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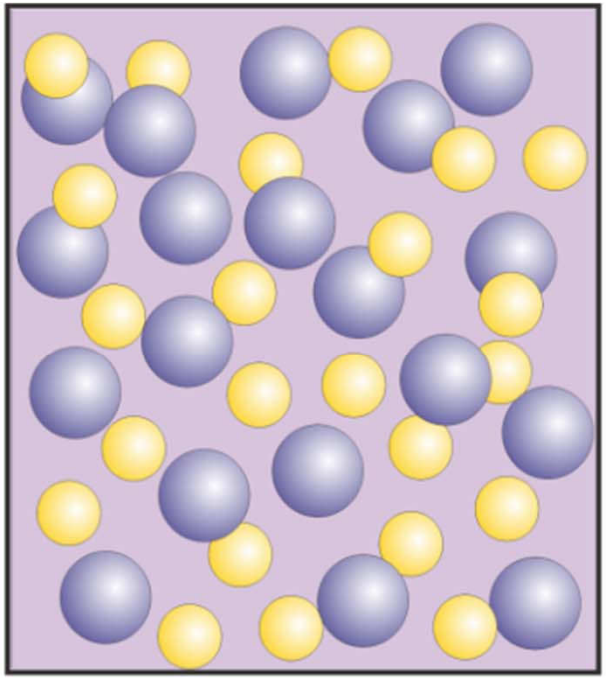
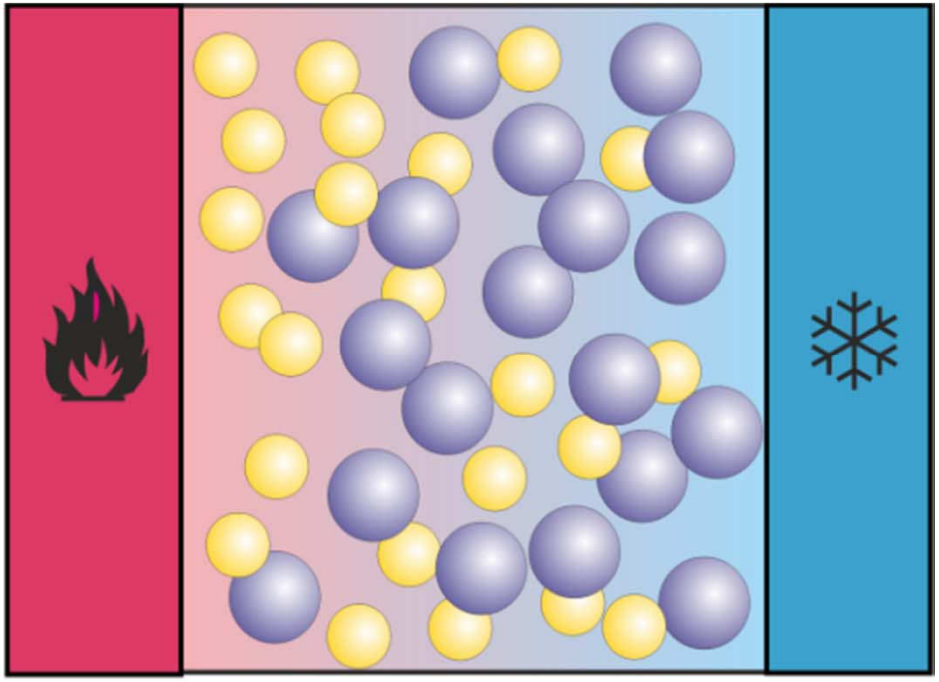
How do hydrogen bonds influence thermophoresis?

21. September 2016| **Simone Wiegand**,
Doreen Niether, Jan K.G. Dhont

Thermophoresis – the effect

(…, thermodiffusion, Soret effect)





