Spectroscopic measurement of associating and solvating binary mixtures for the determination of monomer fraction data towards thermodynamic model improvement

A. E. Burgess, A. J. Burger, and J.T. Cripwell*

Department of Chemical Engineering, Stellenbosch University, Banghoek Road, Stellenbosch 7600, South Africa. Email: *cripwell@sun.ac.za; Tel: +27 21 808 4485

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Introduction

- In the petrochemical, pharmaceutical, and bioprocessing sectors, hydrogen bonding phenomena remains an elusive interaction
- The monomer fraction is considered a direct measure of the extent of hydrogen bonding in associating and solvating systems
- Equations of state (EoS) based on statistical associating fluid theory (SAFT) can predict the fraction of monomers in such mixtures
- Paramount to monomer fraction quantification is the use of spectroscopic data

Aim and Objectives

- Propose multivariate curve resolution with alternating least squares (MCR-ALS) as an alternative method to determine monomer fractions from spectroscopic data towards thermodynamic model improvement by 1) measuring spectroscopic data in associating and solvating systems, 2) comparing to existing literature methods, and 3) assessing SAFT model predictions

## Experimental and spectral analysis
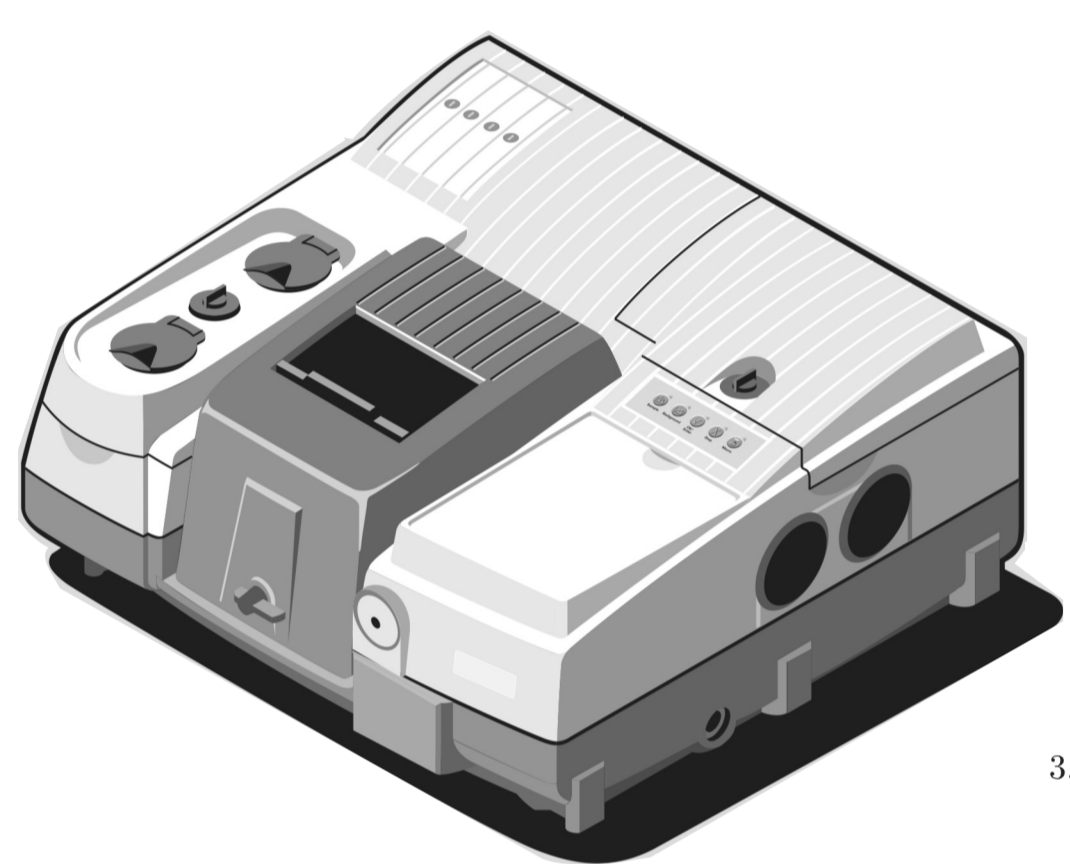
Analytical measurement

- Spectroscopic data generated using a Nicolet 6700 FTIR spectrometer in ATR mode
- Binary mixtures of ethanol in n-hexane, acetone, and C_4 esters are considered
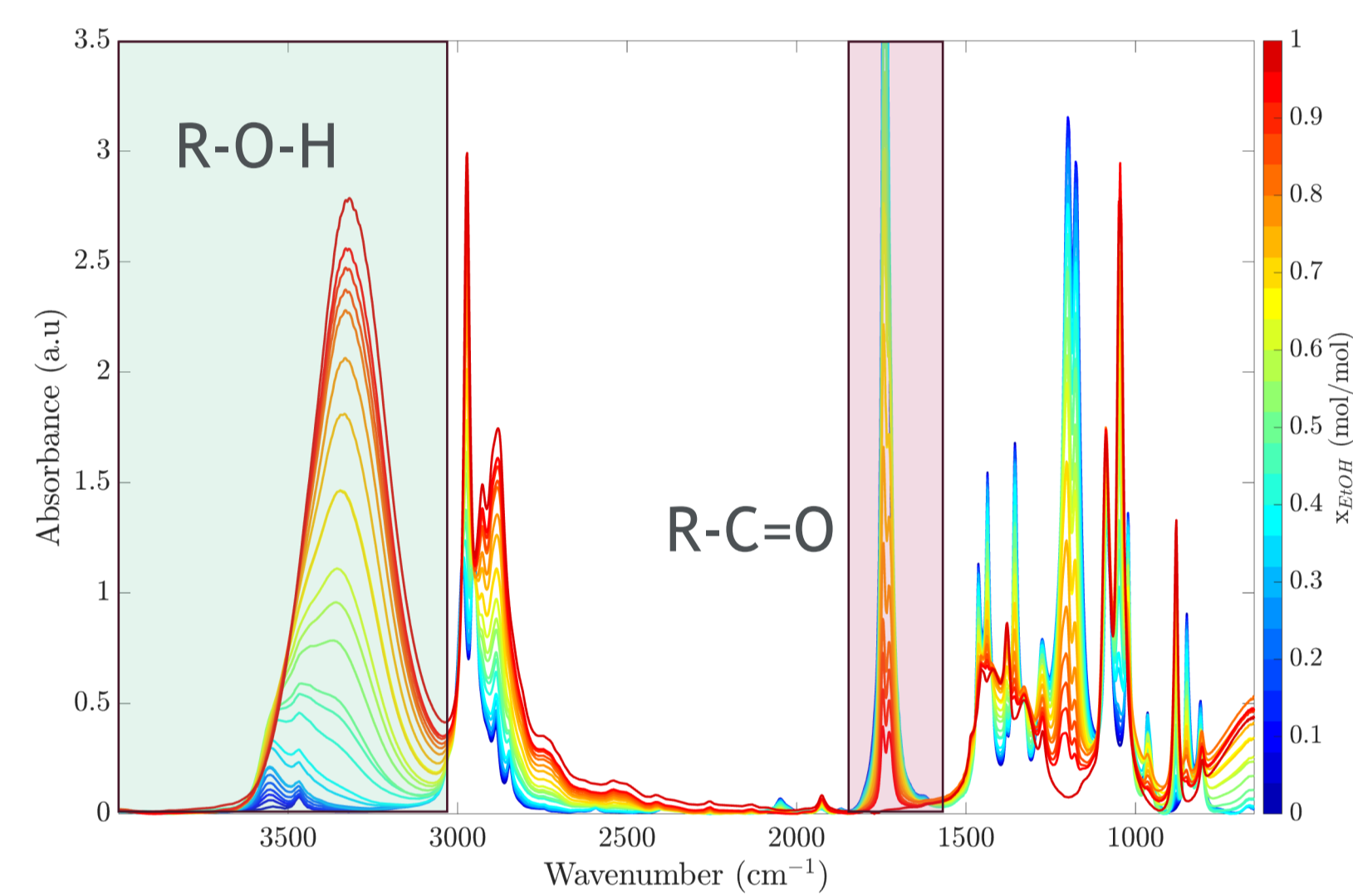
Pre-processing

