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Revealing the Nature of Eutectic Solvents: A Synergy Between DSC and Lock-Free NMR DOSY

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Complex alternative solvents

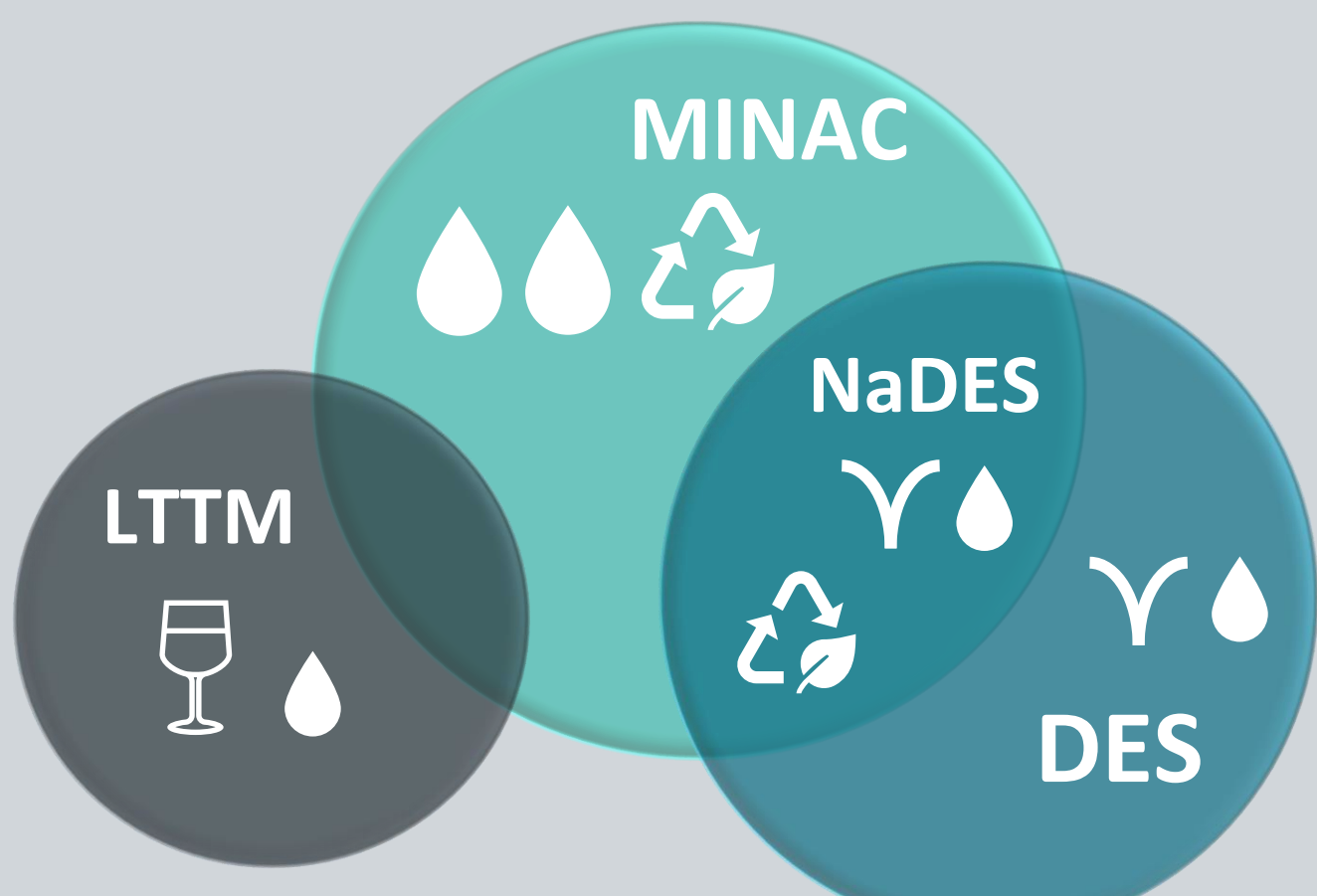
Growing focus on **sustainability** in chemical processes
 Alternative solvents : eco-friendly, **cost-effective**, and versatile

Natural Deep Eutectic Solvents (NaDES)

- deep eutectic point in Solid Liquid Equilibrium, deviation > 10 K from ideality^{1,2}
- Low amount of water (< 40%)
- Overused and misused in literature^{2,4}

Alternative formulated solvents

- Low Transition Temperature Mixtures (LTTMs)³
 - Glass transition instead of eutectic point
- Mixtures of Natural Compounds (MINACs)⁴
 - No thermodynamical requirement
 - High tolerance of water (up to 90%)



Biosourced raw material Authorized water amount Glass transition Deep eutectic point

NaDES, LTTM, MINAC ?

