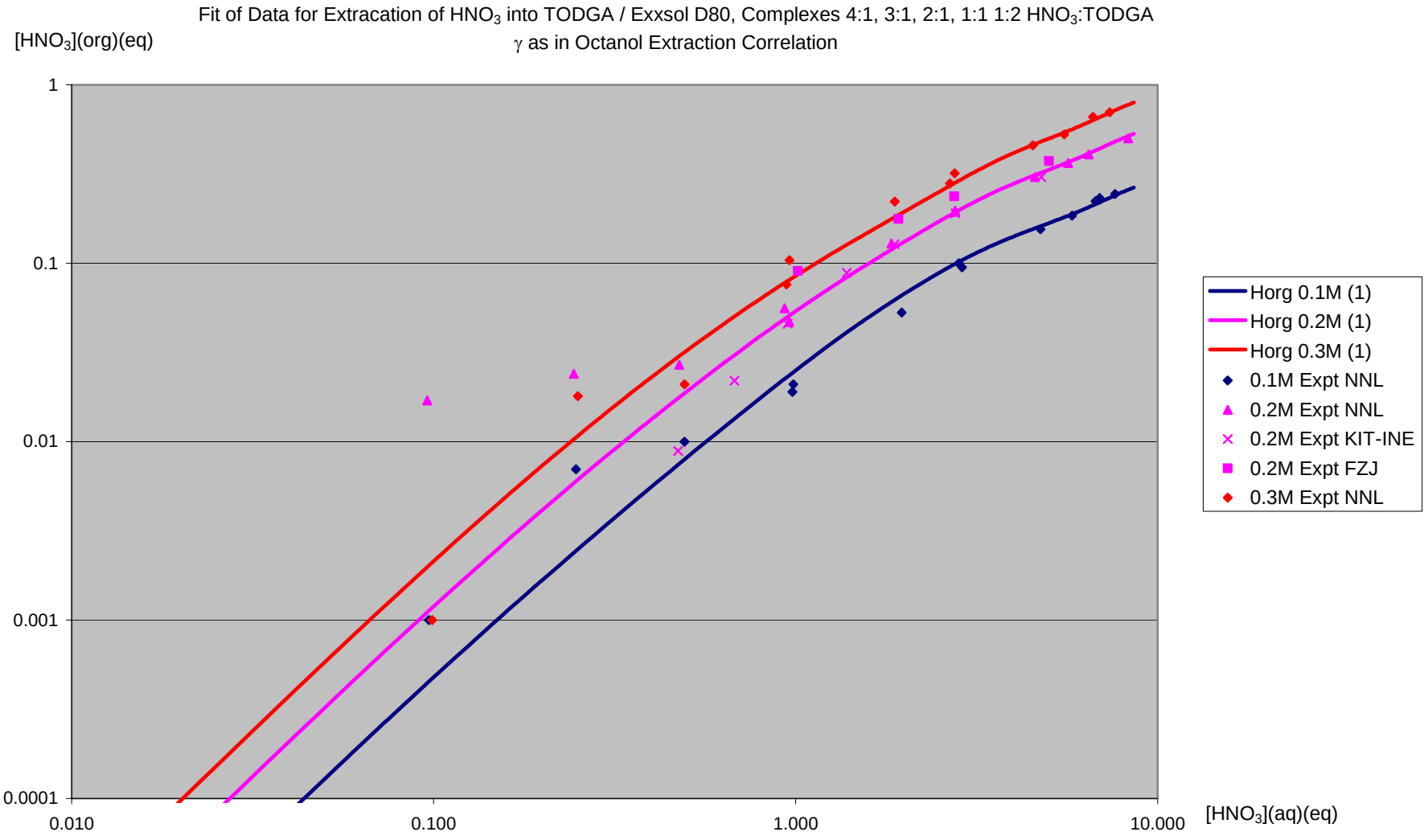
- Data from NNL, KIT-INE and FZJ. 0.05 – 0.4M TODGA, 0 – 8M HNO_3
- Low acidity data widely scattered
- Fitting assumed HNO_3.2TODGA, $nHNO_3$.TODGA (n = 1, 2, 3, 4)
- Fit set $3HNO_3$.TODGA at zero.
- Also tried refitting constants in expression for γ
  - Little benefit found over using same γ expression as for acid extraction into octanol correlation
  - Practically and theoretically attractive to use same γ throughout
- Also attempted including TODGA dimer
  - No benefit from this found

Acid Extraction into TODGA(2)