- Spectral windowing for ethanol and acetone/esters
- Baseline corrections performed by peak-to-peak method
- Spectral subtraction removes solvent features
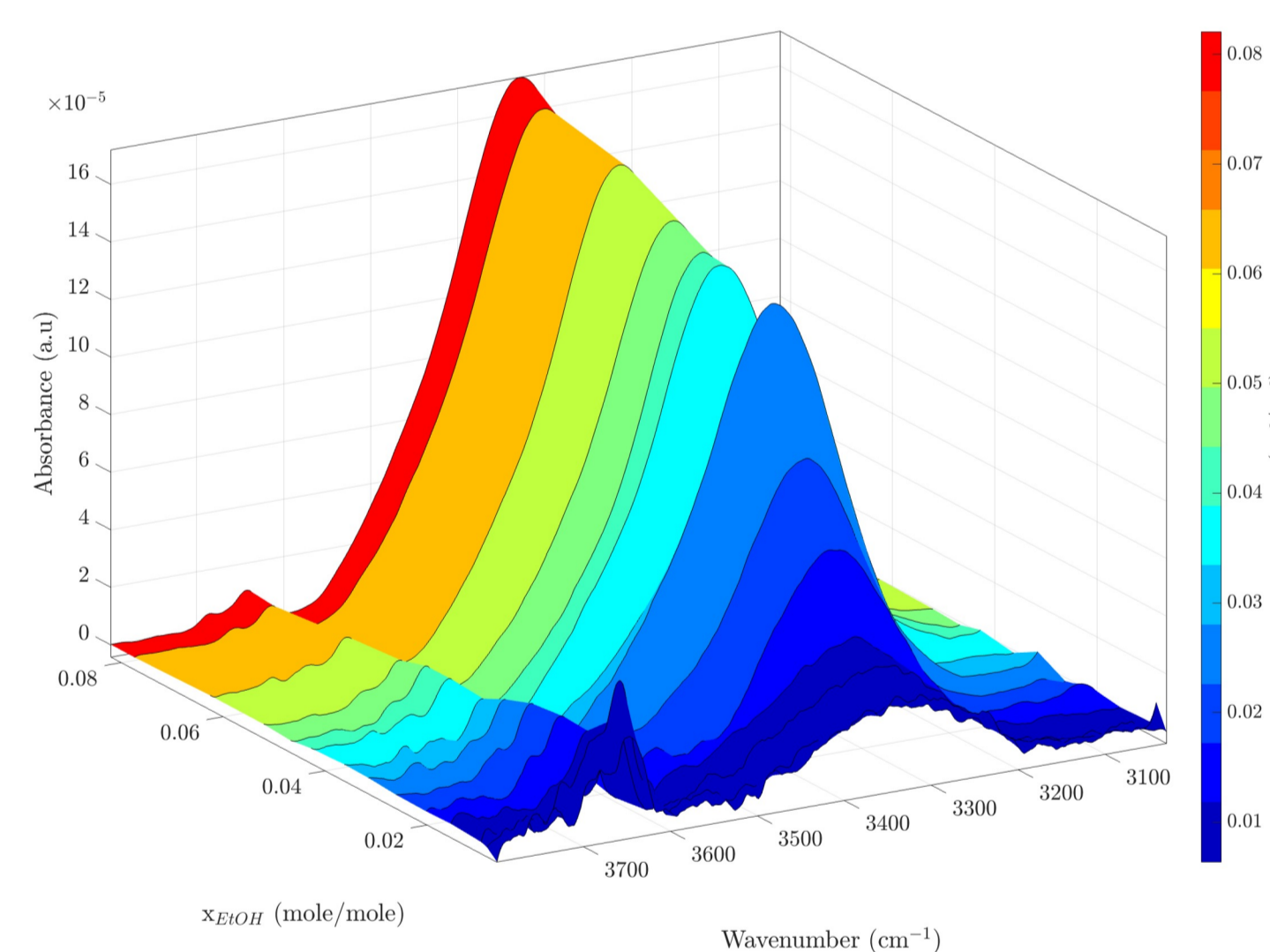
Further pre-processing