Main analysis : differential scanning calorimetry (DSC)
 Analyze full Solid liquid equilibrium
 Sometimes difficult to interpret ?

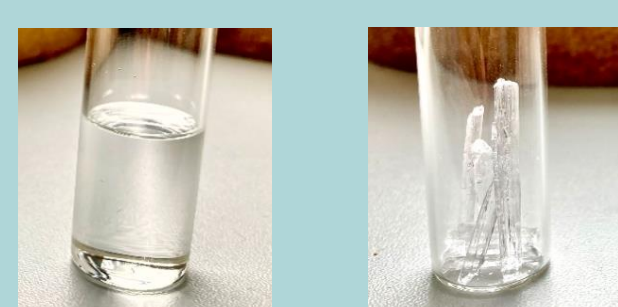
What conclusion if no eutectic or glass transition?

Implement multi-technique approach

COSMO-RS simulation
 differential scanning calorimetry (DSC)
 original lock-free NMR DOSY strategy

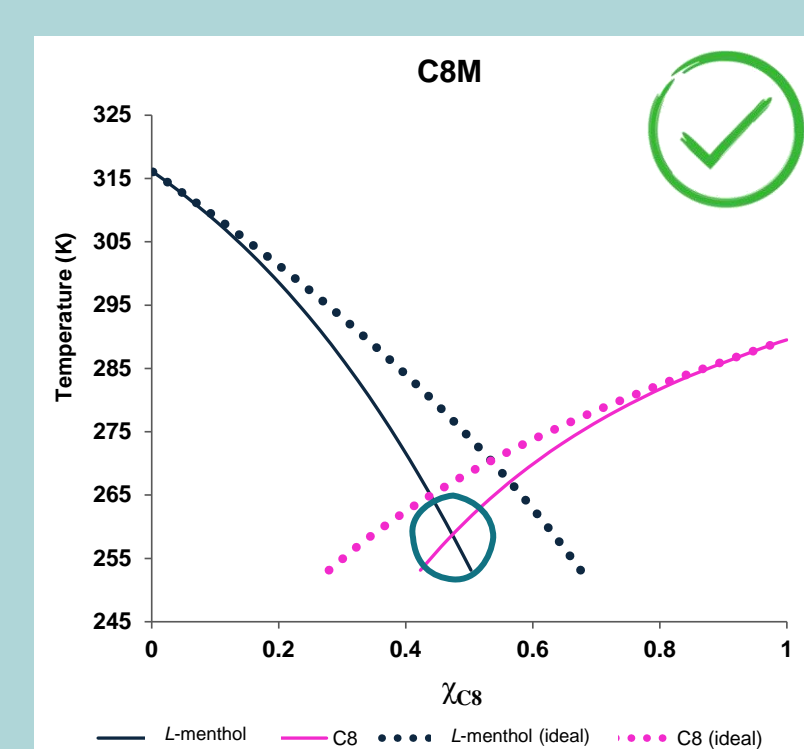
Simple case study

Caprylic acid & L-menthol



caprylic acid (C8) L-menthol (M)