Acid Extraction into TODGA(3)



Low Acid Data Widely Scattered – Difficult to fit well, reduced weights used in fit

Mixed TODGA / Octanol Systems (1)

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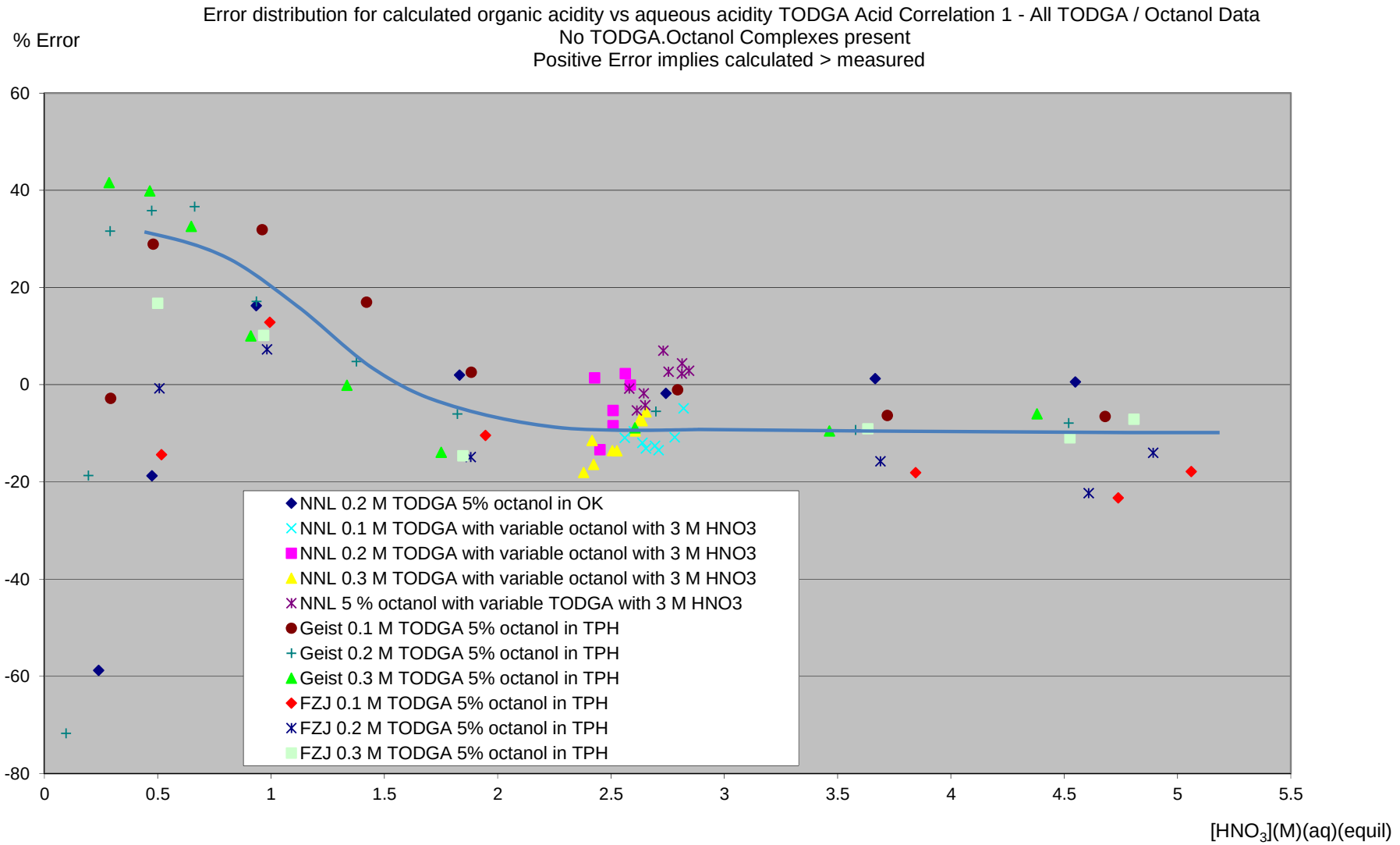
- Data from NNL, KIT-INE and FZJ:
  - 0.05 – 0.4M TODGA, 5 – 50v/v% Octanol, 0 – 5M HNO_3
  - Majority at 5% Octanol
- Significant scatter in low acidity data
- Initially assume that TODGA and Octanol do not interact and extract acid independently of each other. i.e. No synergism or antagonism.
- Combined model:
  - Overpredicts for 0.5 → 1.5M HNO_3
  - Underpredicts for [HNO_3] > 1.5M
  - Data for below 0.5M [HNO_3] too scattered to comment meaningfully