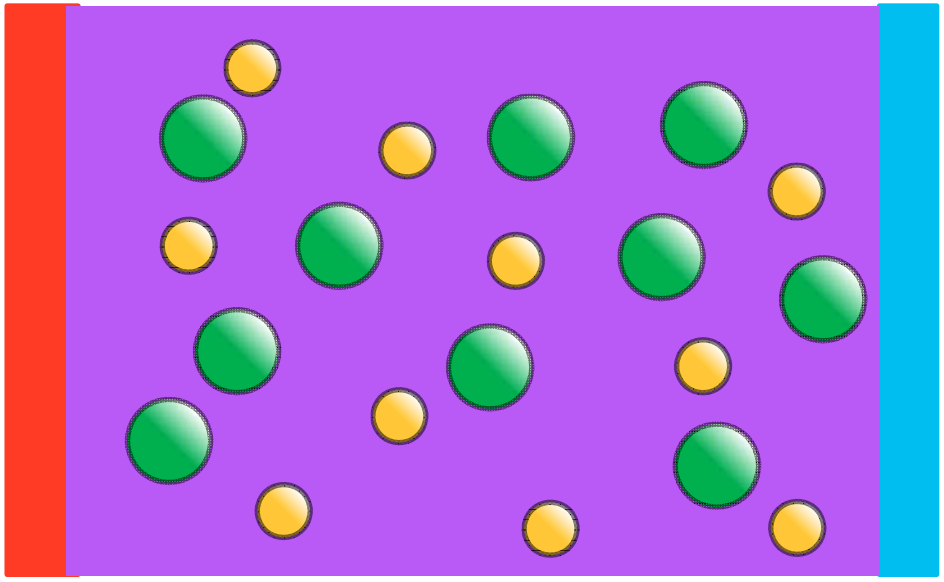
No microscopic understanding

Thermophoresis – the effect

$$\vec{j} = -D\vec{\nabla}w - w(1-w)D_T\vec{\nabla}T$$

Steady state $\vec{j} = 0$

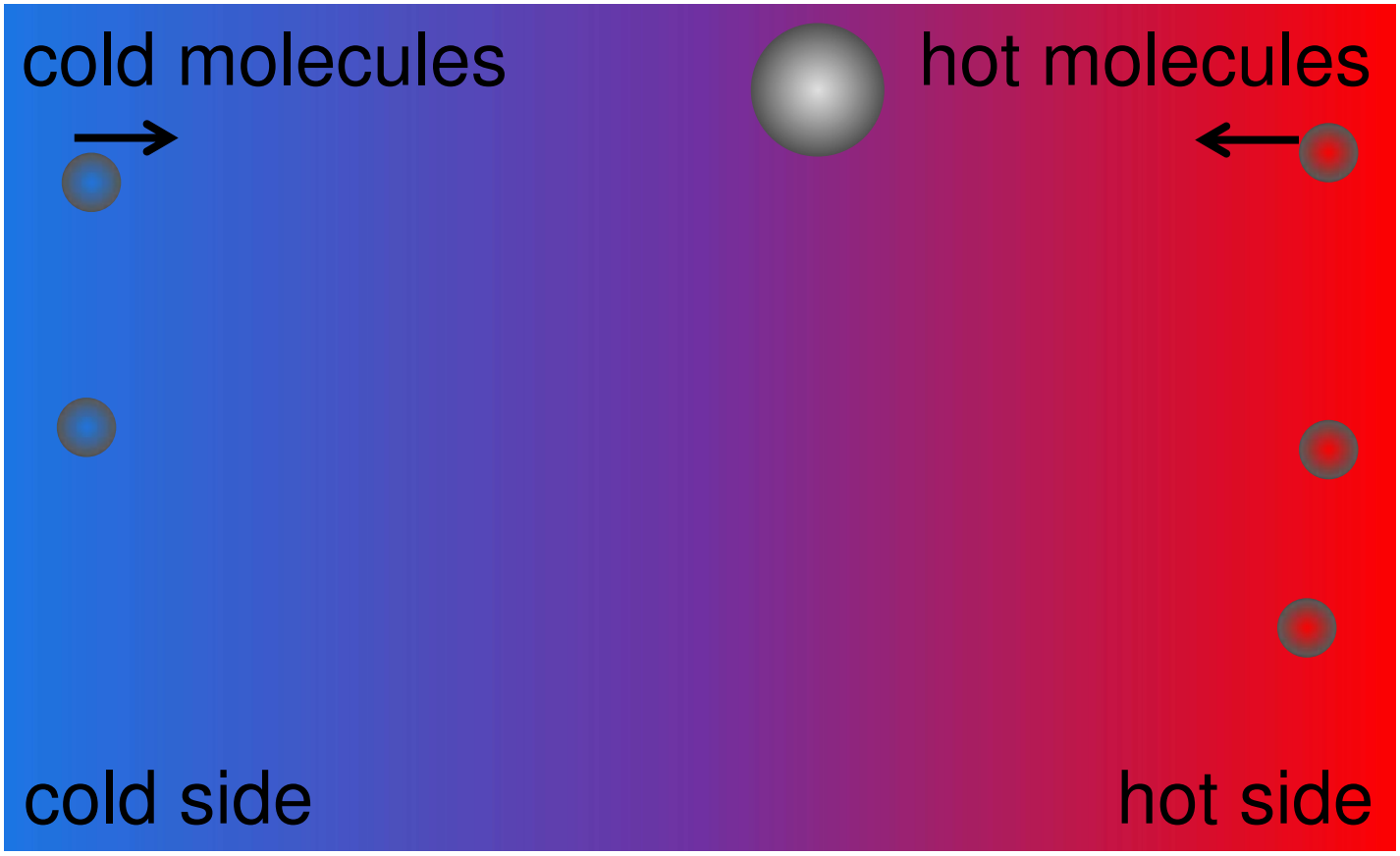
$$S_T = \frac{D_T}{D} \propto \frac{\Delta c}{\Delta T}$$