- Smoothing filters (Savitzky-Golay)
- Concentration normalisation to render molar spectra
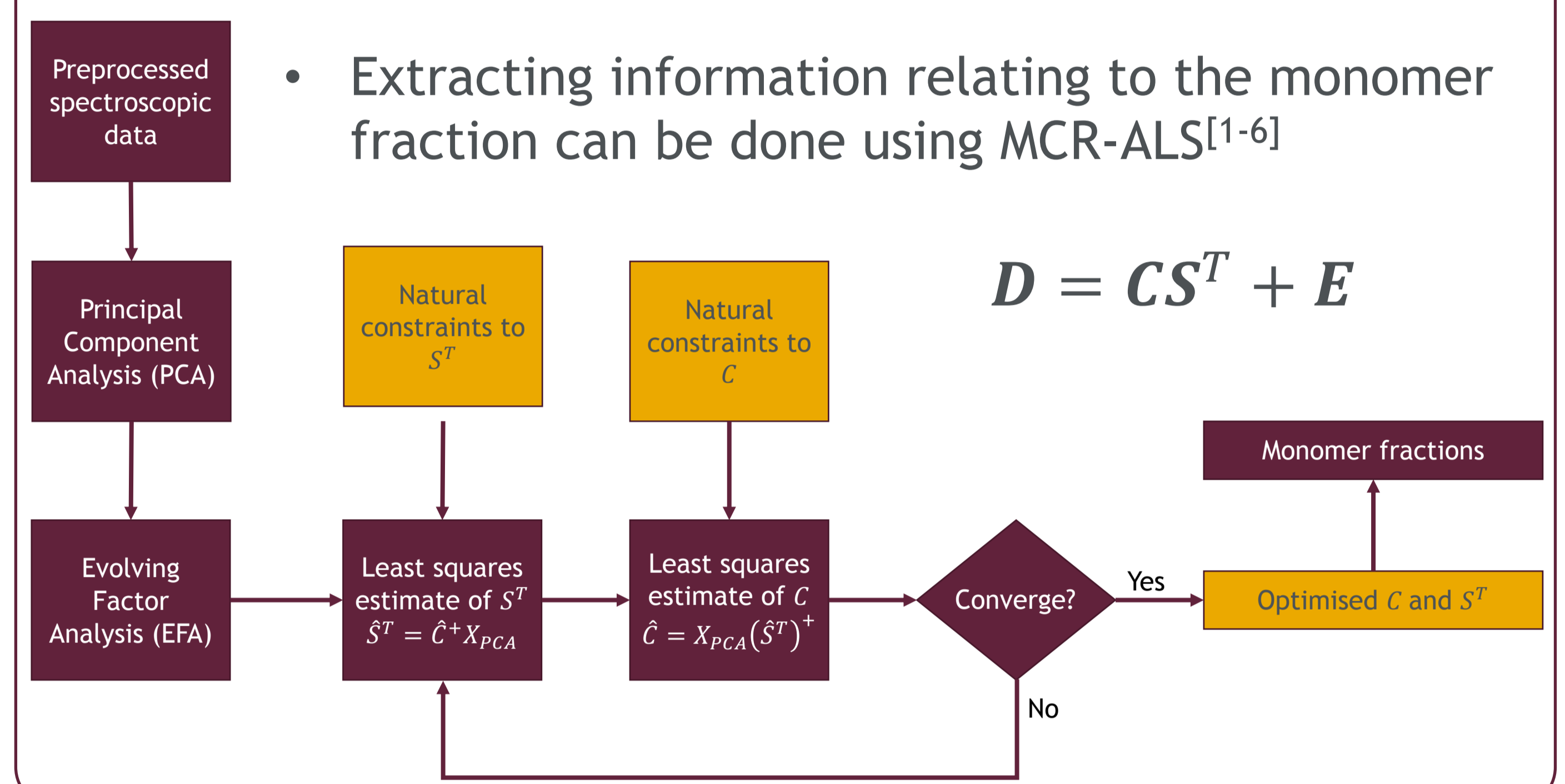- Elucidates small absorbances of dilute spectra and scales large absorbances for concentrated spectra