Mixed TODGA / Octanol Systems (2)



Superposition of Algorithms for extraction of Acid into TODGA and Octanol

Mixed TODGA / Octanol Systems (3)

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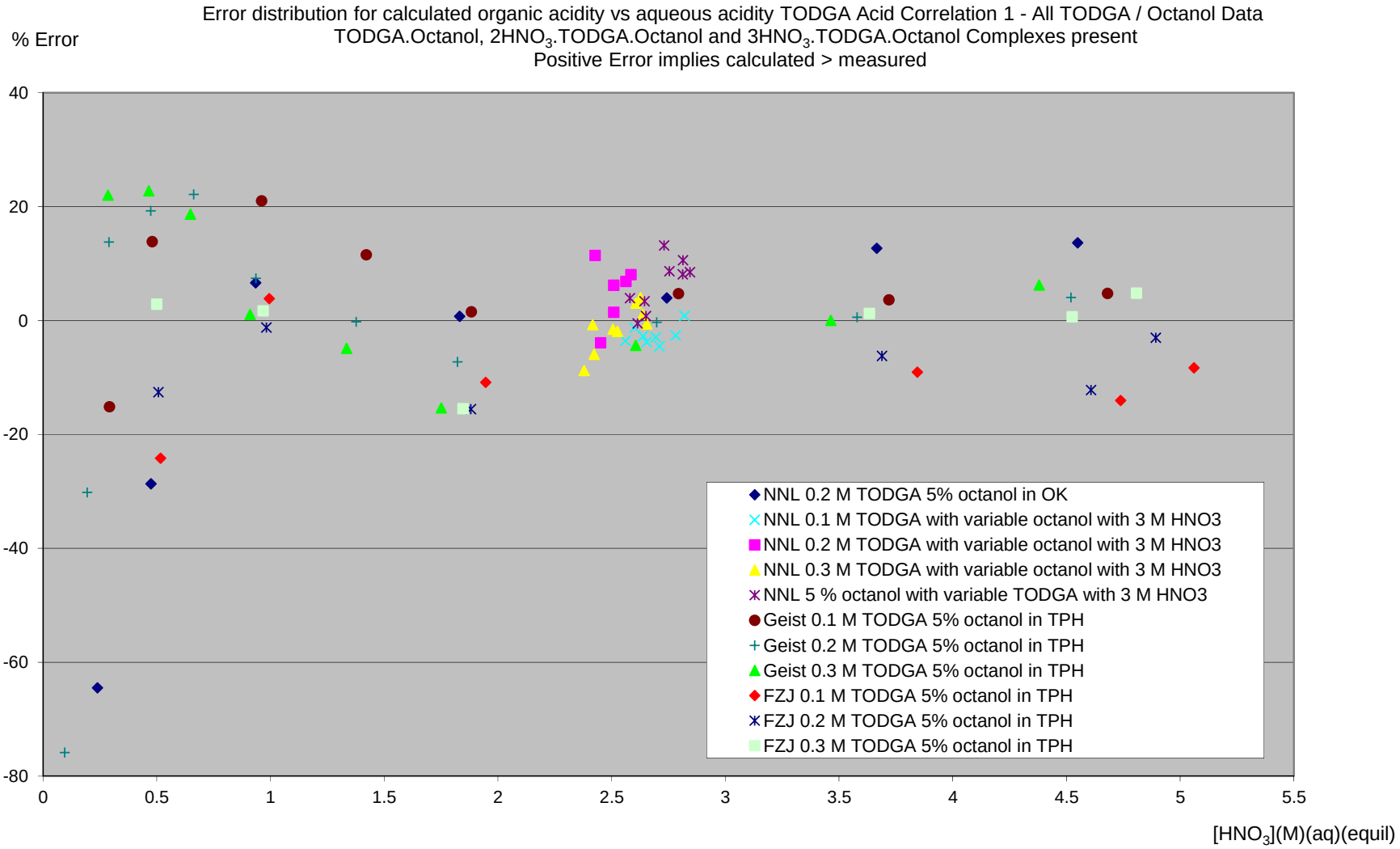
- Suggestion of some Synergistic (higher acidity) and Antagonistic (lower acidity) effects.
- New model developed and fitted with complexes of form