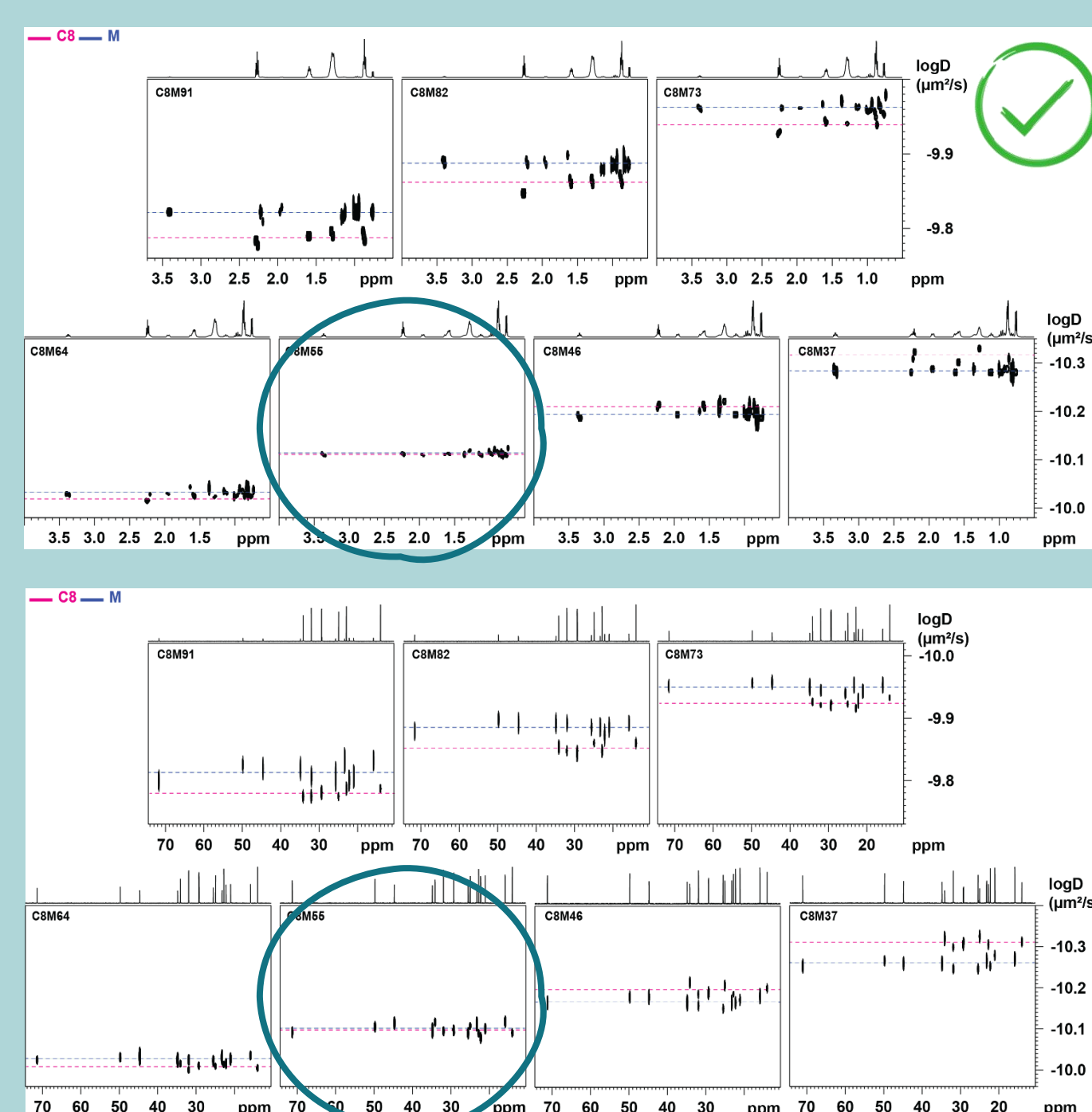
COSMO-RS simulation



Putative eutectic point at 1:1 mol/mol
 Ideality deviation > 10 K

Lock-free ¹H and ¹³C NMR DOSY

Mixture of C8/L-menthol from 9:1 to 3:7 mol/mol
 2D Spectra acquisition **without lock** at 298 K at 500 MHz (¹H) and 125 MHz (¹³C)
 Diffusion measurements with curve fitting processing



