Study of thermoresponsive porphyrins and their supramolecular complexes

Diploma thesis

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ČSSVK7, 2016

Porphine

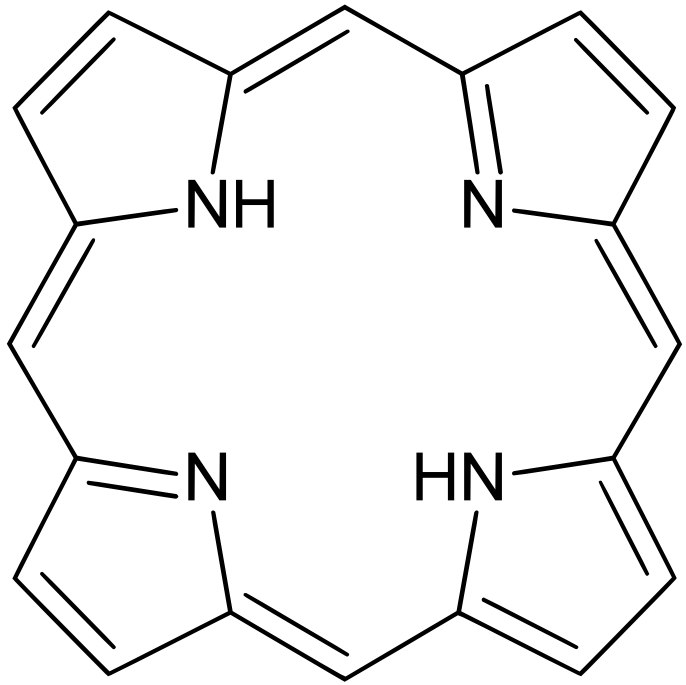
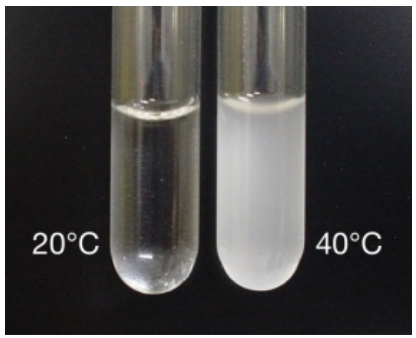


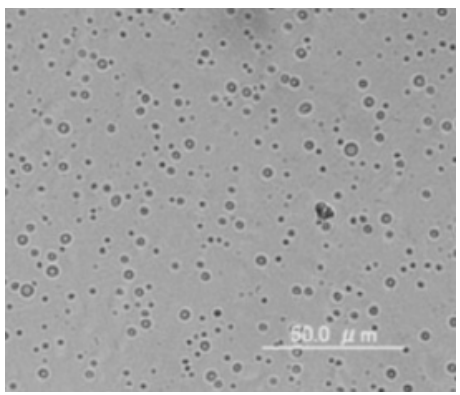
Figure: *Porphine*, the pecursor to all porphyrins. *Porphyrins* are the chemical modifications of porphine.

Phase separation

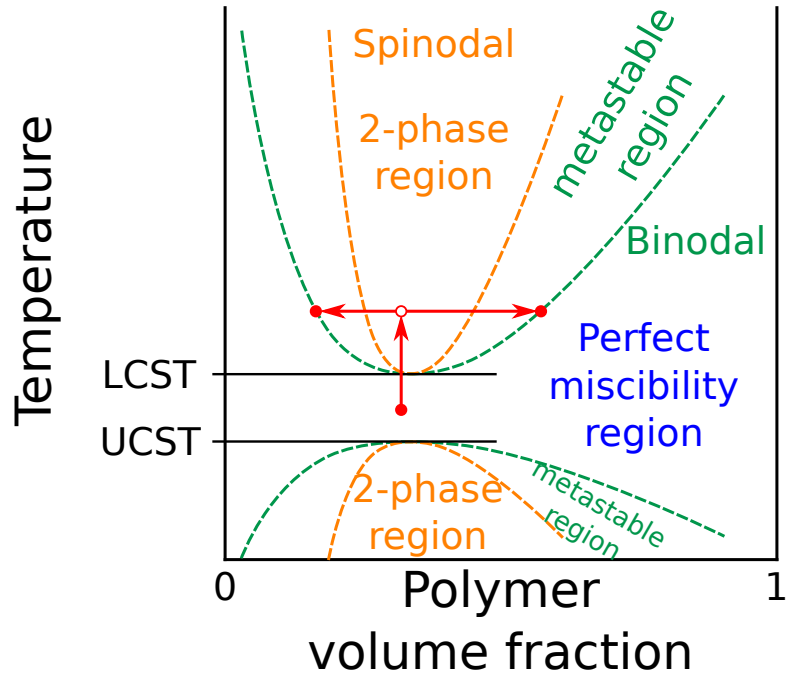
Polyphosphoester
H_2O solution



40°C



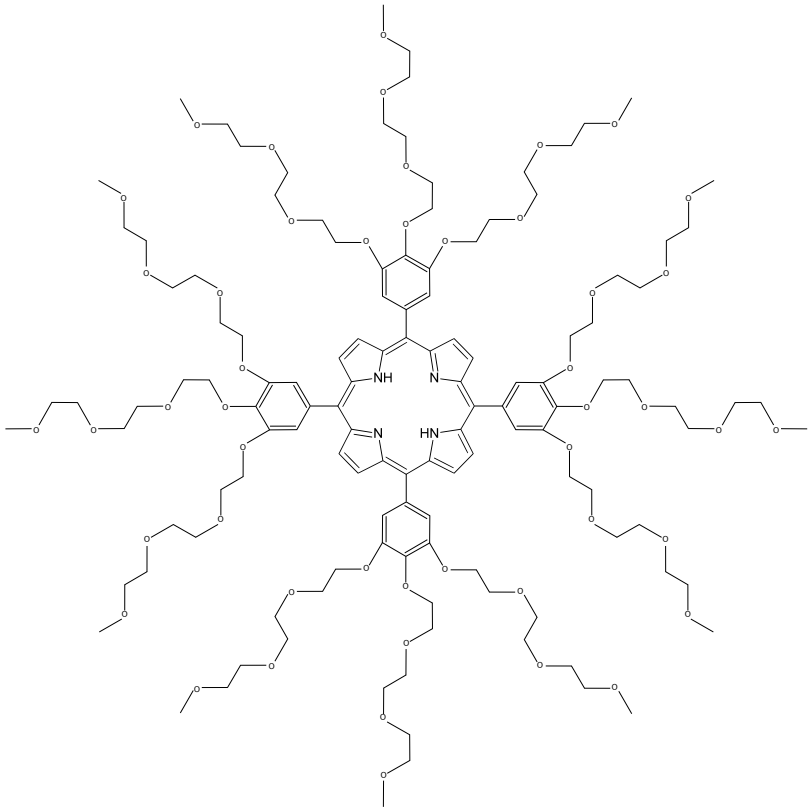
Amphiphilic polymer solution
phase diagram (schematical, example)



Photos: Yasuhiko Iwasaki (2011). Modern Synthesis and Thermoresponsivity of Polyphosphoesters, Biomedical Engineering - Frontiers and Challenges, Prof. Reza Fazel (Ed.), ISBN: 978-953-307-309-5, InTech, DOI: 10.5772/18538. Available here

Compound of interest

3,4,5-TEG-TPP



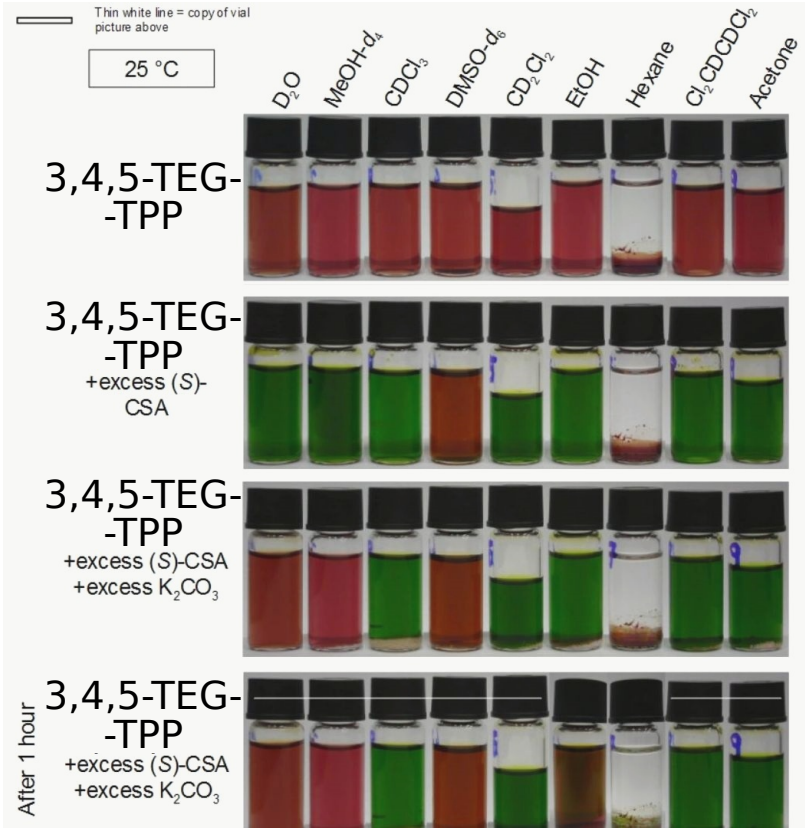


Figure: **3,4,5-TEG-TPP**, a highly symmetric porphyrin with amphiphilic side chains (tetraethylene glycol) – *which make is water-soluble* – and its color in various solvents. The compound was prepared at National Institute of Materials Science in Tsukuba, Japan.