  $nHNO_3$.TODGA.Oct, n = 0, 1, 2, 3

  - n = 0 complex gives antagonism, others synergism
  - Fitting always resulted in elimination of the n = 1 complex
  - New model can largely remove biases for $[HNO_3] > 0.5M$

Mixed TODGA / Octanol Systems (4)



Residuals in Model with TODGA/Octanol Complexes

Mixed TODGA / Octanol Systems – Solvent Phase Acid Speciation

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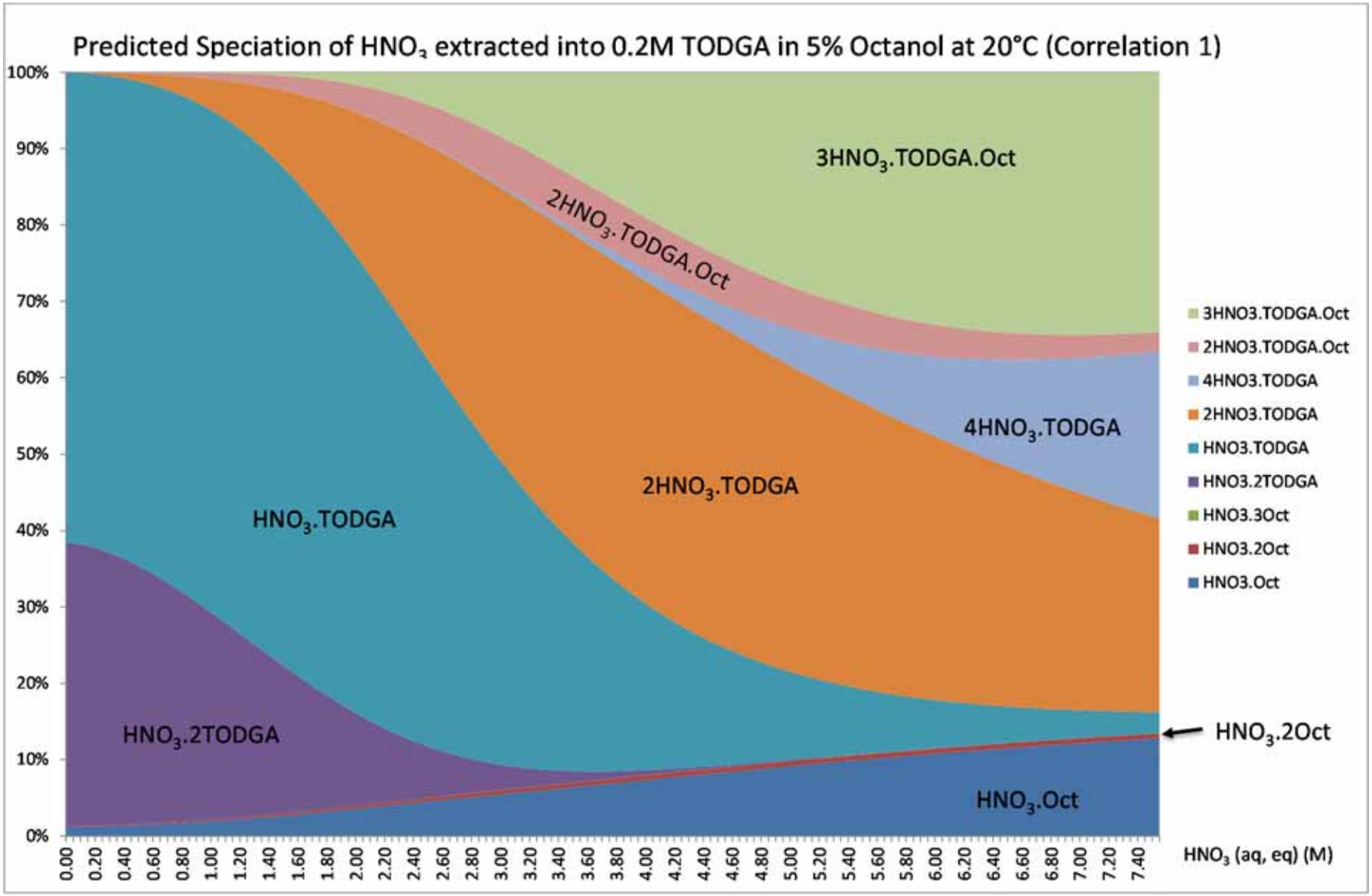
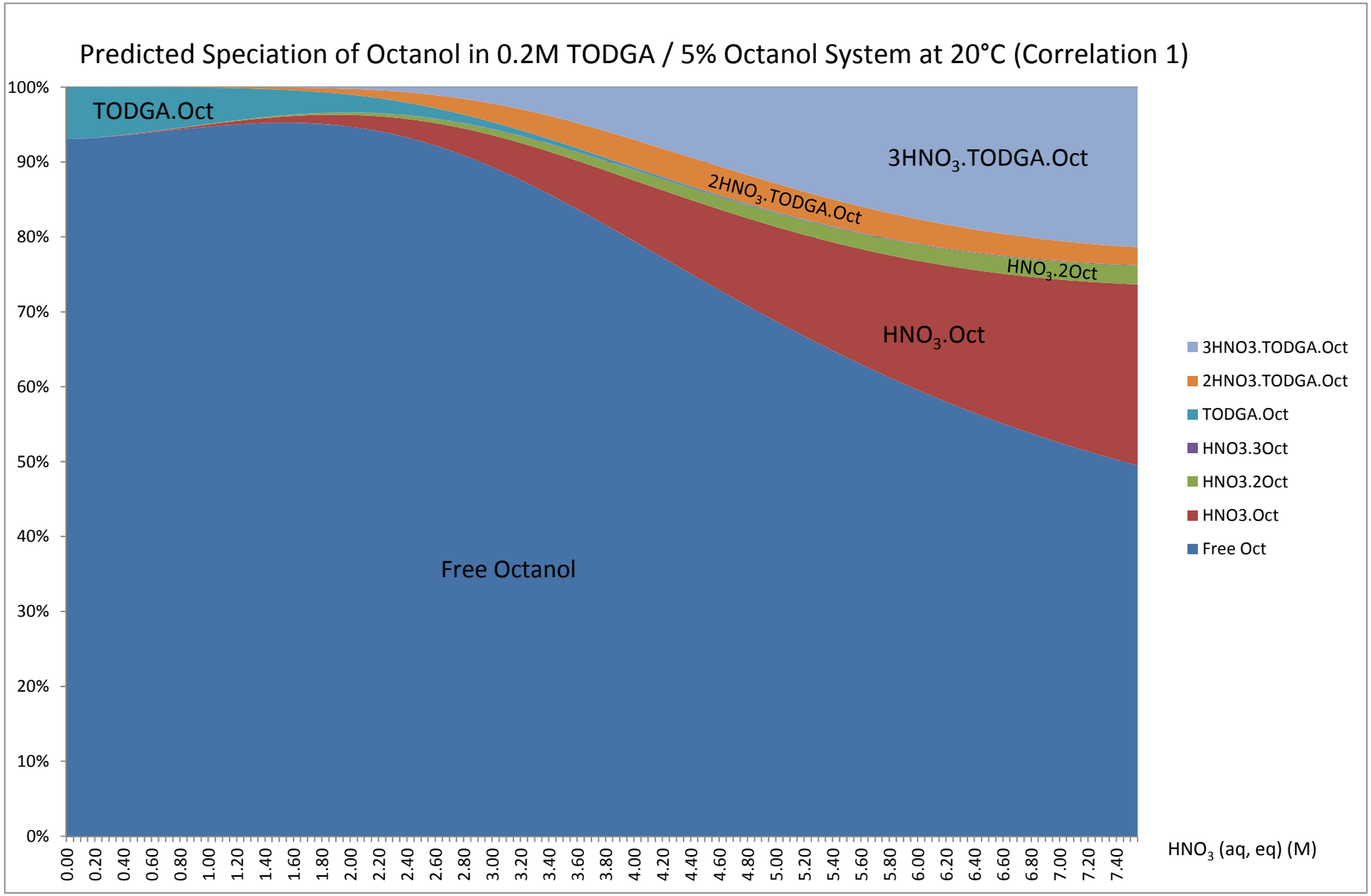


