# Implementation of Wertheim Theory for the Gamma-Phi Approach of Phase Equilibria Modeling

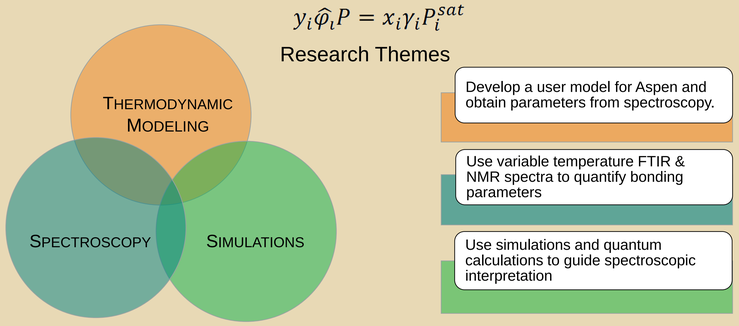
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## 1. Introduction

- Industrial use of polar/bio-derived components requires models that realistically capture the effects of associations, such as hydrogen bonding.
- Equations of state such as SAFT, CPA, ESD provide a fundamental basis for modeling with association with Wertheim Theory[1-2], but require many parameters, and substantial data for parameter fitting.
- The novelty of this work lies in the *simultaneous* use of *thermodynamic modelling, spectroscopy*, and *quantum and molecular dynamics simulations*. This work incorporates Wertheim theory into the Gamma-Phi approach

$$y_i \hat{\varphi}_i P = x_i \gamma_i P_i^{sat}$$

Research Themes




Develop a user model for Aspen and obtain parameters from spectroscopy.

Use variable temperature FTIR & NMR spectra to quantify bonding parameters

Use simulations and quantum calculations to guide spectroscopic interpretation

## 2. NRTL-PA (Plus Association) Model

$$\ln \gamma_k = \ln \gamma_k^{res} + \ln \gamma_k^{comb} + \ln \gamma_k^{assoc}$$

- Traditional $\ln \gamma^{res}$ model. NRTL[3] is used here
- $\ln \gamma^{comb}$ is modified Flory (2/3 power on molar volume)
- $\ln \gamma^{assoc}$ uses Wertheim Theory

$$\ln \hat{\varphi}_k = (2(\sum y_i B_{ik}) - B)P/(RT);$$

$$B = B^{free} + B^{bound} + B^{polar} + B^{assoc}$$

- $\hat{\varphi}$ from Hayden-O'Connell[4], though Wertheim adaptation is in development

## 3. Wertheim Theory

- $X_i^B = n_{free}^B / n_{total}^B$ is the fraction of acceptor (A) or donor (D) sites *free*.

Site balance

$$X^{B_i} = \left(1 + \sum_{\substack{mating \\ sites\ E_j}} x_{E_j\ host} N_{E_j} X^{E_j} \rho \Delta^{B_i E_j}\right)^{-1}$$

Example sites on alcohol (2B model)




Association constant

$$\Delta^{B_i E_j} = g(\rho) K^{B_i E_j} \left[\exp\left(\frac{\varepsilon^{B_i E_j}}{RT}\right) - 1\right]$$

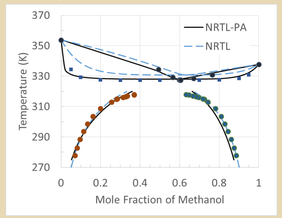
$K^{B_i E_j}$ and $\varepsilon^{B_i E_j}$ parameters can be fitted to match spectroscopic results

$g(\rho)$ uses CPA or SAFT model (CPA form applied here but matching SAFT values of $\Delta^{B_i E_j}$ at $\rho$ and *T)*

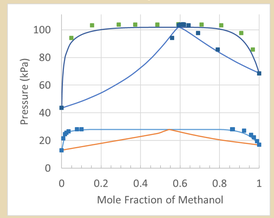
$$\ln \gamma_k{}^{assoc} = \sum_{\substack{sites\ B_i \\ on\ k}} N_{B_i} \left[\ln\left(\frac{X^{B_i}}{X^{B_i,0}}\right) - \frac{1}{2}(1 - X^{B_i,0})\right] + \frac{1}{2}\frac{\rho}{\rho_k} \sum_{\substack{all \\ sites\ B_i}} x_{B_i\ host} N_{B_i} (1 - X^{B_i})$$

## 4. Representative Model Capabilities

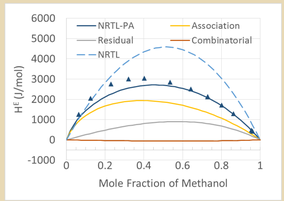
Implemented as an Aspen Plus user model. Common bonding schemes are utilized, e.g. 1A, 2B, 3B, 4C. Bonding scheme and parameters are user-configurable. All methanol + cyclohexane plots use the same parameter set.
Association parameters as shown in Panel 6 were not adjusted.