Data analysis

- Greek letters [11] different bonds, monomer = α bond
- Non-negativity in concentration and spectral profiles
- Spectral normalisation and selectivity enforced
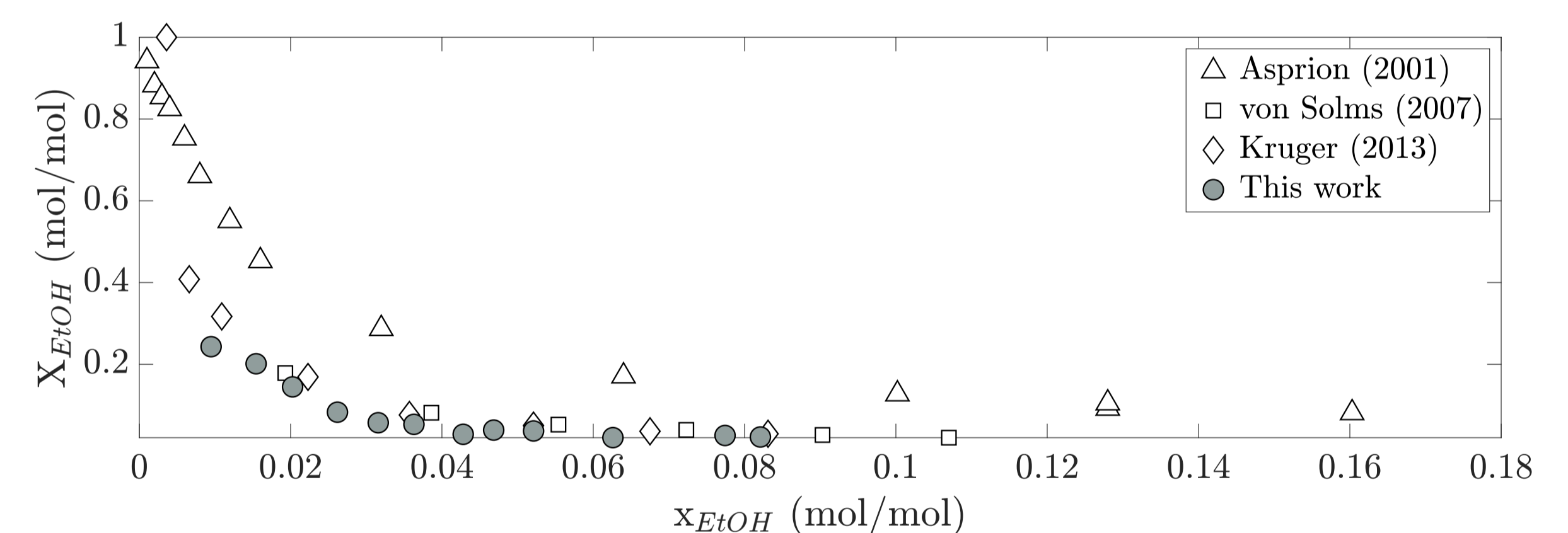- Lack of fit (LOF) of 1.99% and variance captured (VAR) of 99.96%
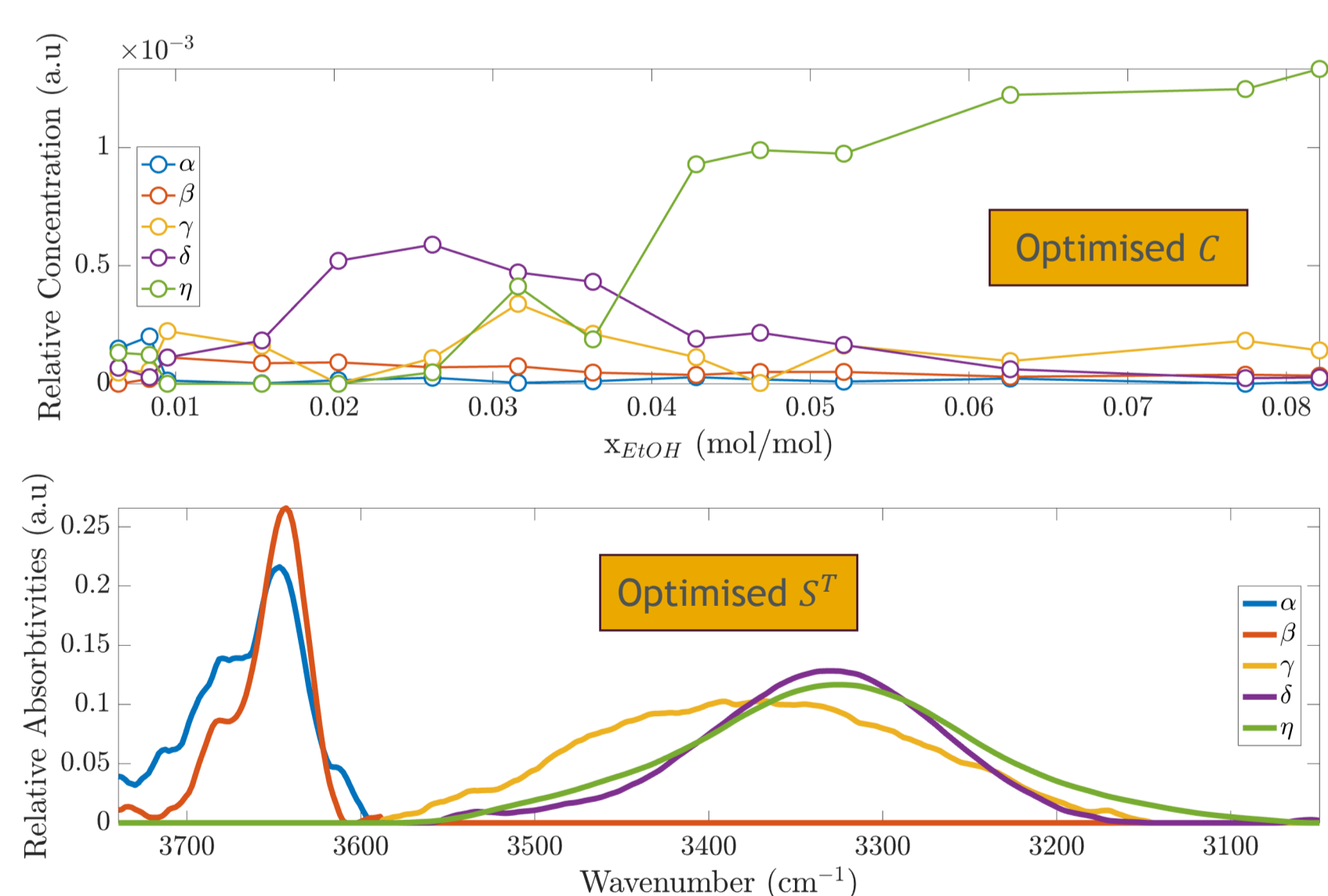
Theory: SAFT and MCR-ALS