Mixed TODGA / Octanol Systems – Octanol Speciation



Mixed TODGA / Octanol Systems – TODGA Speciation

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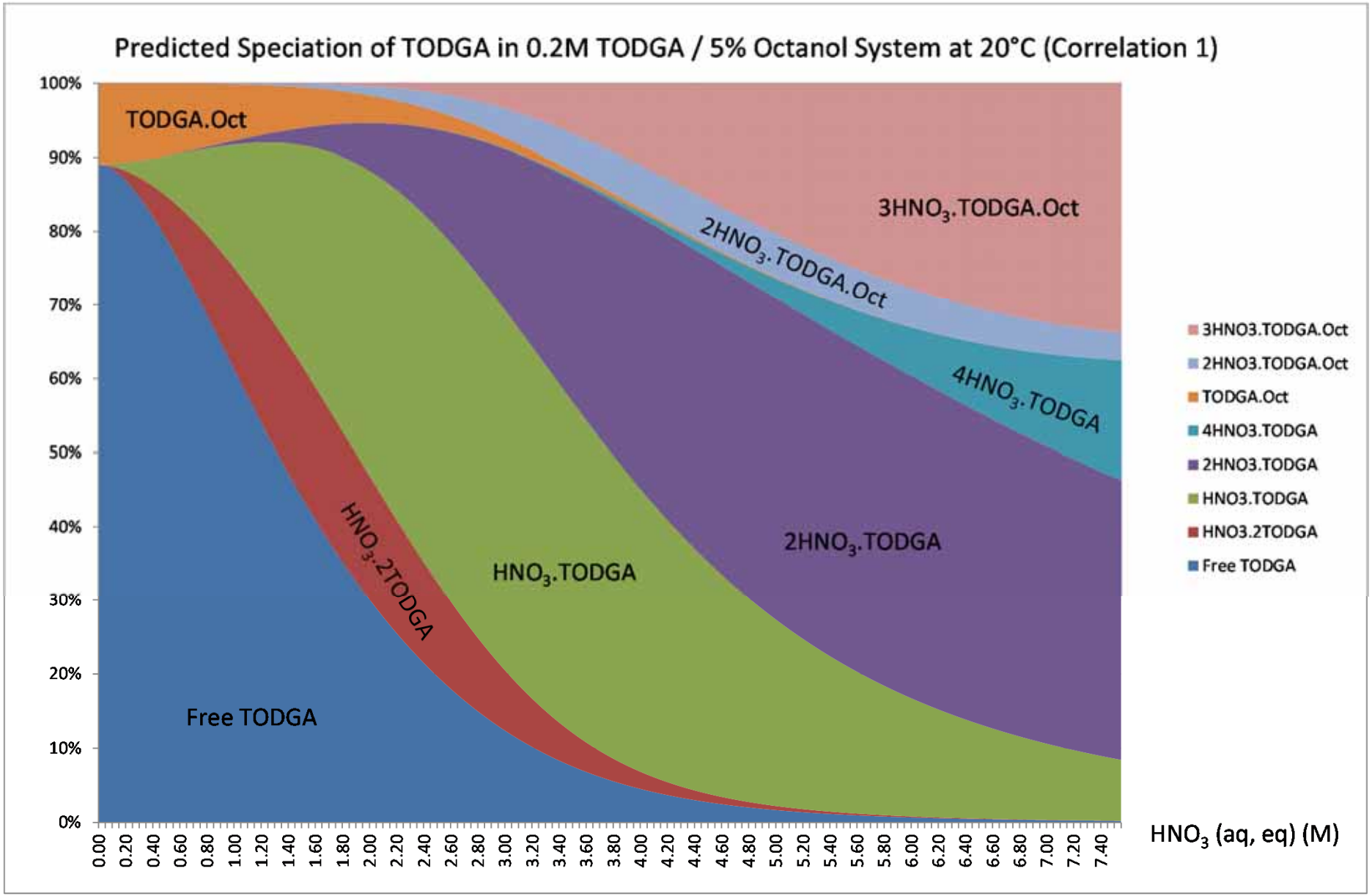

Outstanding Issues

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- Model is based on data in range 20 – 25°C
- Ideally have data for a wider range of temperatures so temperature dependence can be included.

- The model is based on data with acid as the only extracting species.
- Model will be required to work with metal loaded systems
  - Need to consider systems in which $[H^+] \neq [NO_3^-]$ implying need to distinguish $\gamma_{H^+}, \gamma_{NO_3^-}$
  - Some subtle issues related to dilation arise in systems with multiple extracting species

Summary / Conclusions

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- Acid Extraction into Octanol / Diluent can be modelled to a high degree of accuracy assuming HNO_3.nOct, n = 1, 2, 3
- Acid Extraction into TODGA / Diluent can be modelled to good accuracy assuming HNO_3.2TODGA and nHNO_3.TODGA, n = 1, 2, 4.
- Combining the two models suggests some synergistic and antagonistic effects
- These can be incorporated in model by inclusion of nHNO_3.TODGA.Oct complexes, n = 0, 2, 3
- Wide scatter of data at low acidity makes validation in this region difficult