D - diffusion coefficient,
w - concentration,
D_T - thermodiffusion coeff.,

$\vec{j}$ – flux,
T – temperature,
S_T –Soret coefficient

Mass effect: animation

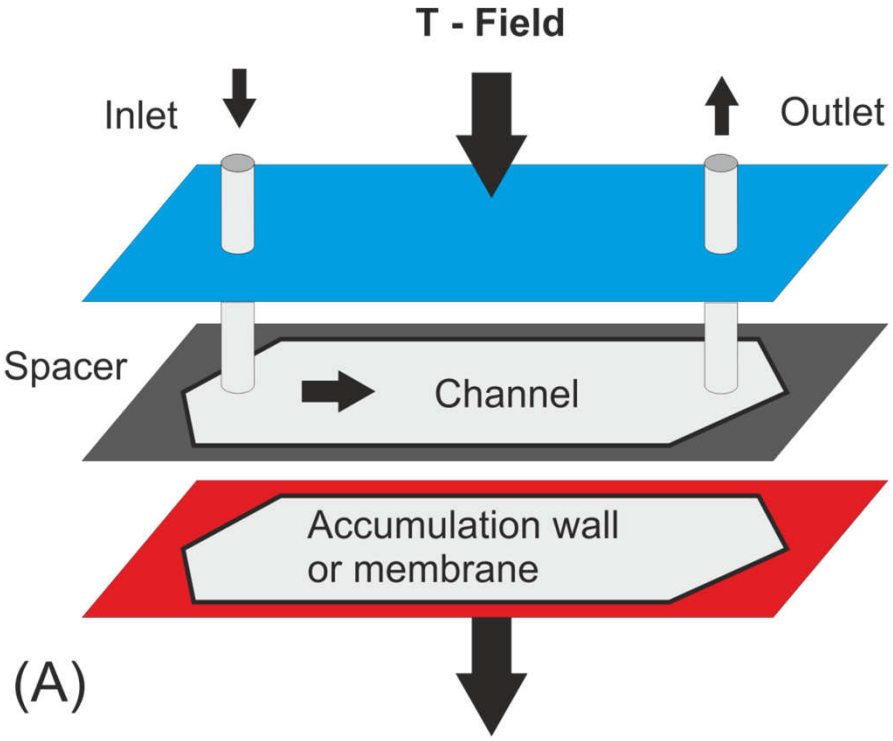


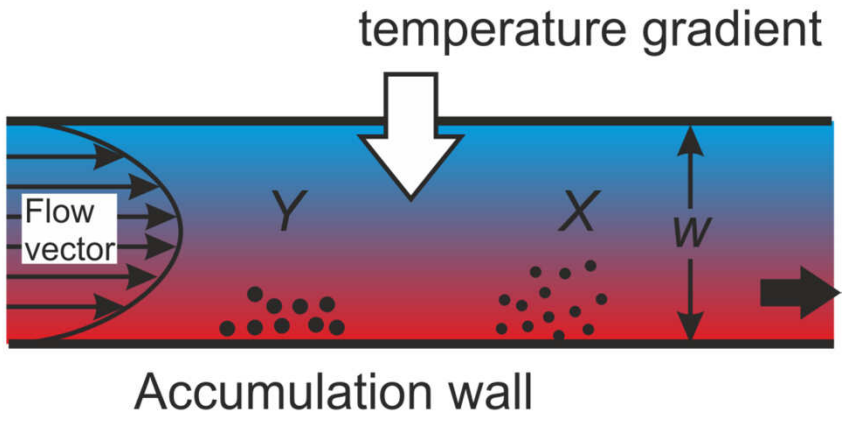
"kinetic gas model"
higher momentum transfer from the warm side

⇨ **Enrichment of the heavy particles on the cold side**

Thermophoresis: Where is it used?

Application examples: "Characterization of Soft Matter"
Thermal field flow fractionation

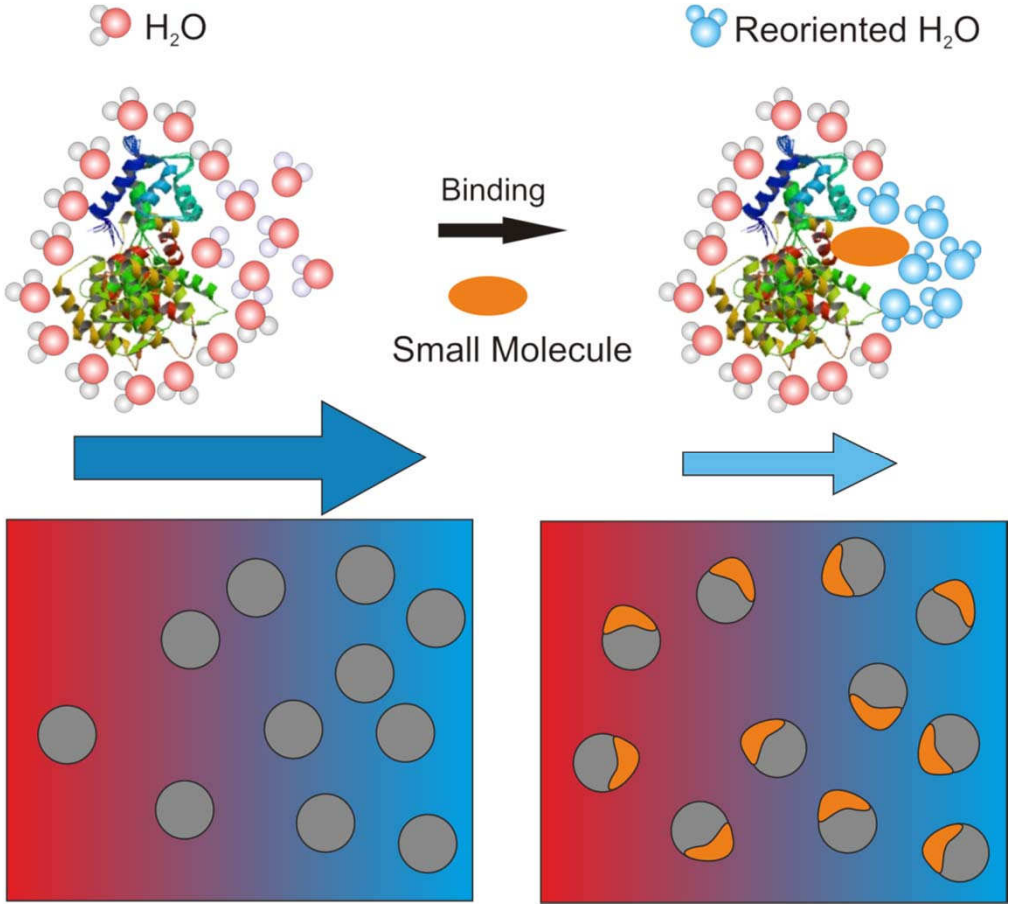




SW., *Introduction to thermal gradient related effects*, in *Functional Soft Matter*, J.K.G. Dhont, et al., Editors. 2015, Forschungszentrum Jülich: Jülich. p. F4.1-F4.24.

Thermophoresis: Where is it used?