Motivation

- possible applications:
  - solvent purification (phase separation + decantation)
  - impurity and enantiomeric excess detection by NMR
  - functional pigment
  - nanotube solubilization
- extension of Flory-Huggins theory
- we study one of the few *non-polymeric* compounds showing this behavior
- the compound:
  - is similar to other, natural porphyrins (heme, chlorophyll, vitamin B_{12})
  - has *significantly higher water solubility*
  - also undergoes:
    - stacking
    - positive ion binding (metals, H^+)
    - visible light absorption dependent on the chemical environment of the conjugated electron system (solvent, bound ions)

Each of the properties affects the others. How? How much?

Goals

- quantify the dependence of phase separation of **3,4,5-TEG-TPP** on temperature and concentration
- apply the Flory-Huggins theory of polymer solutions to find the binodal and spinodal of the phase separation (i.e. phase diagram)
- examine how acidity (i.e. availability of H^+ ligands) affects the supramolecular interactions of **3,4,5-TEG-TPP**

Methodology

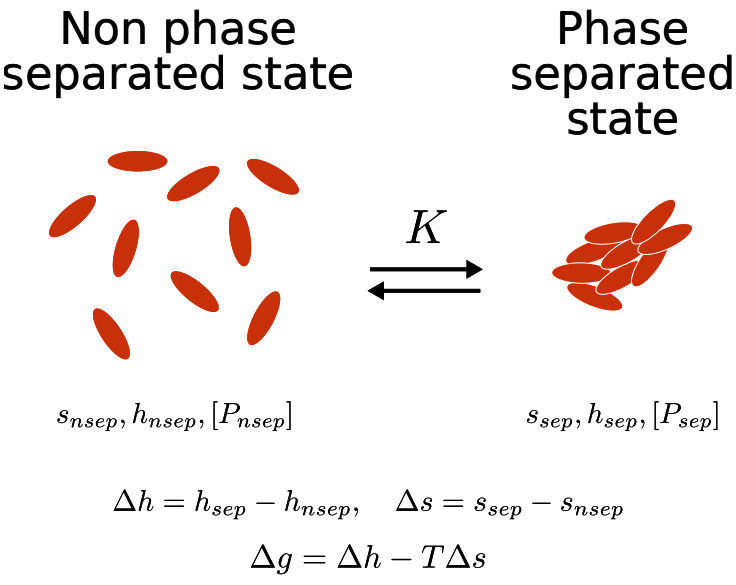
Nuclear Magnetic Resonance

- highly local method (spatial scale $\approx$ chemical bond lengths)
  $\rightarrow$ information characterizes the vicinity of nuclei accurately, morphology of the sample is largely irrelevant
- "polls" every active nucleus and returns *the sum* of responses
  $\rightarrow$ signal is proportional to the number of nuclei with given chemical environment
- allows us to *prove* that we are really working with what chemists say we are working with (^{1}H ^{13}C 1D, 2D correlations
  $\rightarrow$ peak assignment)
- variable temperature measurements/titrations for porphyrin at various concentrations
  $\rightarrow$ get infromation about thermodynamics, stoichiometry and volume of coordinating units

Definitions of observables

Phase-separated porphyrin fraction - f_{sep}

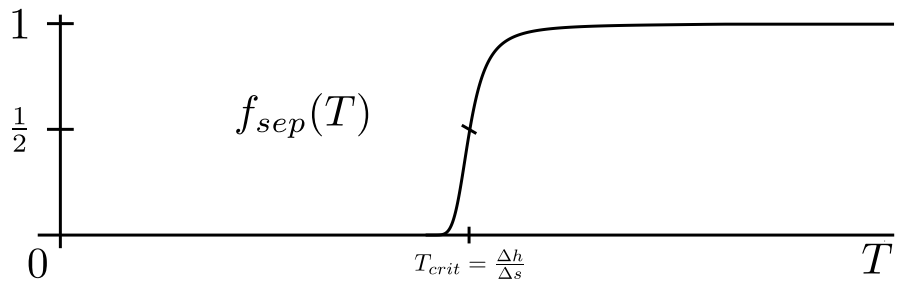
f_{sep} – theoretical, as a function



$$K = \frac{[P_{sep}]}{[P_{nsep}]} = \mathrm{e}^{-\frac{\Delta g}{RT}} = \mathrm{e}^{-\frac{\Delta G}{NRT}}$$

$$f_{sep} := \frac{[P_{sep}]}{[P_{sep}]+[P_{nsep}]} = \frac{1}{1+\frac{1}{K}}$$

$$\boxed{f_{sep} = \frac{1}{1+\mathrm{e}^{\frac{\Delta h}{RT} - \frac{\Delta s}{R}}}}$$

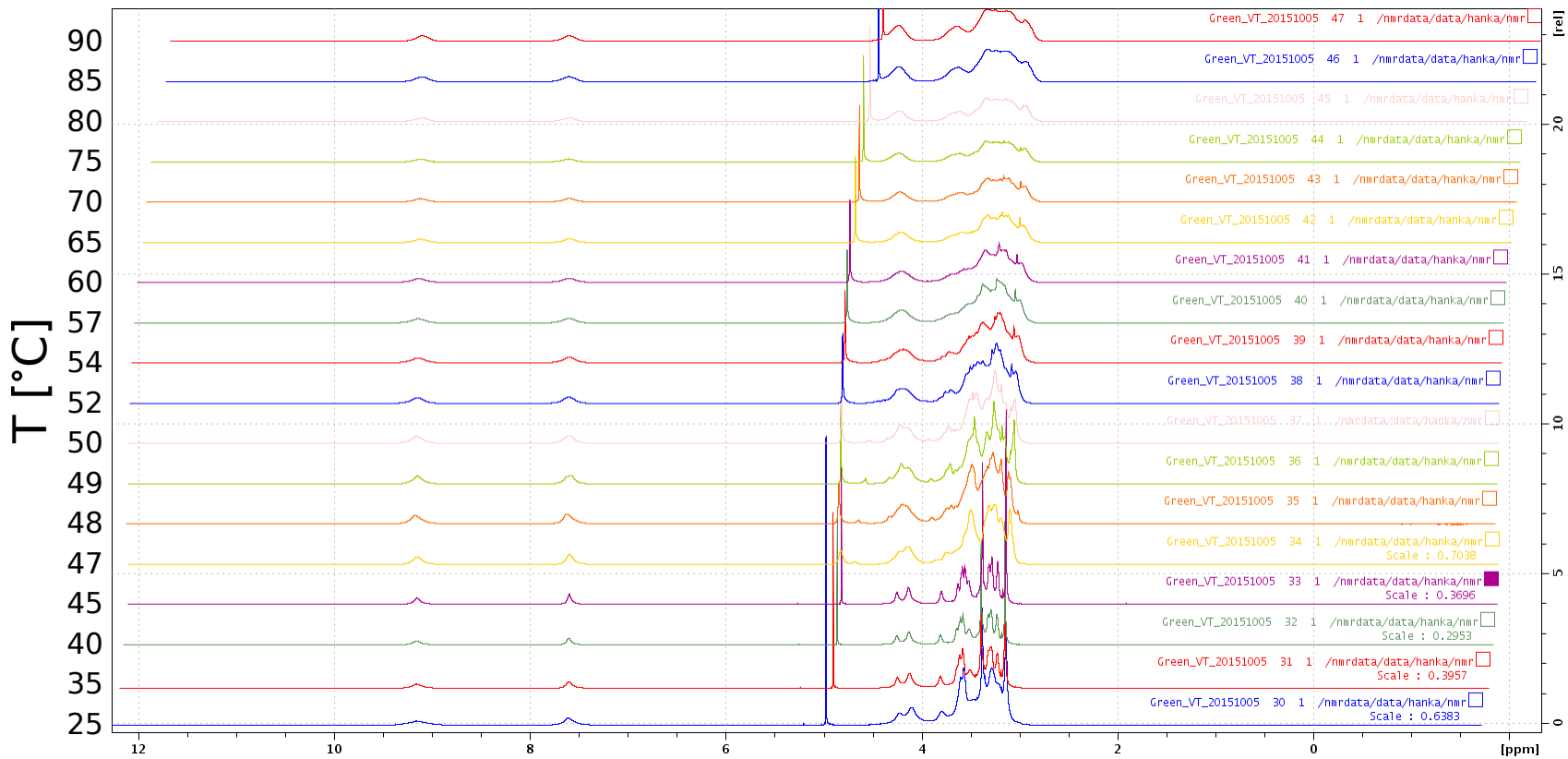


This function is uniquely given by the $(\Delta h, \Delta s)$ pair acquired by fitting each of the VT series!