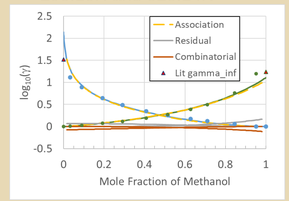

Methanol + cyclohexane at 101.3 kPa[5,6]



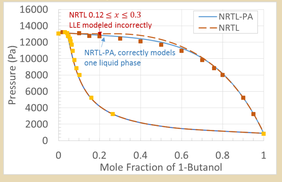

Methanol + cyclohexane at 298.15K and 328.14K[7,8]



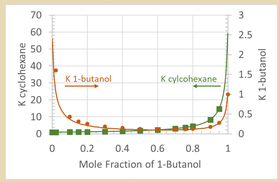

Methanol + cyclohexane at 416.3K[9]




Methanol + cyclohexane at 328.14 K[7,10]




1-Butanol + cyclohexane at 298.15K[11]



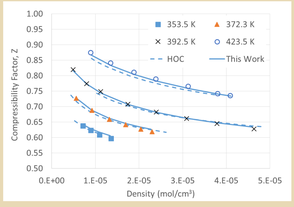

1-Butanol + cyclohexane at 298.15K[11]

## 5. Gas Phase Modeling Progress

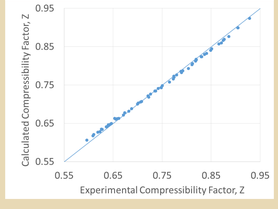
Acetic acid modeling

$$Z = 1 + (B^{free} + B^{bound} + B^{polar})\rho + 2\rho g \Delta^{CC} (X^C)^2$$

1A model, Jog/Chapman[12] method for $B^{polar}$




Acetic acid Z at four temperatures[13]

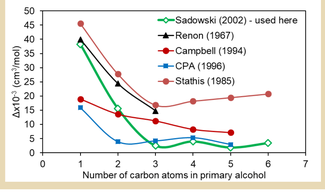



Z parity plot at nine temperatures[13]

## 6. Association Constant Uncertainty

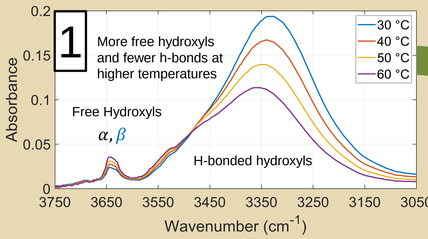
Association constants in literature vary significantly. Values at 298.15 K shown here[14-18].

Spectroscopic methods also have uncertainty. Can spectroscopic methods be improved?



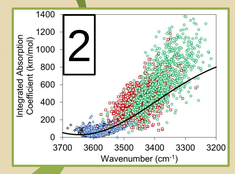

## 7. Quantum-Guided Spectroscopy

Using Beer's law to determine fraction of unbonded sites.
$A = (\epsilon l)c$. $A$ – absorbance. $\epsilon$ – extinction coefficient, $l$ – path length, $c$ - concentration.



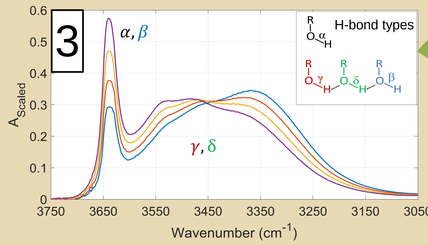

Spectra of 20 mol% 1-butanol in cyclohexane at 30–60 °C

1. Spectra after subtracting solvent and background
2. Extinction coefficient based on quantum calculations. Clusters were generated from MD and a smooth curve was adjusted to fit the parity in plot 4.



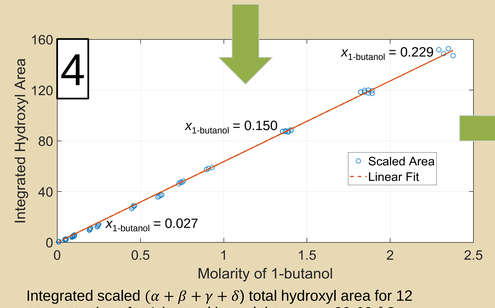

- Molecular simulations
  - Amber 94 Force Field
  - H-bond types identified
- Quantum Calculations
  - Gaussian 09 code
  - Hydroxyl vibrations at B3LYP/6-31G* level

Predicted (points) and adjusted (line) extinction coefficients as a function of wavenumber

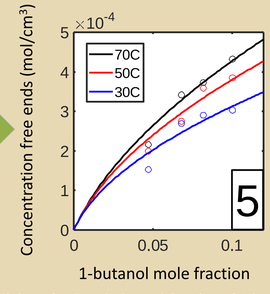



Scaled spectra of 20 mol% 1-butanol in cyclohexane at 30–60 °C

3. Scaled absorbance after considering path length and extinction coefficient
$A_{scaled} = A/(\epsilon l)$
4. Integrated areas validate Beer's law across *entire* scaled OH band.
5. Fitting of Wertheim association constant to $\alpha, \beta$ area fraction.




Integrated scaled ($\alpha + \beta + \gamma + \delta$) total hydroxyl area for 12 concentrations for 1-butanol in cyclohexane at 30-60 °C




Fitting of unbonded $\alpha + \beta$ fraction of 1-butanol sites with Wertheim model

## 8. Future Work

- Public release of Aspen user model for NRTL-PA late summer
- Extend thermodynamic model to complex systems of industrial interest including mixtures with water
- Curve fit spectra for various binary mixtures and further refine spectral interpretation to determine association Δ parameters
- Extend vapor phase model beyond carboxylic acids.

## Acknowledgement, References

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- Poster copy and references available at https://www.egr.msu.edu/reactivedist/news/ppeppd-19

Poster copy, References