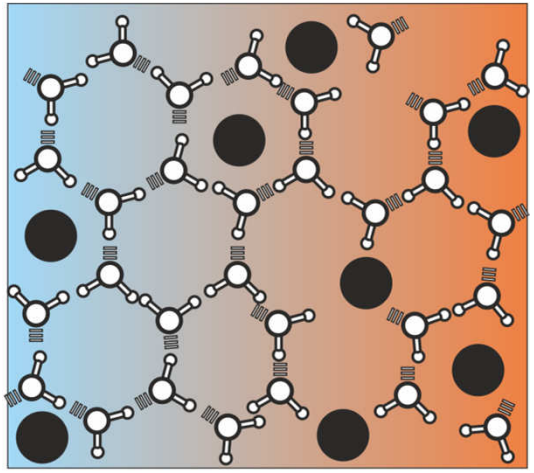
Application examples: “Biochemical reactions” Microscale thermophoresis



Microscale Thermophoresis: Technology and Applications
//NanoTemper GMBH

Hydrogen bonds: temperature effect

Assuming local thermodynamic equilibrium



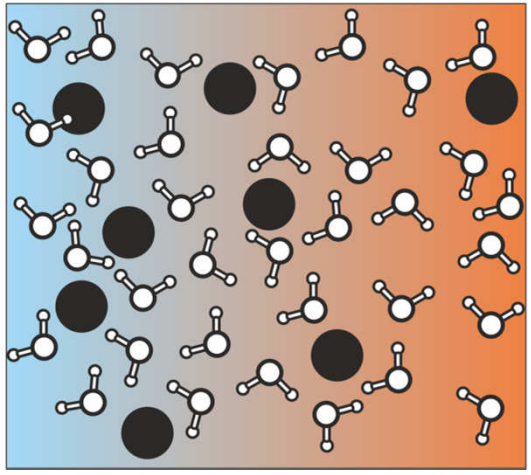
At low temperatures:

minimization of the free energy

$$F = U - TS$$

by forming hydrogen bonds ($\Delta U<0$).

→ water goes to the cold side



At high temperatures:

minimization of the free energy

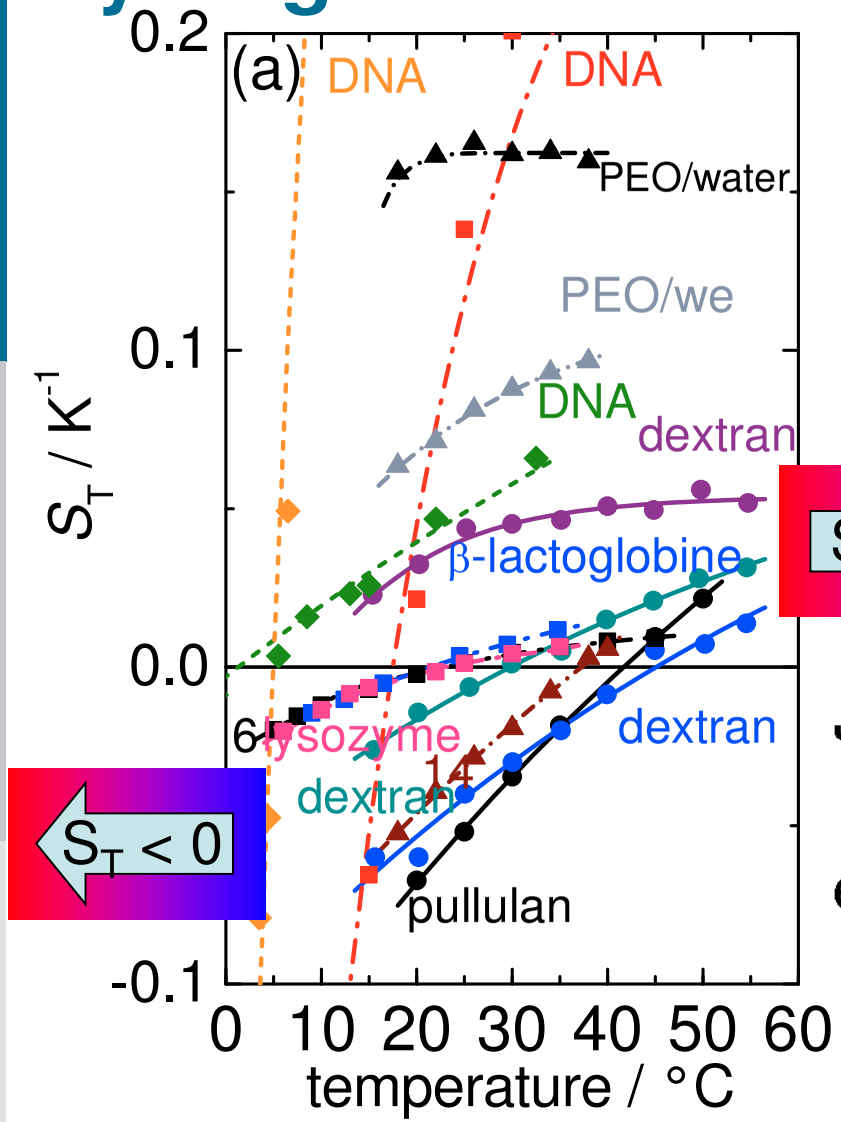
$$F = U - TS$$

by entropy production ($\Delta S>0$).

→ water goes to the warm side

[Wang, Z., H. Kriegs, and SW J. Phys. Chem. B, **116** (2012) 7463.]

Hydrogen bonds: temperature effect



Many, but not all aqueous systems show a similar temperature dependence

$$S_T(T) = S_T^{\infty}\left[1 - \exp\left(\frac{T^{\pm} - T}{T_0}\right)\right]$$