Definitions of observables

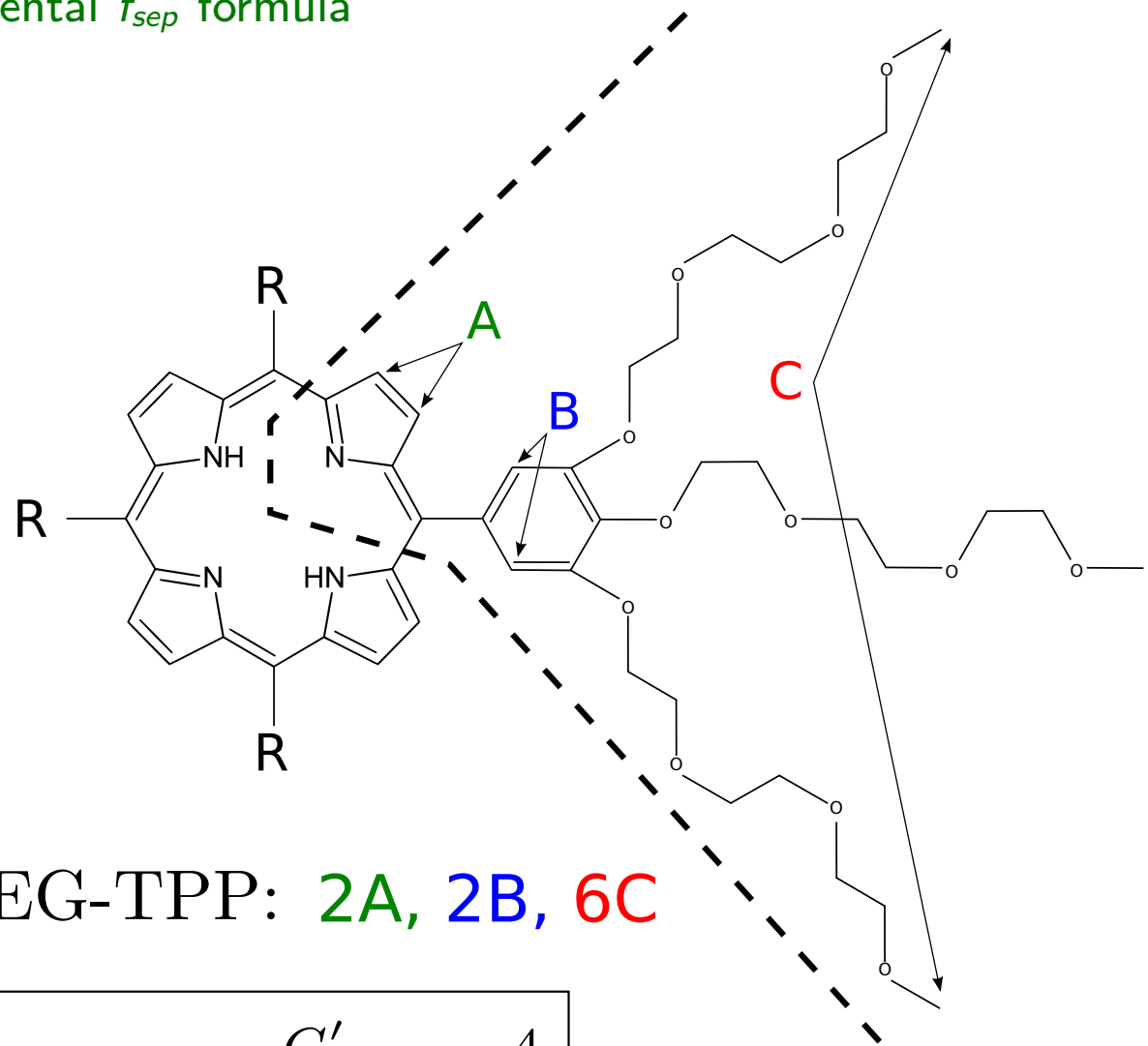
Variable Temperature series - VT

- set of 1D zg spectra for the same sample
- measured at a set of pre-defined temperature points
- points typically more dense near a region of interest, where the phenomenon we want to observe occurs (phase separation)



Definitions of observables

^{1}H site naming, experimental f_{sep} formula



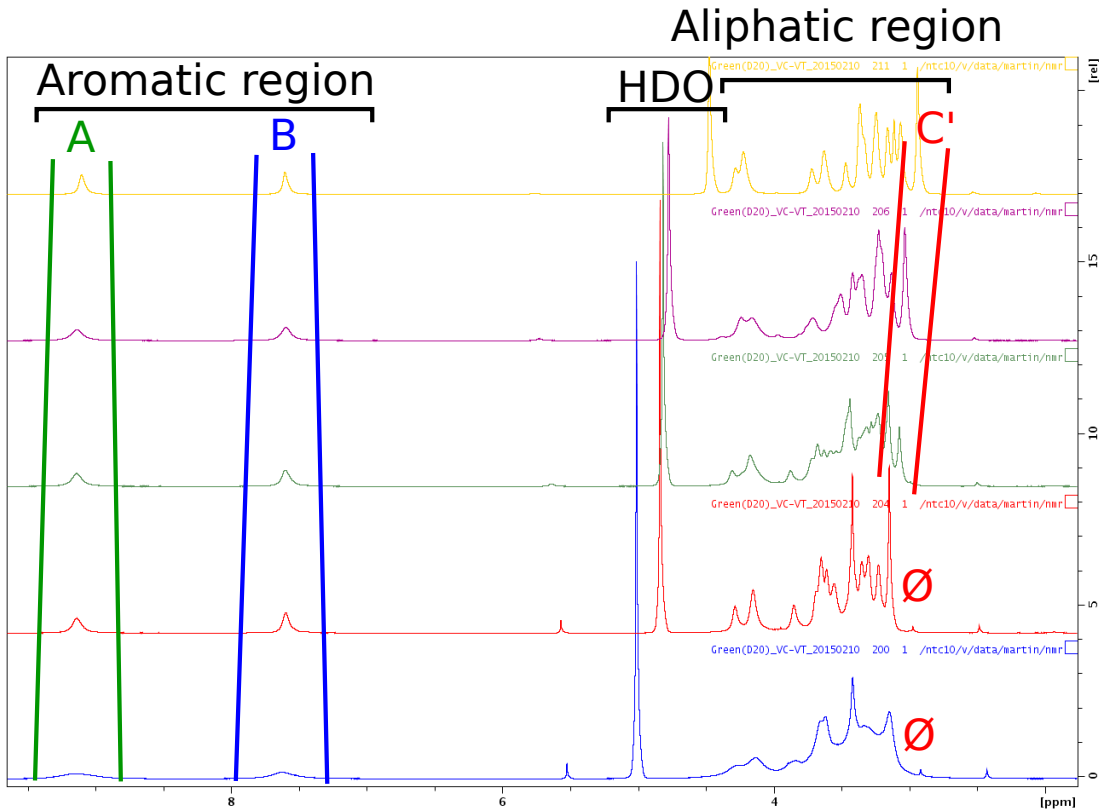
$\frac{1}{4}$ 3,4,5-TEG-TPP: 2A, 2B, 6C

$$f_{sep} = \frac{C'}{A+A'+B+B'} \frac{4}{6}$$

Definitions of observables

^{1}H VT regions of interest

- peak areas are proportional to number of nuclei of given type
- integrate/fit peaks to find their areas
  (we used Lorentzian/pseudo-Voigt fitting)
- areas known $\rightarrow$ phase-separated fraction calculation
- $f_{sep} = \frac{C'}{A+A'+B+B'} \frac{4}{6}$



Definitions of observables

From f_{sep} to T_{ONSET}

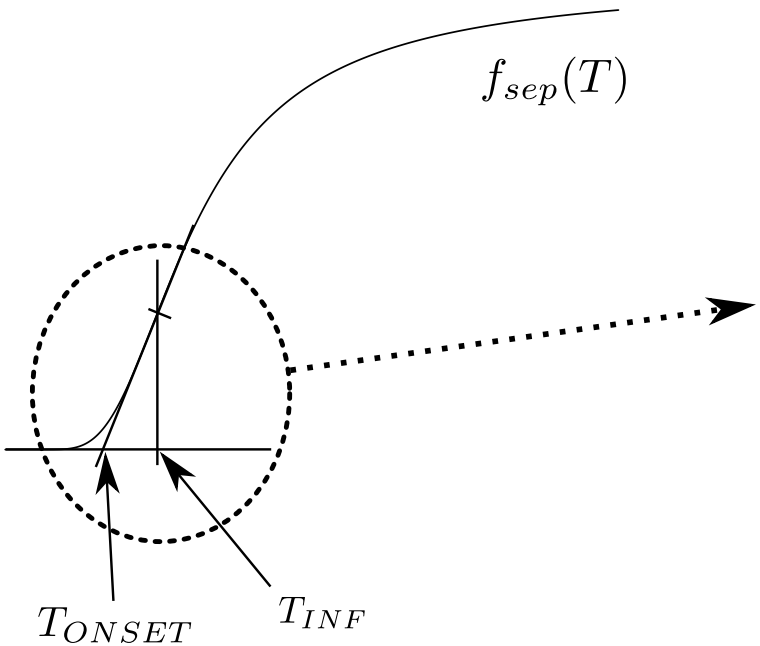
- fitting: (exp. points) $\mapsto$ (function, parameters)
- fitting experimental f_{sep} of each VT series with theoretical f_{sep} gives us the $(\Delta h, \Delta s)$ pair for each VT series
- purpose: the result can be handled analytically and numerically (calc. value/derivatives at any point) to find T_{ONSET}
- result: (ϕ_P, T_{ONSET}) are experimental points on binodal in Flory-Huggins theory; we are going to fit binodal in the next step