- Fraction of molecules not H-bonded = monomer fraction (X_i) related to SAFT free site fraction (X^k)

$$X_i = \prod_k X^k$$

- Single calibration[7] and multiple calibration[8] methods yield different monomer fraction results

- Extracting information relating to the monomer fraction can be done using MCR-ALS[1-6]

$$D = CS^T + E$$

Preprocessed spectroscopic data → Principal Component Analysis (PCA) → Evolving Factor Analysis (EFA) → Least squares estimate of S^T $\hat{S}^T = \hat{C}^+ X_{PCA}$ → Natural constraints to S^T → Least squares estimate of C $\hat{C} = X_{PCA}(\hat{S}^T)^+$ → Natural constraints to C → Converge? → Yes → Optimised C and S^T → Monomer fractions / No → loop

Results

Associating with non-associating (ethanol in n-hexane)

- MCR-ALS determined monomer fraction shows excellent agreement with trends of single calibration literature set.

Solvating with associating (Acetone with ethanol)
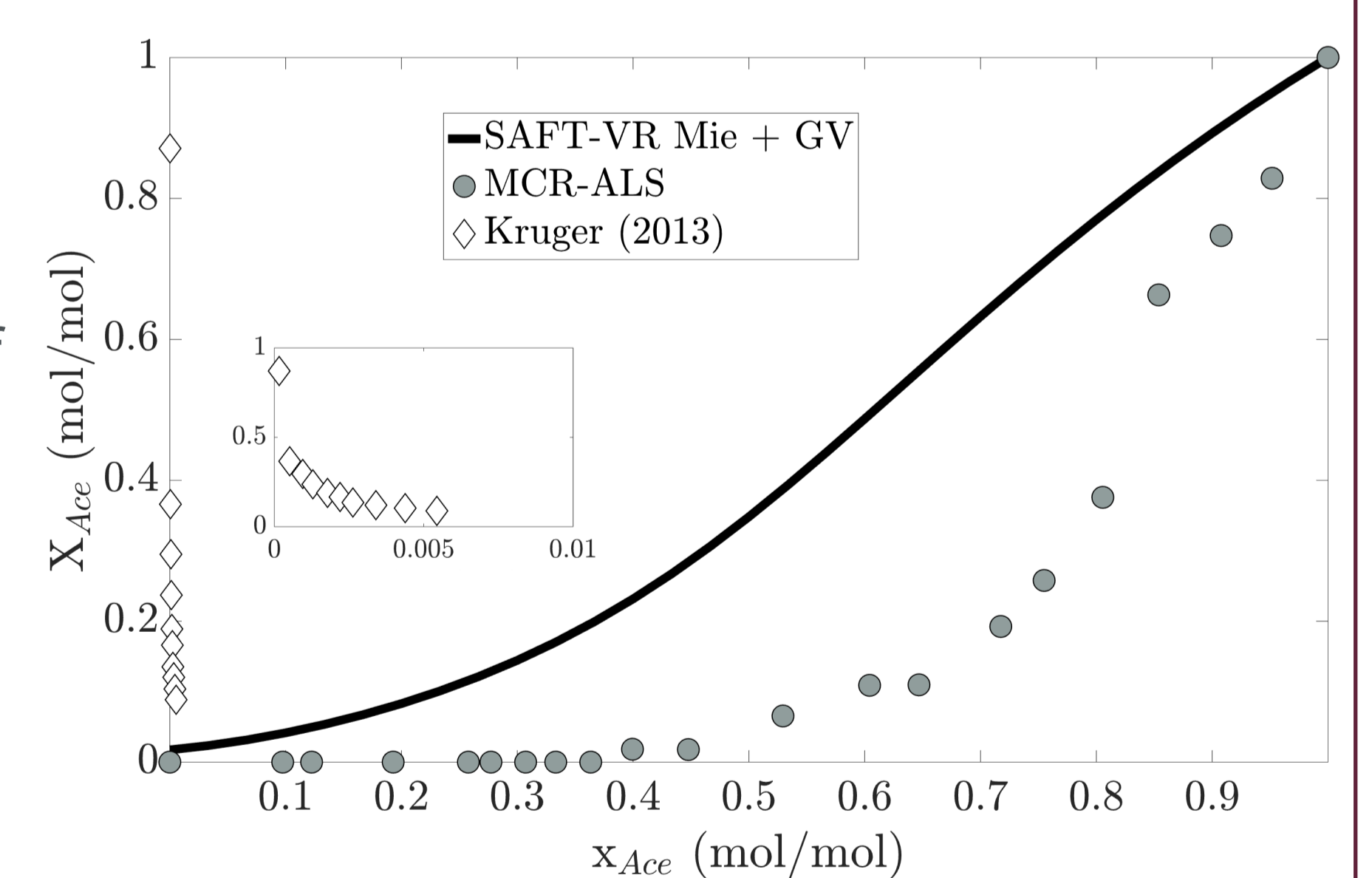
- Monomer fraction of acetone (cross association) – "N scheme"[10]
- SAFT-VR Mie + GV qualitatively agrees with monomer fraction (MCR-ALS)
- Scope for model improvement -> paramertise SAFT-VR Mie + GV with monomer fraction data -> assess phase equilibria

Conclusions and future work

- Monomer fractions by MCR-ALS method for ethanol in n-hexane are comparable to single point calibration not multiple calibration
- SAFT-VR Mie + GV acetone monomer fraction predictions qualitatively agree with MCR-ALS not multiple calibration[9]
- Extensions to other solvating systems of ethanol in esters of similar chain length will be considered
- New association parameters will be determined using measured monomer fraction data and will be used to asses phase equilibria

References: [1] Elsevier, Oxford, 2009, vol. 2, pp. 249-259. [2] Technometrics, 1971, 13,617. [3] J. Chemom., 1990, 4,1. [4] Anal. Chim. Acta, 2003, 500, 195. [5] Rev. Anal. Chem., 2006, 36, 163. [6] Anal. Chim. Acta, 2013, 765, 28-36. [7] Fluid Phase Equilibria 261 (2007) 272-280. [8] Fluid Phase Equilibria 186 (2001) 1-25. [9] Fluid Phase Equilibria 400 (2015) 87-94. Fluid Phase Equilibria 483 (2019) 1-13. [11] Journal of Physical Chemistry A 124 (2020) 3077-3089

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