empirical parameter $S_T^{\infty}, T^{\pm}$ and T_0

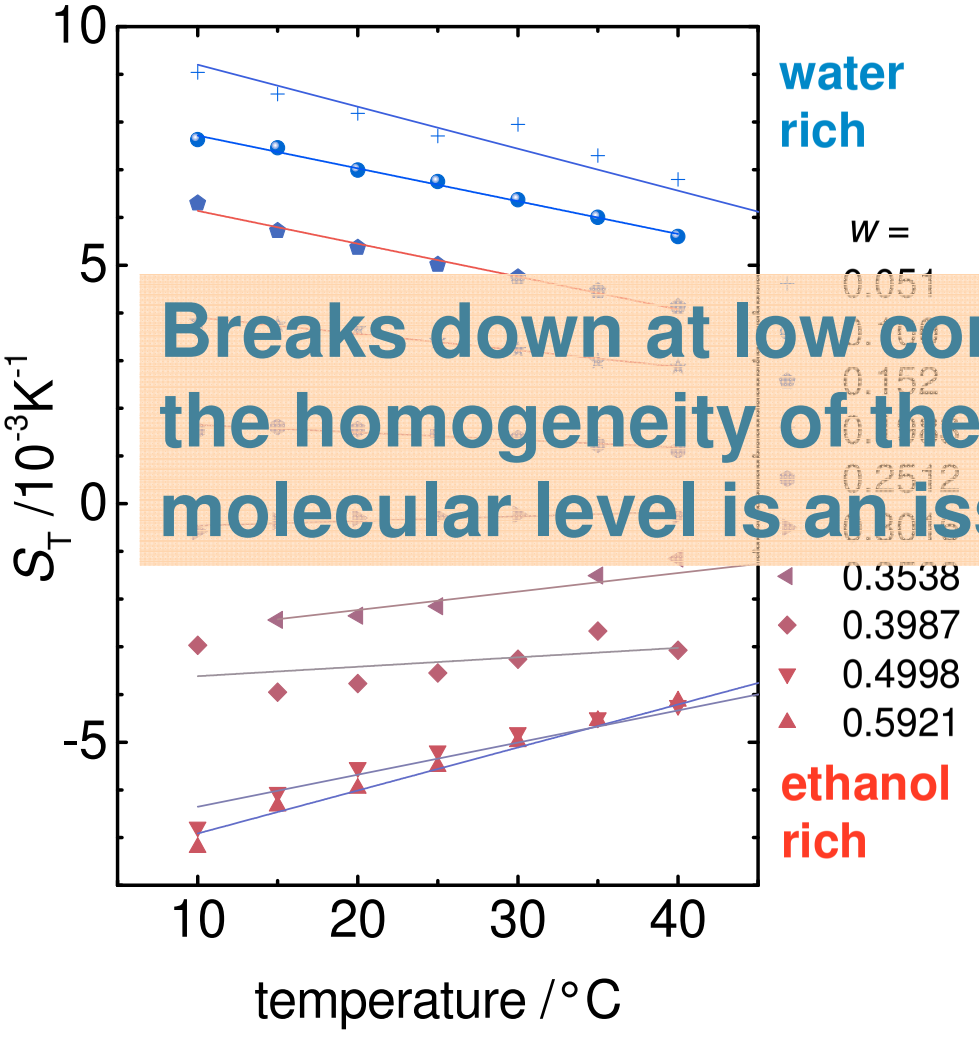
[Iacopini et al., Eur. Phys. J. E, **19**(2006) 59]

[Kishikawa, Y., SW, and R. Kita, Biomacromolecules, **11** (2010) 740]

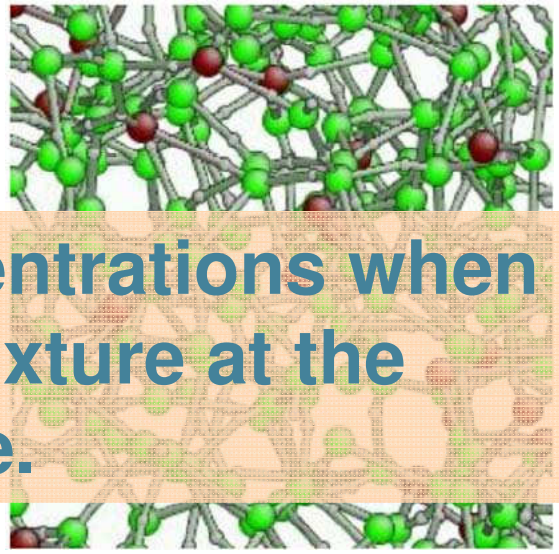
Validity of the empirical formula?

$$S_T(T) = S_\infty\left[1 - \exp\left(\frac{T_\pm - T}{T_0}\right)\right]$$

ethanol/water



Breaks down at low concentrations when the homogeneity of the mixture at the molecular level is an issue.



20 mol % ethanol

- "pure water rings are formed"
- **clumping** of like molecules

A. Königer, et al., Philos. Mag., **89** (2009) 907.

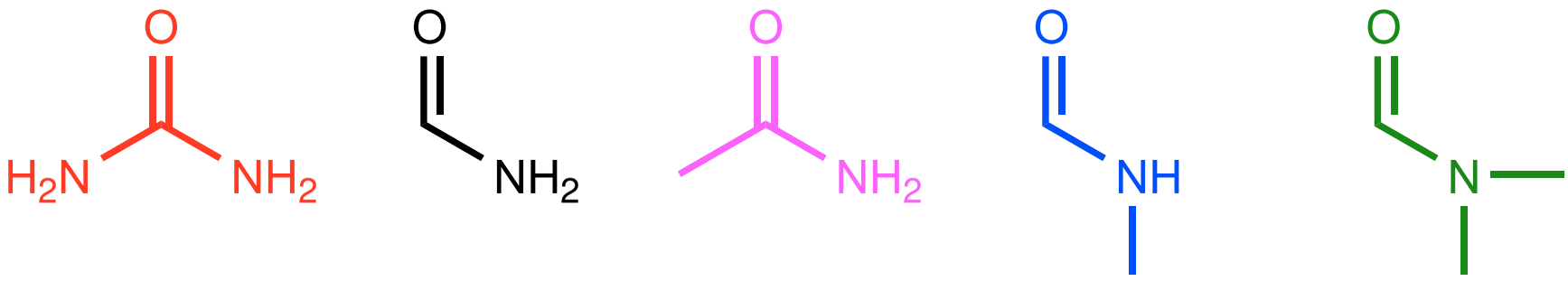
[O. Gereben, Journal of Molecular Liquids, 211 (2015) 812-820]