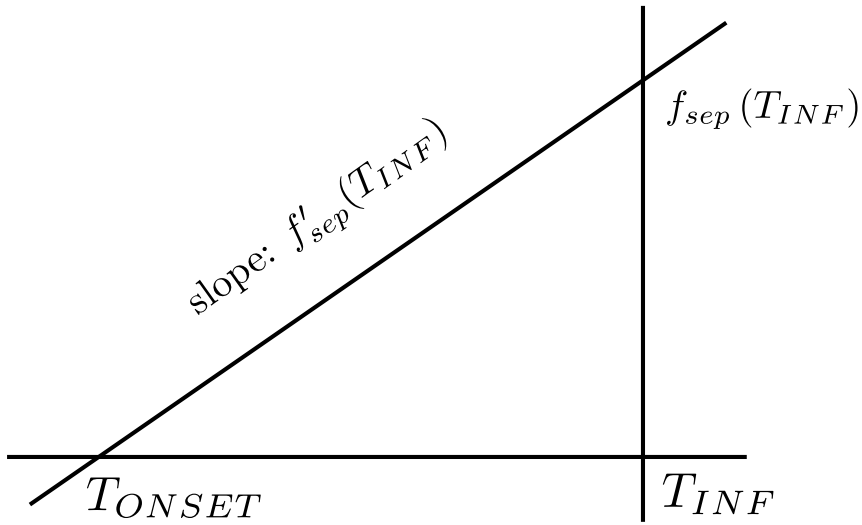
Definitions of observables

Temperature of phase separation onset - T_{ONSET}

$T_{INF}: \quad (\partial_{TT} f_{sep})\,|_{T=T_{INF}} = 0$

Temperature of the inflex point of f_{sep}





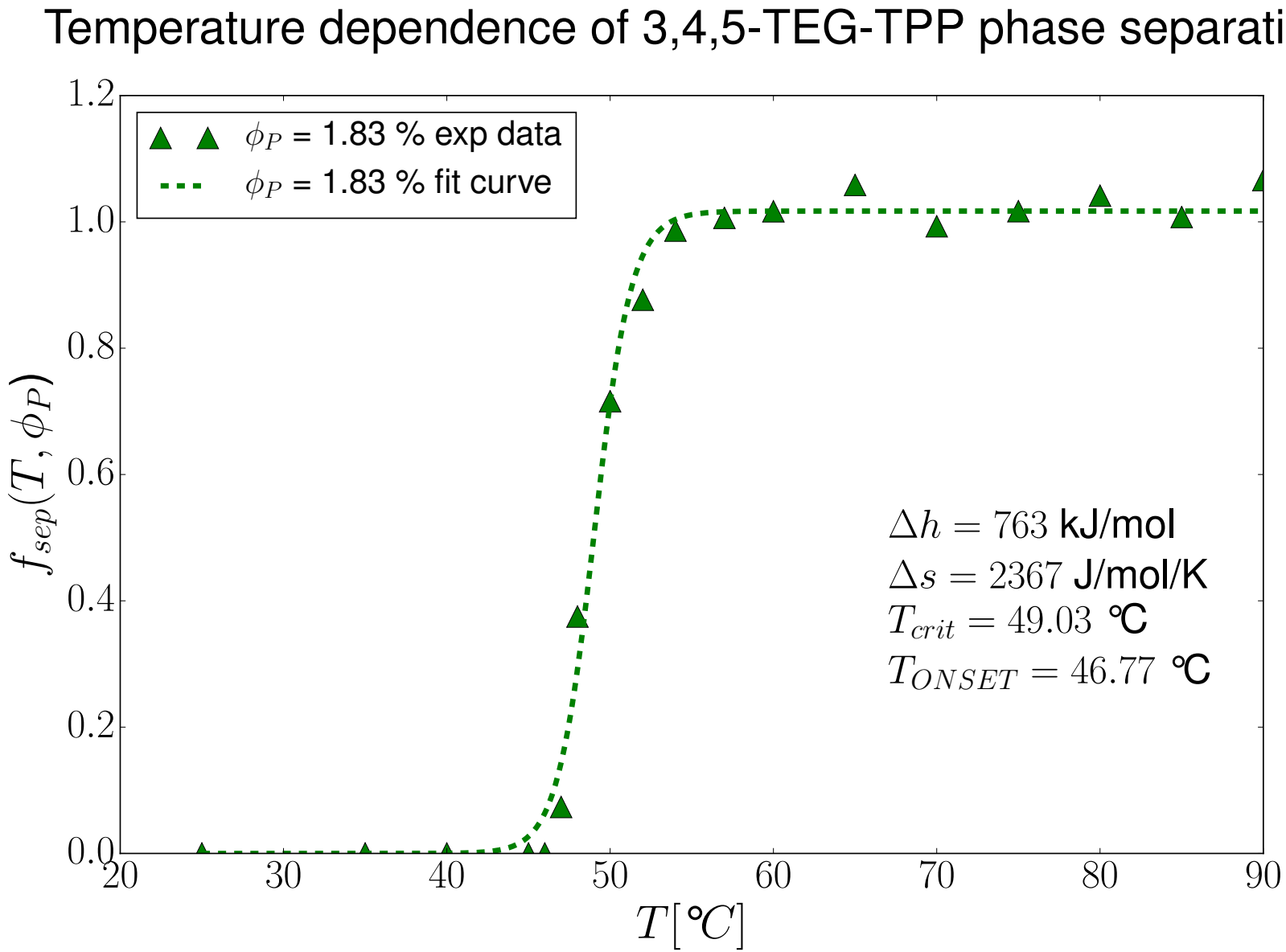
$$T_{ONSET} = T_{INF} - \frac{f_{sep}(T_{INF})}{f'_{sep}(T_{INF})}$$

T_{INF} ... numerically

T_{ONSET} is the most important quantity to be determined here!

Example

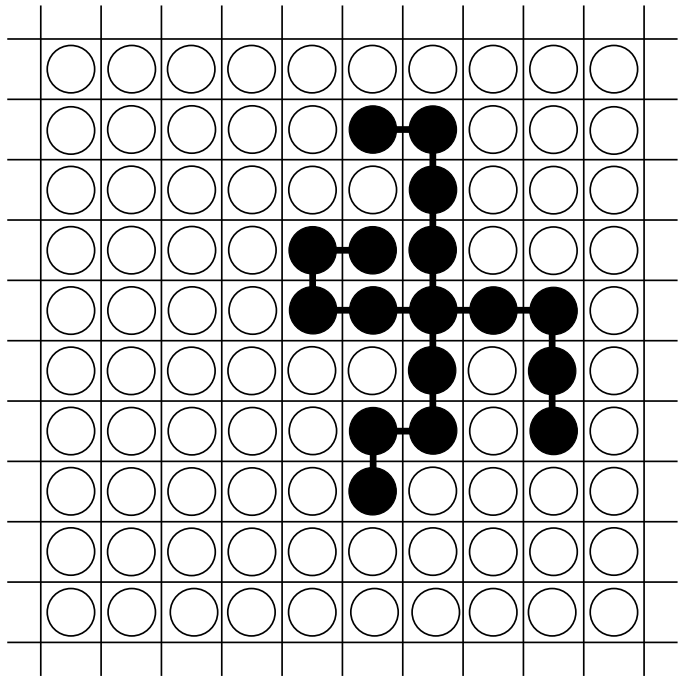
f_{sep}, T_{ONSET} for one VT



Definitions of observables

Polymer solution in Flory-Huggins theory

Star-like macromolecule in Flory-Huggins theory



○ ... solvent molecule

● ... polymer "tile" with a similar volume to the volume of a solvent molecule

r ... number of black tiles per molecule

ϕ_P ... ratio of solute tiles to all tiles

Definitions of observables

Phase diagram derived from Flory-Huggins Gibbs energy of mixture

Indices:

compound: 1 – solvent; 2 – porphyrin

phase after separation: α – solvent-rich; β – porphyrin-rich

Variables:

$$\phi_1 = \frac{V_1}{V_1 + V_2} = \frac{n_1}{n_1 + rn_2} \qquad N = n_1 + rn_2$$

$$\phi_2 = \frac{V_2}{V_1 + V_2} = \frac{rn_2}{n_1 + rn_2} \qquad \chi = A + \frac{B}{T}$$

Gibbs energy of a polymer solution:

$$\Delta G_{mix} = Nk_B T \left[\phi_1 \ln \phi_1 + \frac{\phi_2}{r} \ln \phi_2 + \chi \phi_1 \phi_2 \right]$$

Binodal:

$$f_1 = 0 = \ln(1 - \phi_2^\alpha) - \ln(1 - \phi_2^\beta) + \left(1 - \frac{1}{r}\right)\left(\phi_2^\alpha - \phi_2^\beta\right) + \chi\left[(\phi_2^\alpha)^2 - (\phi_2^\beta)^2\right]$$

$$f_2 = 0 = \ln(\phi_2^\alpha) - \ln(\phi_2^\beta) - (1 - r)\left(\phi_2^\alpha - \phi_2^\beta\right) + \chi\left[(1 - \phi_2^\alpha)^2 - (1 - \phi_2^\beta)^2\right]$$