Two diffusion lines in all mix

Except ratio 1:1 mol/mol
 A unique line of diffusion

Not an effect of viscosity
 two diffusion lines before and after

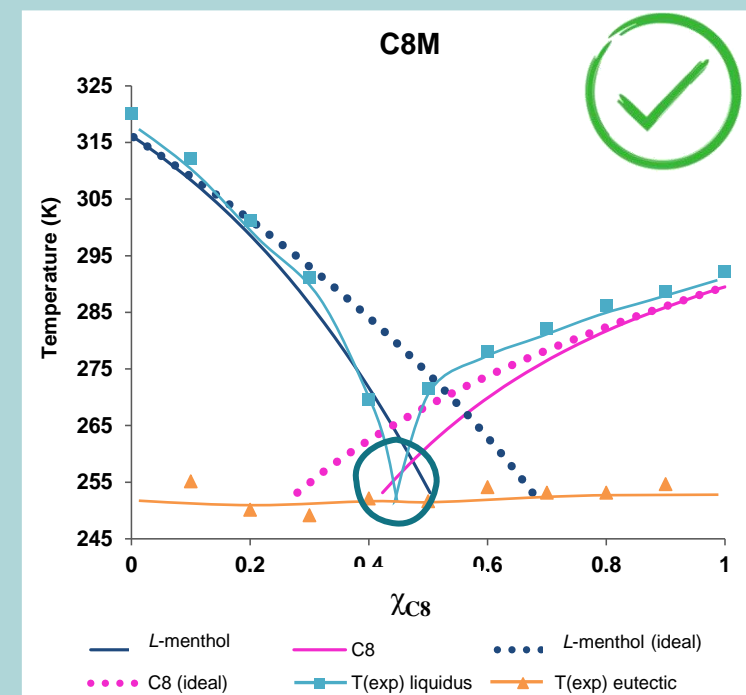
- behave as a pure substance
- Proof of an interactions network

DSC analysis

Heating step at a scan rate of a 2K/min from -60°C to 50°C

Confirmation of both COSMO-RS prediction and DOSY NMR measurement

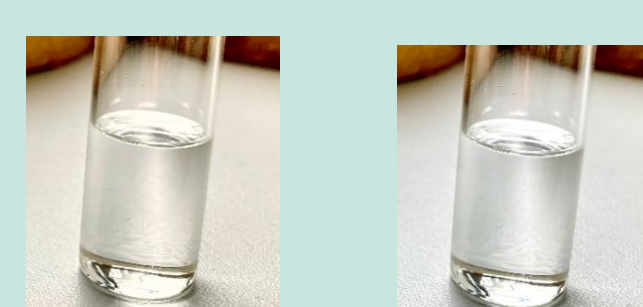
C8/Menthol at 1:1, mol/mol
 Type V NaDES



- Lock-free NMR DOSY could be trusted to find an eutectic point
- First real proof of the low interaction network inside a NaDES

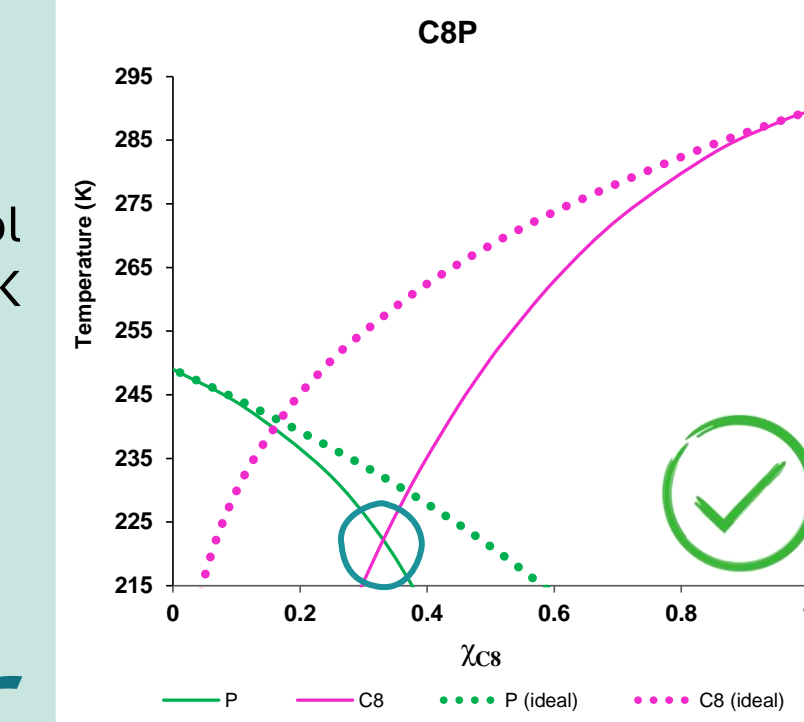
Let's get trickier ! Two liquids

Caprylic acid & 1,3-propanediol



caprylic acid (C8) 1,3-propanediol (P)