Systematic study of amides

Why amides? *".. serve as model of the peptide bond "*

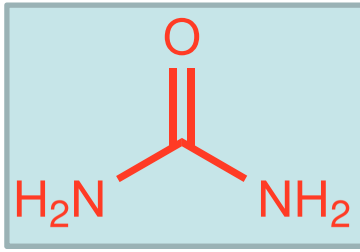
[Y. Lei et al. JPC A, **107** (2003) 1574]

Urea **Formamide** **Acetamide** **N-Methyl-formamide** **N,N-Dimethyl-formamide**



More hydrophilic

Temperature dependence



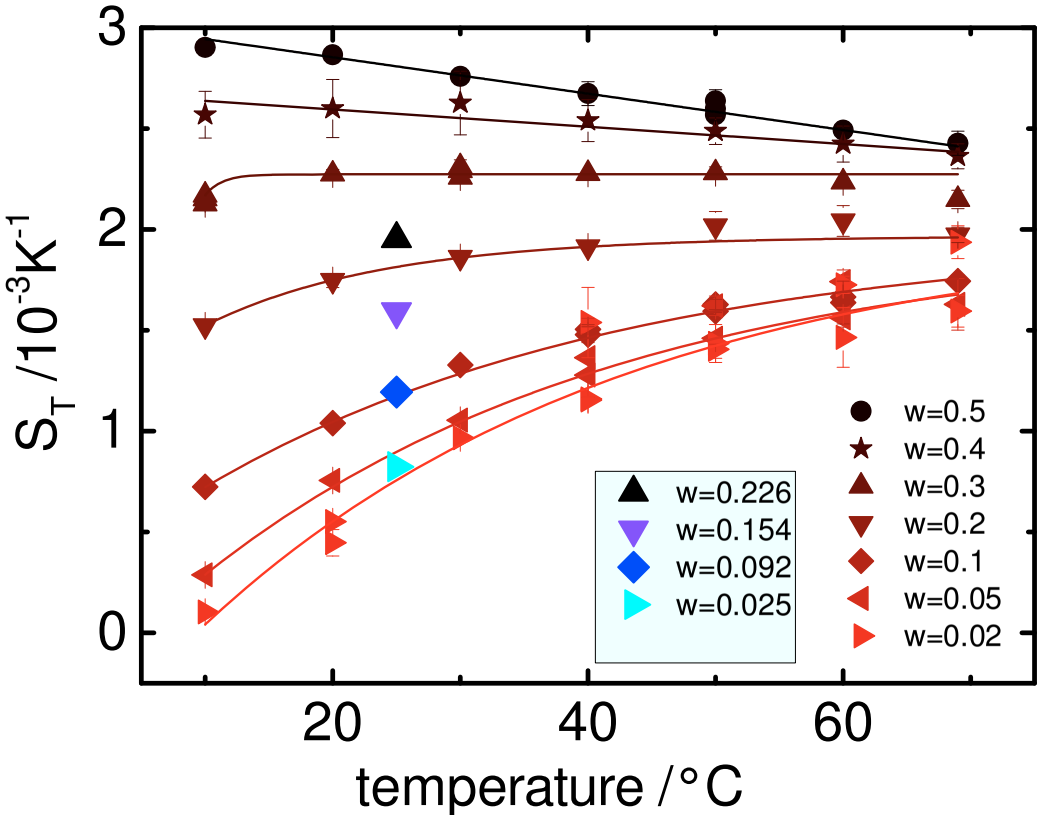
urea in water

- at low concentrations ($w \leq 0.3$):

$$S_T(T) = S_0\left[1 - \exp\left(\frac{T_\pm - T}{T_0}\right)\right]$$

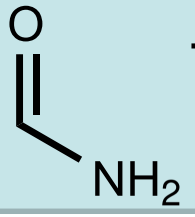
- more flexible fit function needed to describe T-dependence at higher concentrations:

$$S_T(T) = S_0 + a \cdot \exp(-b \cdot T)$$



[Story and Turner, Faraday Trans., 65 (1969) 1810]