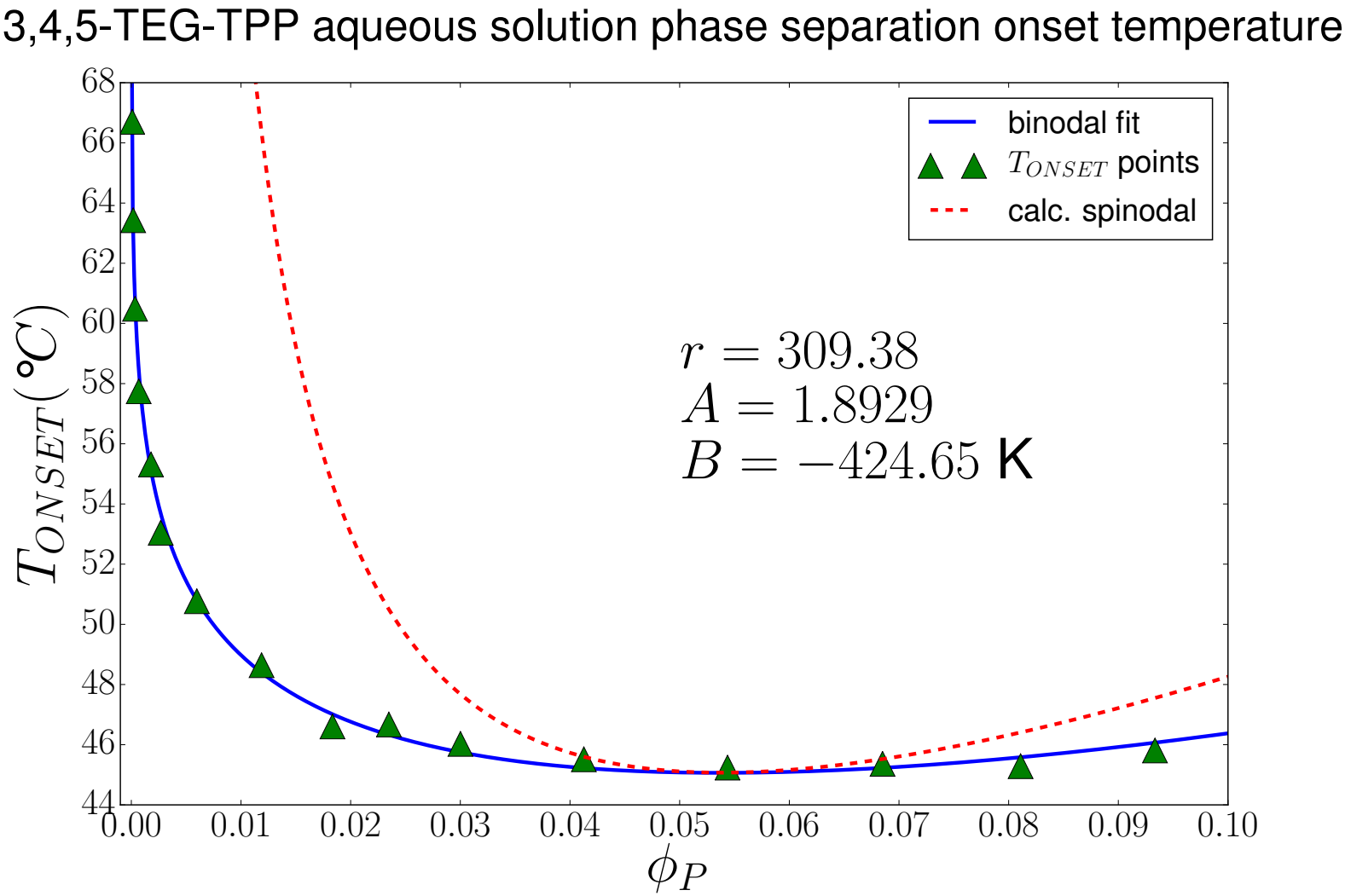
Spinodal:

$$T = \frac{B}{\frac{1}{2}\left(\frac{1}{r\phi_P} + \frac{1}{1-\phi_P}\right) - A}$$

- solve for (ϕ_1, χ) pairs numerically (2D Newton's algorithm)
- calculate $T(\chi)$ and use it as a fitting function $T(\phi)$ for experimental T_{ONSET}
- result: parameters r, A, B; r is the ratio of solute-to-solvent "tile volumes"