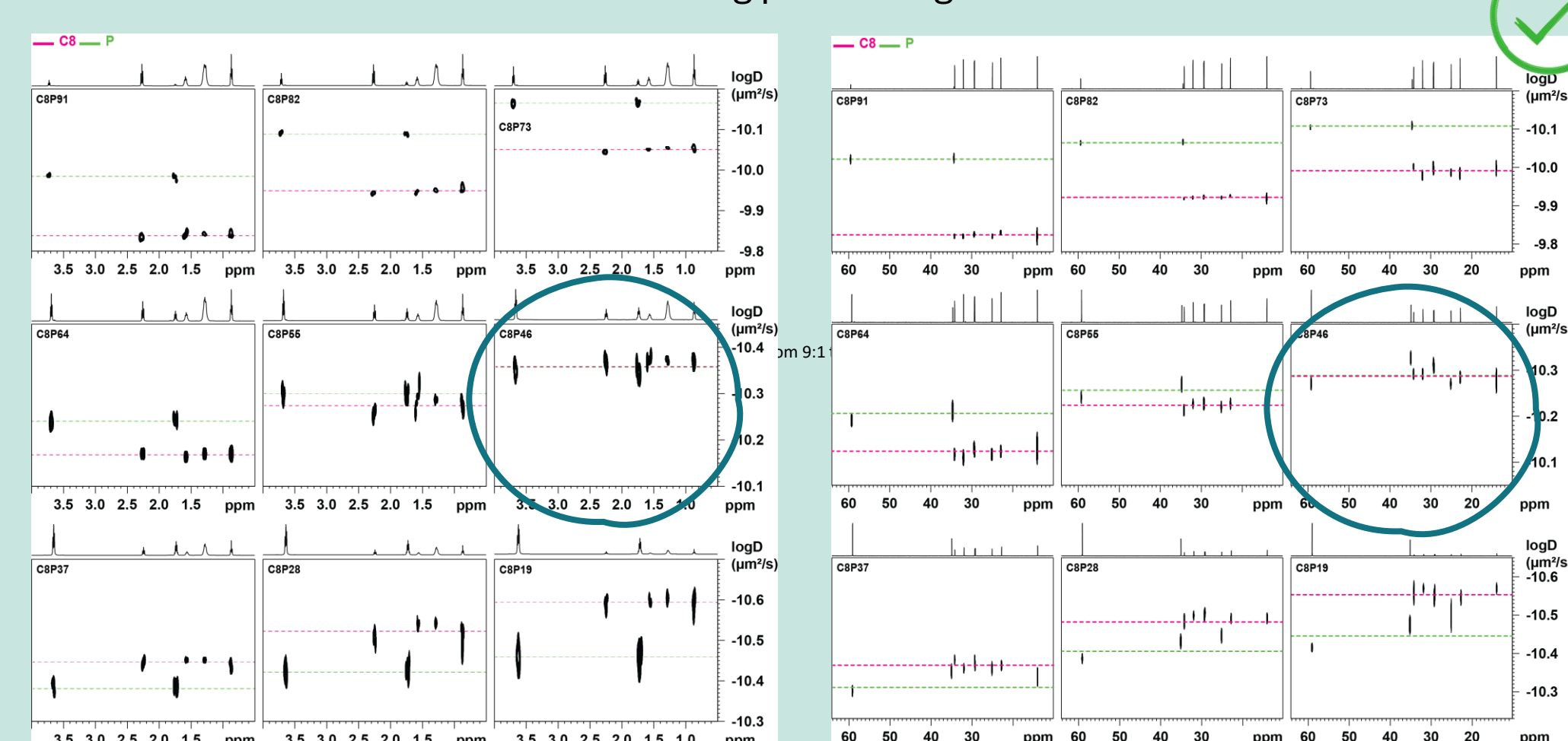
COSMO-RS simulation



Putative eutectic point at 1:2 mol/mol
 Ideality deviation > 10 K

Lock-free ¹H and ¹³C NMR DOSY

Mixture of C8/P from 9:1 to 1:9 mol/mol (liquids are cool for that!)
 2D Spectra acquisition **without lock** at 298 K at 500 MHz (¹H) and 125 MHz (¹³C)
 Diffusion measurements with curve fitting processing