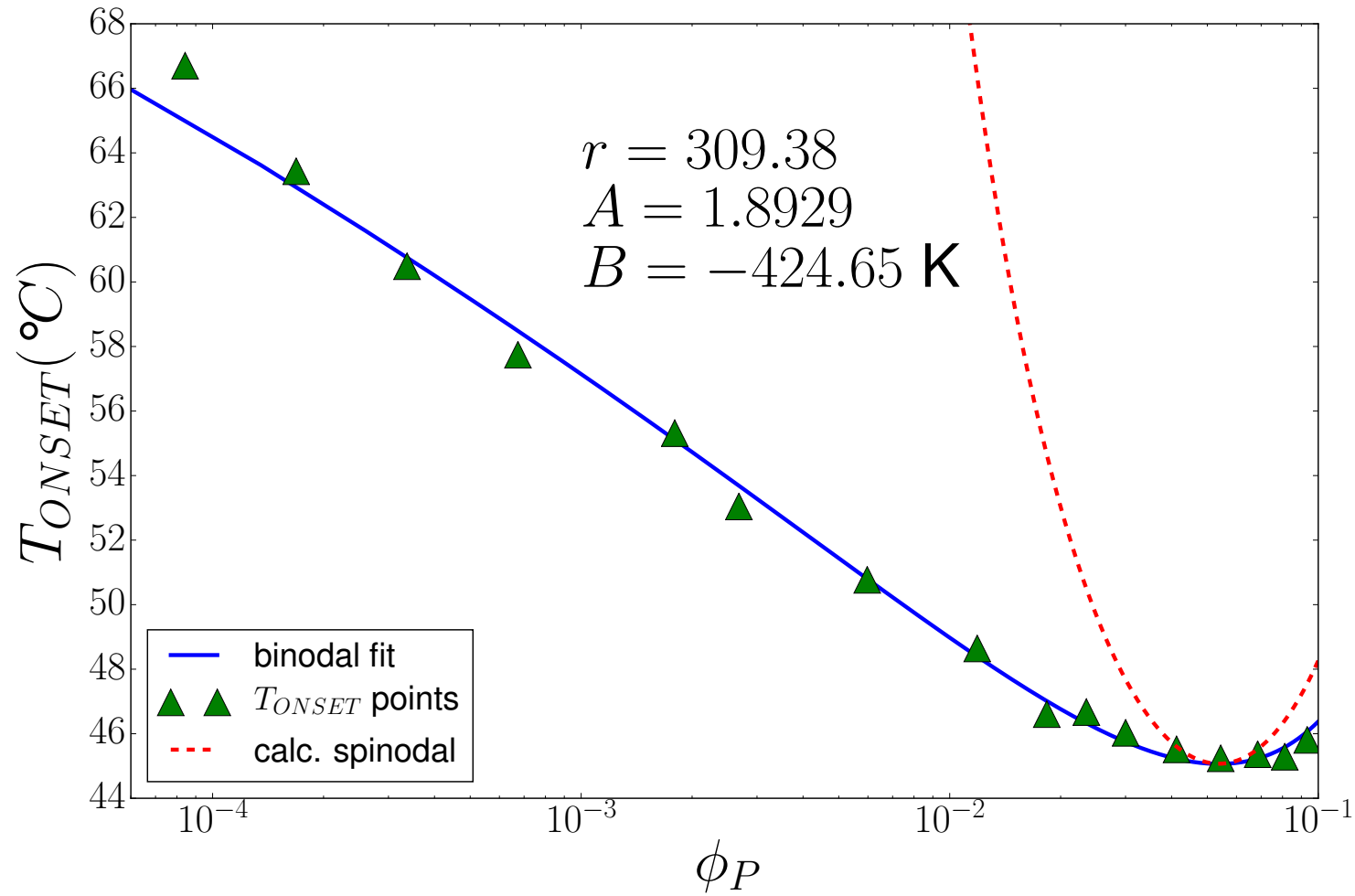
Results

Phase diagram



Results

Phase diagram



Results

Acidity and phase separation

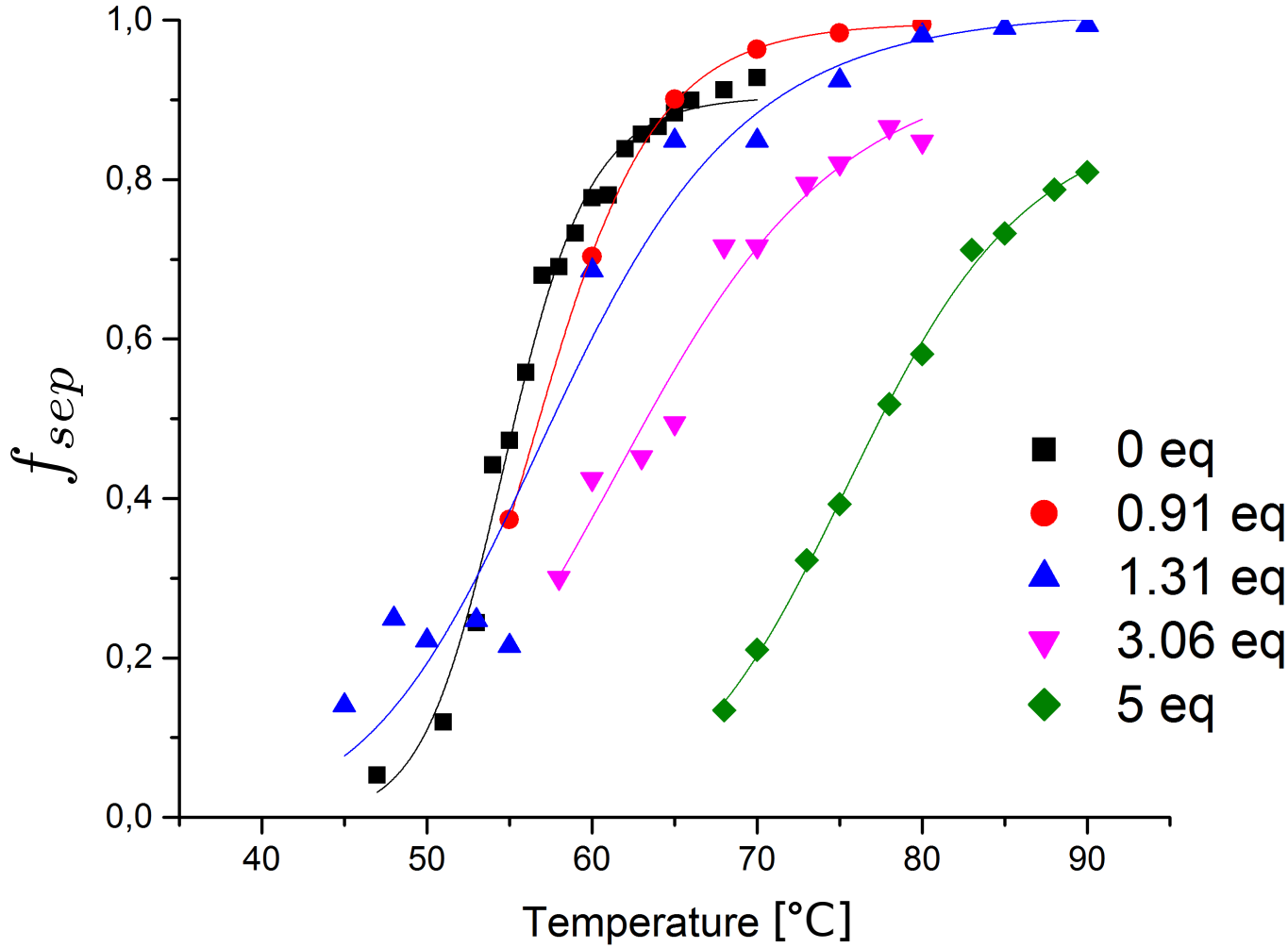


Figure: Phase separation temperature dependence, for various amounts of S-camphorsulfonic acid. Curves shift to the right with increasing acidity, implying T_{ONSET} also increases.

Results

Acidity and transitory complexes

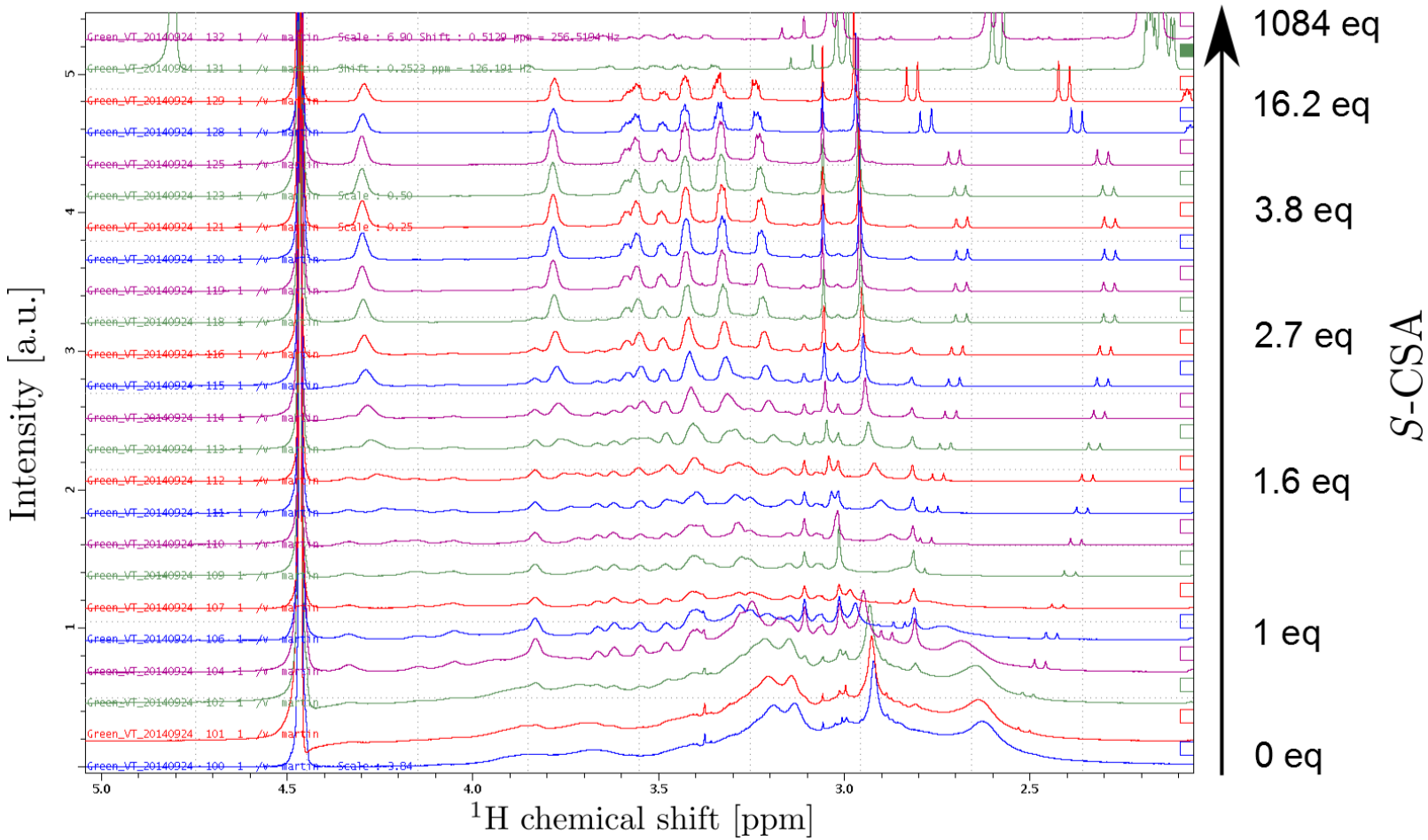


Figure: Room temperature titration using S-camphorsulfonic acid. Acidity causes molecules to adopt identical forms and increases their mobility.

Results

Acidity and transitory complexes

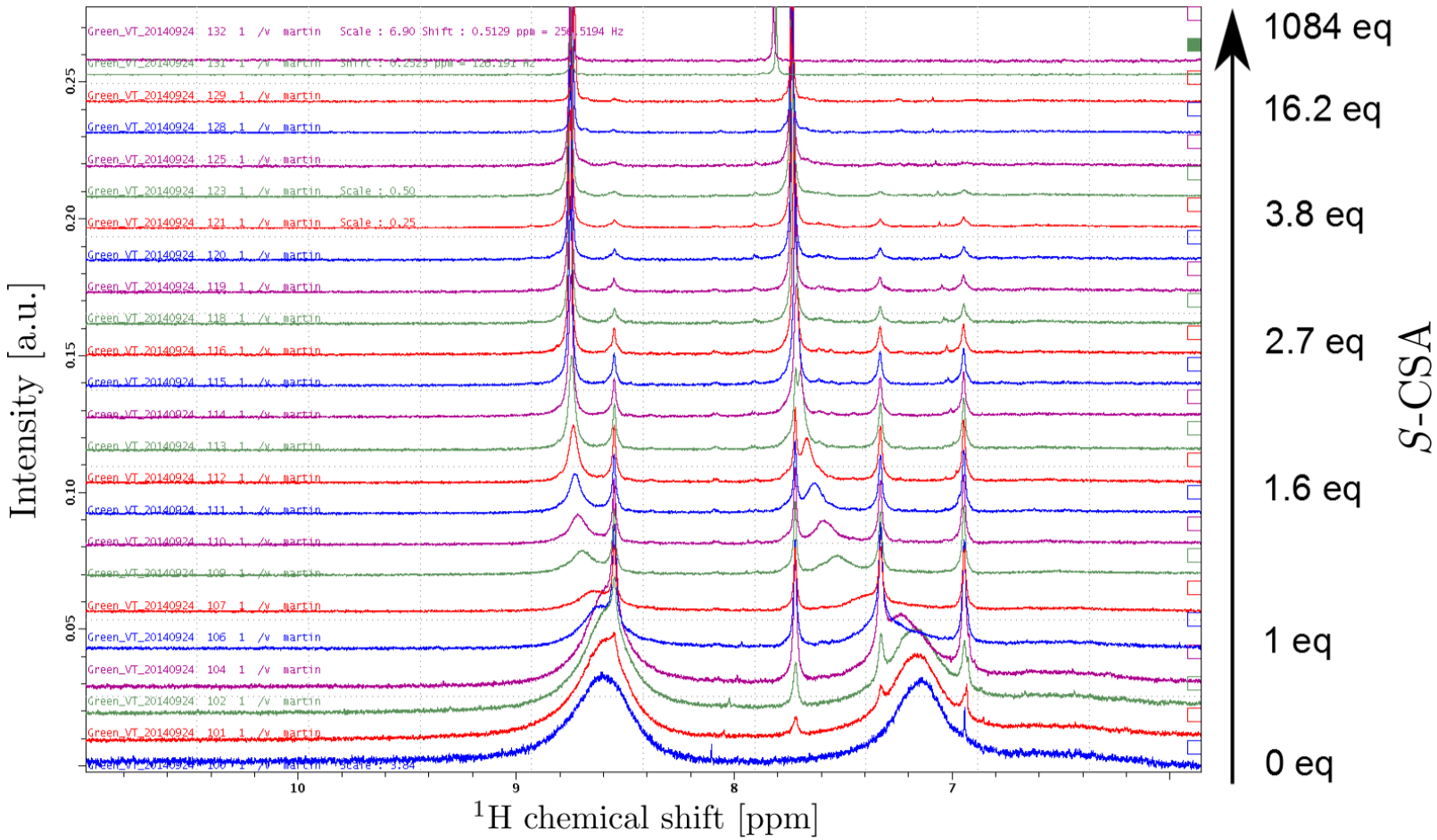
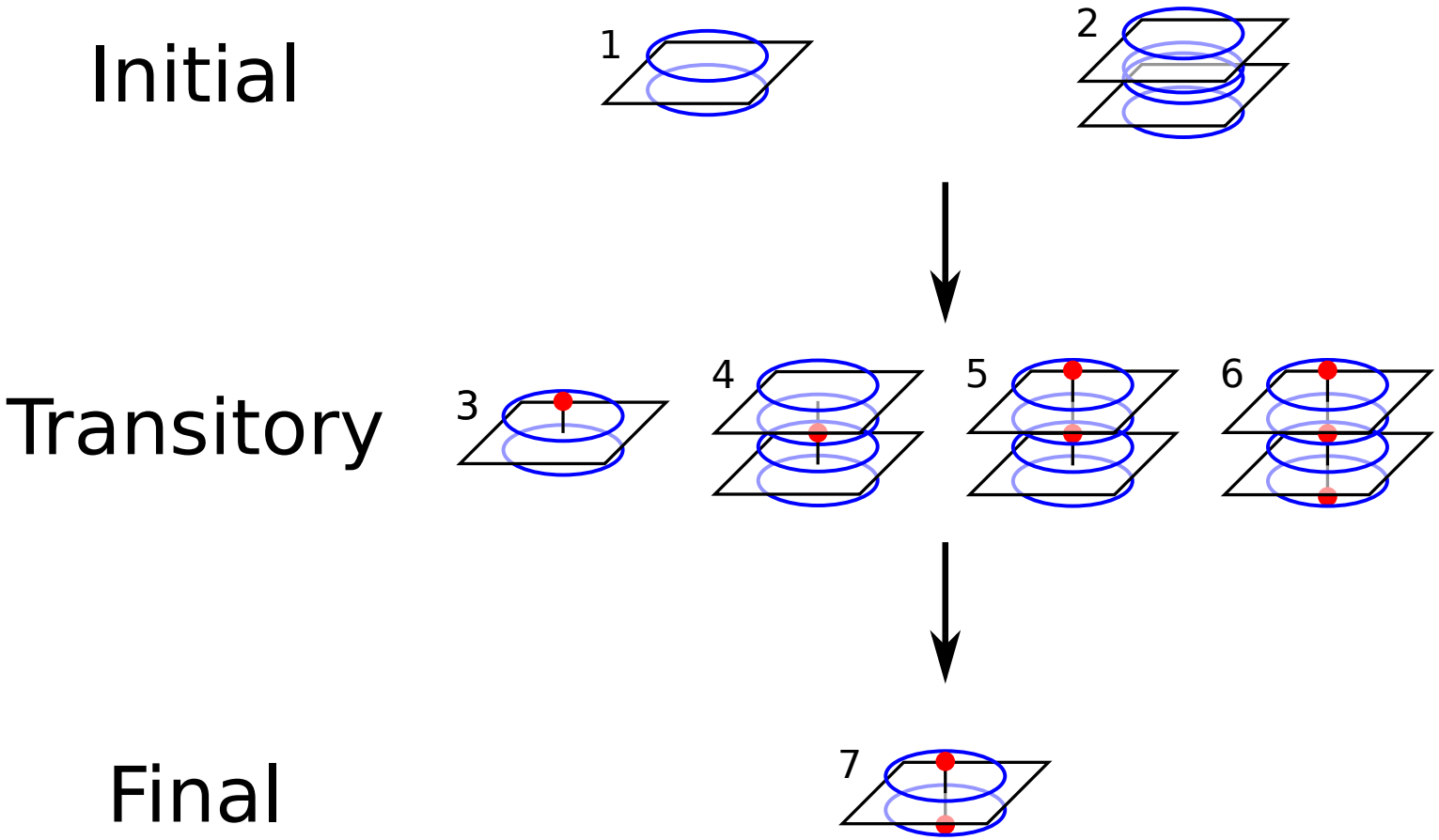


Figure: **3,4,5-TEG-TPP** molecules adopt transitory forms when **3,4,5-TEG-TPP** and **S-CSA** concentrations are comparable.

Results

Acidity



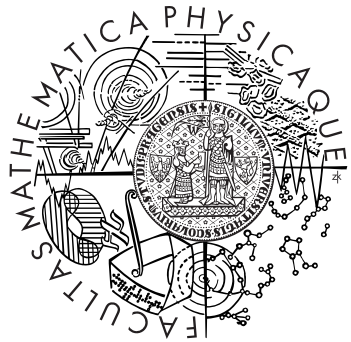
Conclusions

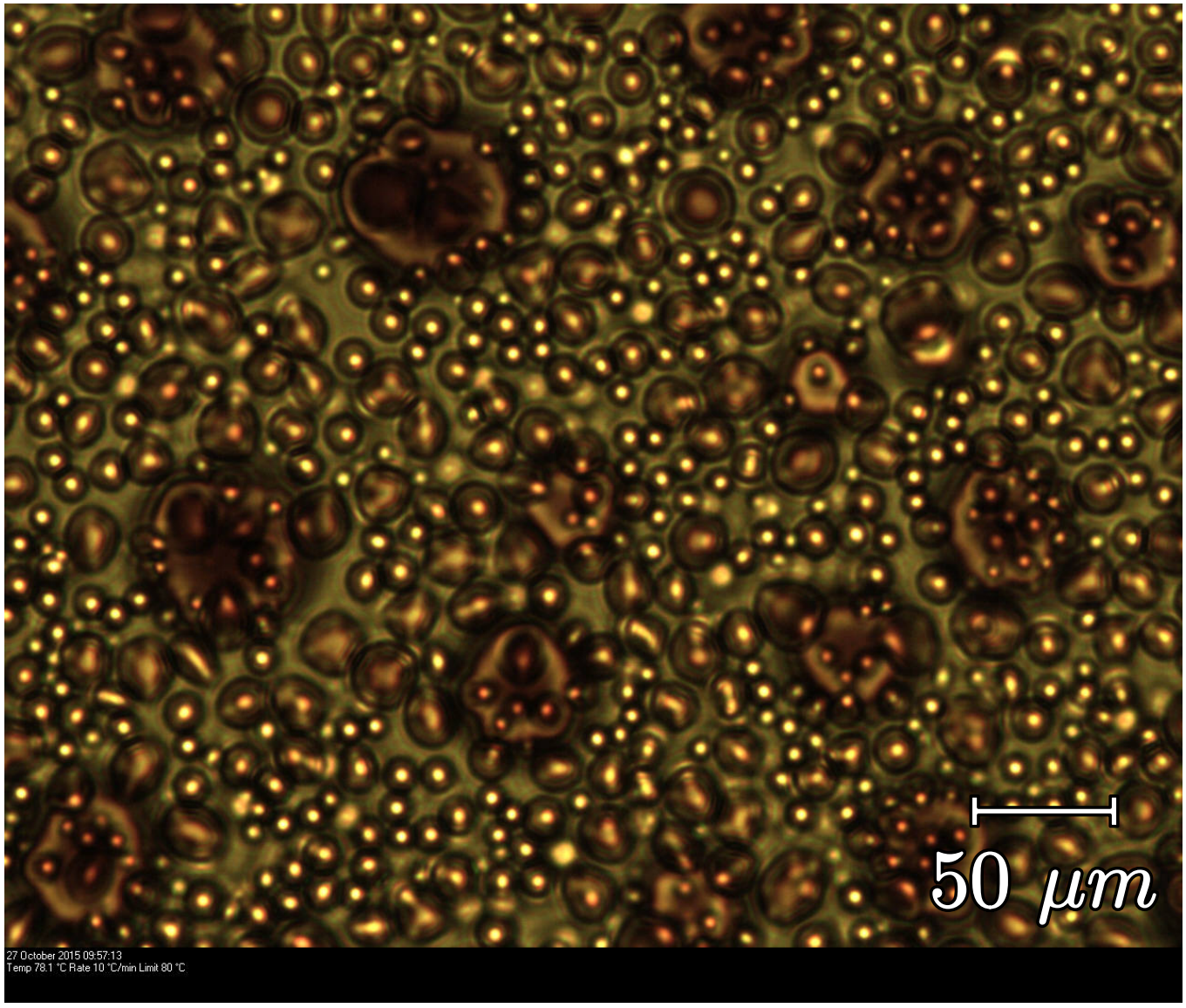
- phase separation:
  - phase diagram measured
  - fitted using Gibbs energy and binodal from Flory-Huggins theory
  - **3,4,5-TEG-TPP** molecules form dimers in aqueous solution
    $\rightarrow$ stacking
- acidity:
  - breaks down these dimers
  - H^+ create various transitory complexes with **3,4,5-TEG-TPP**, but only one final complex
  - increases the phase separation onset temperature
    $\rightarrow$ H^+ ligands cause Coulombic repulsion between **3,4,5-TEG-TPP** molecules