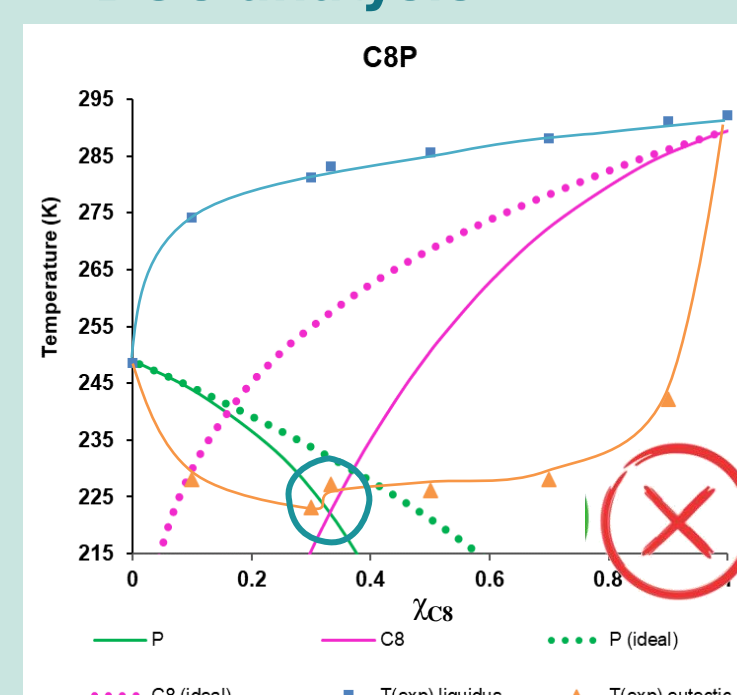


Two diffusion lines in all mix

Except ratio 4:6 mol/mol : A unique line of diffusion

- behave as a pure substance
- Strong intermolecular interactions network

DSC analysis



Heating step at a scan rate of a 2K/min from -125°C to 35 °C

What the hell is that??

Monotectic-like phase diagram
 suggest a solid-solution nature

Small curve break at ratio close to 4:6, mol/mol

Not a NaDES nor a LTTM : MINAC is OK
 BUT act as a pure substance

- DOSY success in finding the maxima of intermolecular interactions
- New generation of complex solvents?
- Further investigations in progress

Conclusions

Crucial role of comprehensive characterization

- in the study of complex alternative solvents

Integrative approach **combining DSC, NMR DOSY, and theoretical modeling**

- able to **uncover critical differences** between NaDES and other types

Major step in the design and application of sustainable solvents

- Lock free NMR DOSY: innovative approach
- First **network of intermolecular interactions proof**

Prospects

MINAC nomenclature

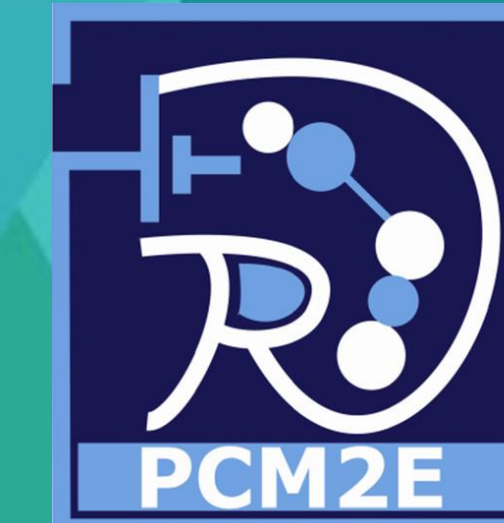
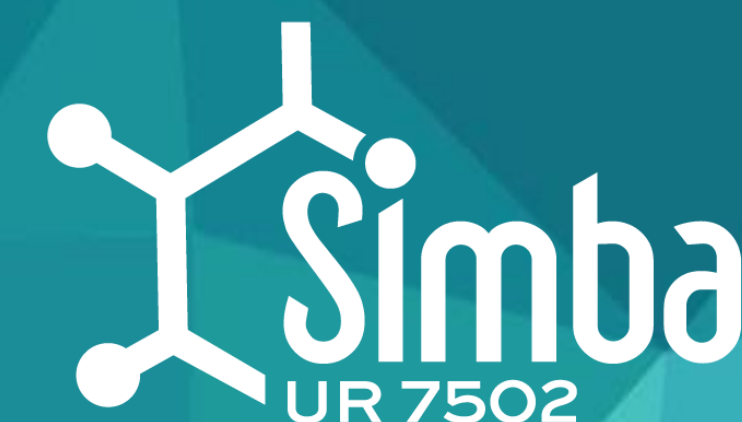
- flexible and inclusive term for mixtures of natural metabolites

too vague as it stands

needs to be refined

New generation of complex solvents based on alkanediol?

DRX imaging, viscosity, density measurements are in progress



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