Further research suggestions

- less symmetrical porphyrins (already in progress)
- interaction with metal ions

Thank you for your attention

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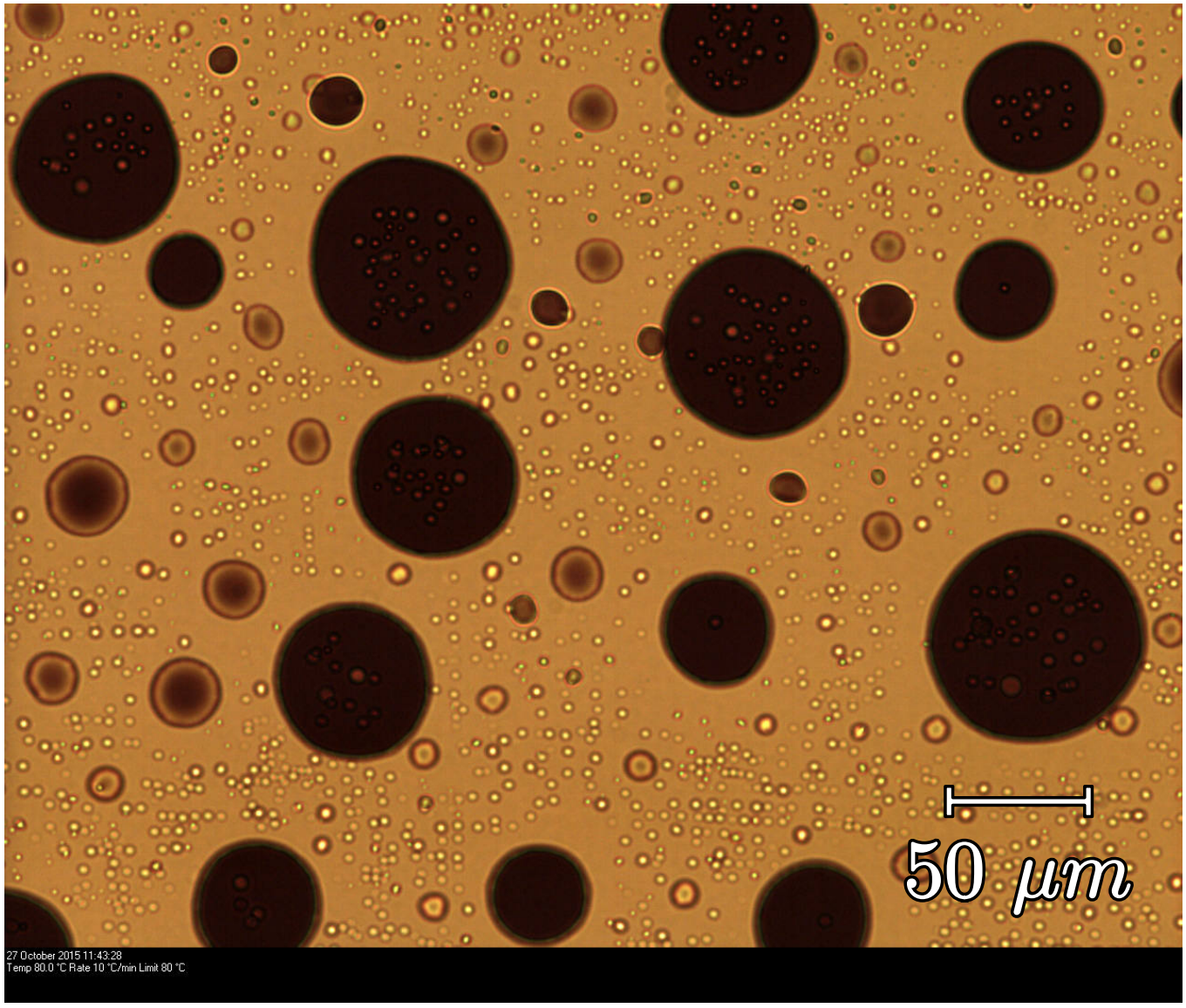
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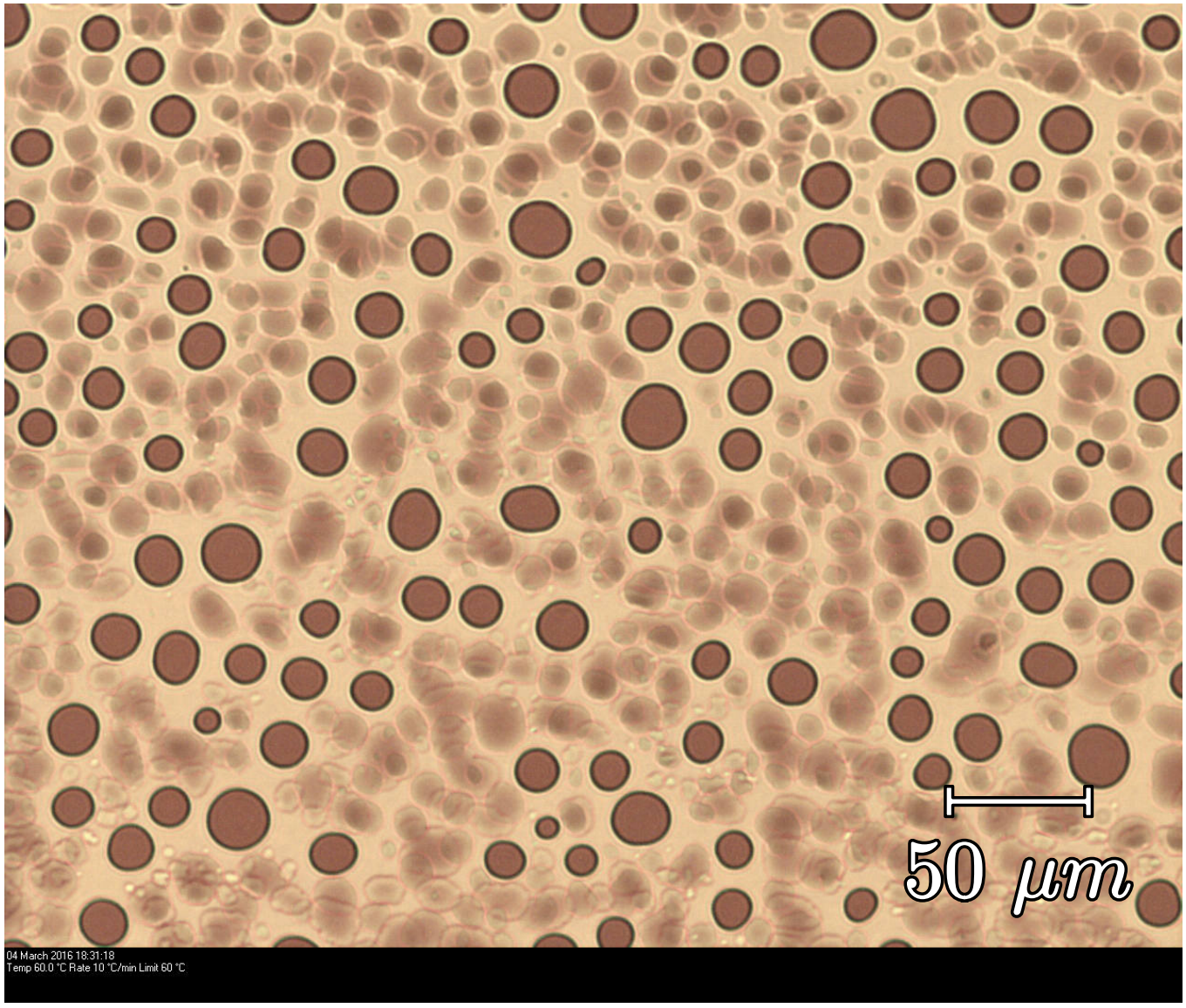
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