Temperature dependence



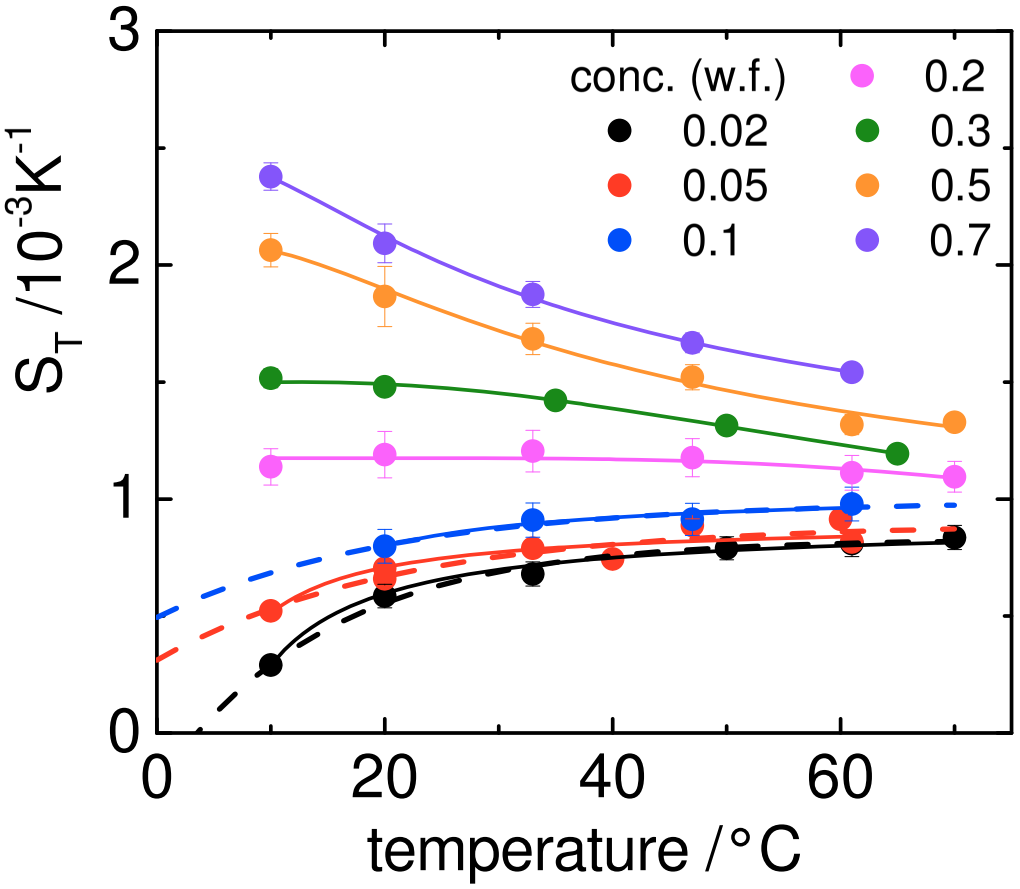
formamide in water

- at low concentrations (***w* < 0.2**):

$$S_T(T) = S_\infty \left[1 - \exp\left(\frac{T_\pm - T}{T_0}\right)\right]$$

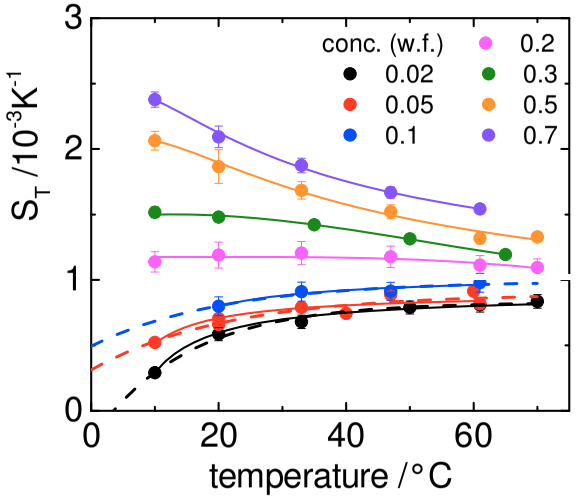
- more flexible fit function needed to describe T-dependence at higher concentrations:

$$S_T(T) = S_{T\infty} + a \cdot \exp(-b \cdot T)$$



[Niether, Afanasenkau, Dhont, SW, PNAS, **113**(2016) 4272]

Structural explanation



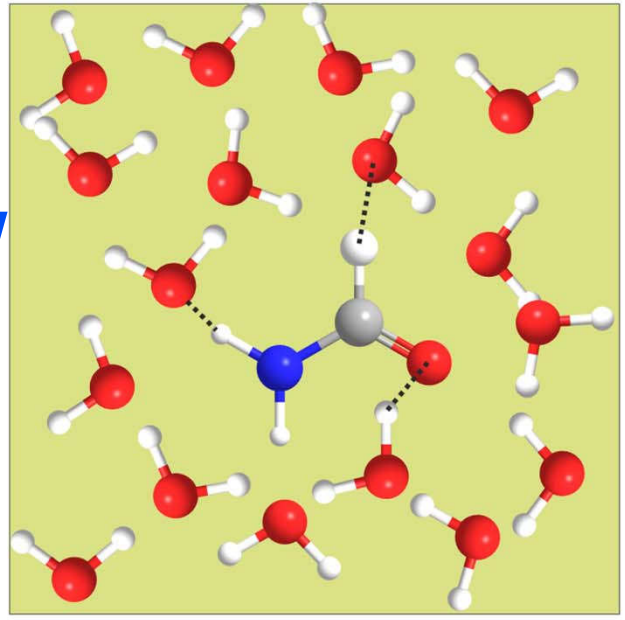
Molecular dynamic simulations
[Elola & Ladanyi, JCP 125,(2006) 184506]

conc. = ?

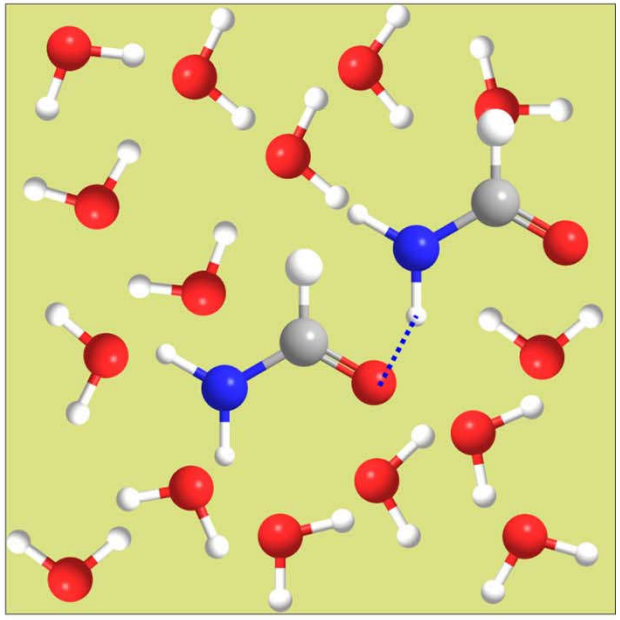
suggest the following picture:

low *w*

only FA-W hydrogen bonds



slope $S_T > 0$

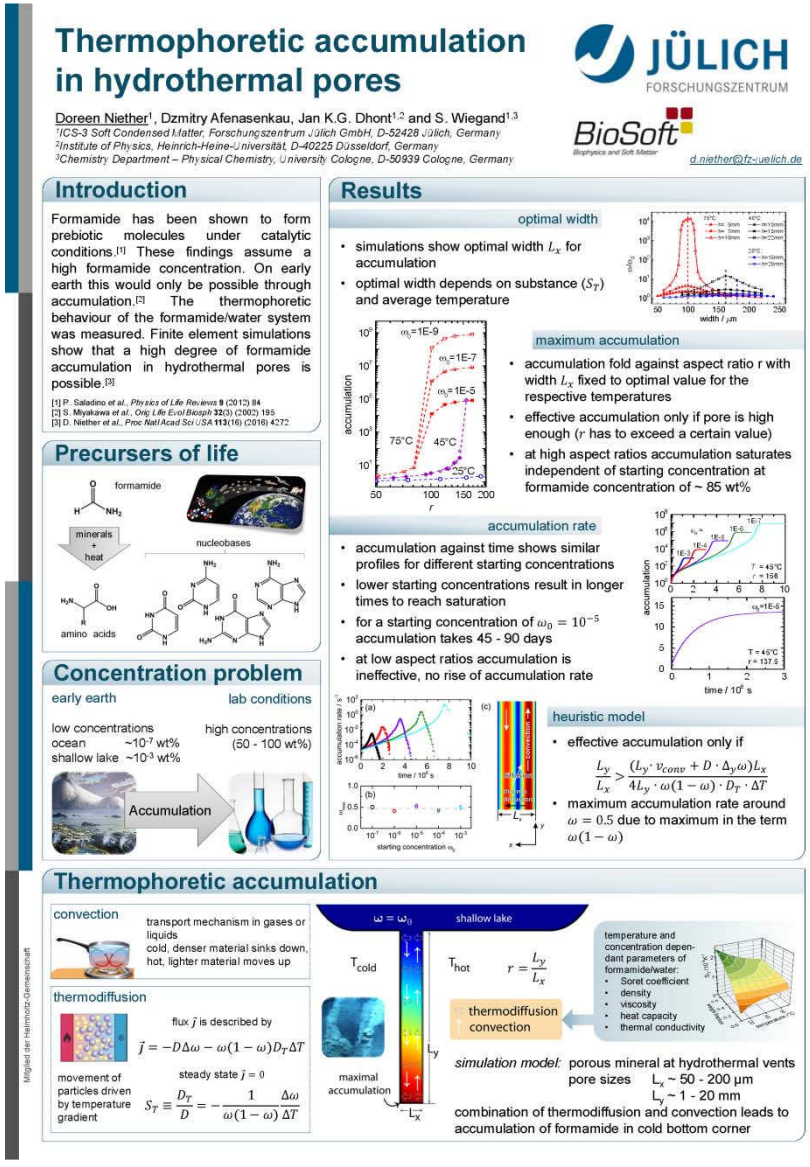


slope $S_T < 0$

higher *w*

also FA-FA hydrogen bonds

POSTER – P02-057



Thermophoretic accumulation in hydrothermal pores

Doreen Niether[1], Dzmitry Afenasenkau, Jan K.G. Dhont[1,2] and S. Wiegand[1,3]
[1]ICS-3 Soft Condensed Matter, Forschungszentrum Jülich GmbH, D-52428 Jülich, Germany
[2]Institute of Physics, Heinrich-Heine-Universität, D-40225 Düsseldorf, Germany
[3]Chemistry Department – Physical Chemistry, University Cologne, D-50939 Cologne, Germany
d.niether@fz-juelich.de

Introduction

Formamide has been shown to form prebiotic molecules under catalytic conditions.[1] These findings assume a high formamide concentration. On early earth this would only be possible through accumulation.[2] The thermophoretic behaviour of the formamide/water system was measured. Finite element simulations show that a high degree of formamide accumulation in hydrothermal pores is possible.[3]

[1] P. Saladino et al., Physics of Life Reviews 9 (2012) 84
[2] S. Miyakawa et al., Orig Life Evol Biosph 32(3) (2002) 195
[3] D. Niether et al., Proc Natl Acad Sci USA 113(16) (2016) 4272

Precursers of life

formamide
minerals + heat
nucleobases
amino acids

Concentration problem

early earth: low concentrations, ocean ~10^{-7} wt%, shallow lake ~10^{-3} wt%
lab conditions: high concentrations (50 - 100 wt%)
Accumulation

Results

optimal width

- simulations show optimal width L_x for accumulation
- optimal width depends on substance (S_T) and average temperature

maximum accumulation

- accumulation fold against aspect ratio r with width L_x fixed to optimal value for the respective temperatures
- effective accumulation only if pore is high enough (r has to exceed a certain value)
- at high aspect ratios accumulation saturates independent of starting concentration at formamide concentration of ~ 85 wt%

accumulation rate

- accumulation against time shows similar profiles for different starting concentrations
- lower starting concentrations result in longer times to reach saturation
- for a starting concentration of $\omega_0 = 10^{-5}$ accumulation takes 45 - 90 days
- at low aspect ratios accumulation is ineffective, no rise of accumulation rate

heuristic model

- effective accumulation only if $\frac{L_y}{L_x} > \frac{(L_y \cdot v_{conv} + D \cdot \Delta_y \omega) L_x}{4 L_y \cdot \omega(1-\omega) \cdot D_T \cdot \Delta T}$
- maximum accumulation rate around $\omega = 0.5$ due to maximum in the term $\omega(1-\omega)$

Thermophoretic accumulation

convection
transport mechanism in gases or liquids
cold, denser material sinks down, hot, lighter material moves up

thermodiffusion
flux $\vec{j}$ is described by $\vec{j} = -D\Delta\omega - \omega(1-\omega)D_T\Delta T$
movement of particles driven by temperature gradient
steady state $\vec{j} = 0$
$S_T \equiv \frac{D_T}{D} = -\frac{1}{\omega(1-\omega)} \frac{\Delta\omega}{\Delta T}$

$\omega = \omega_0$ shallow lake
T_{cold} T_{hot} $r = \frac{L_y}{L_x}$
maximal accumulation
thermodiffusion
convection
temperature and concentration dependant parameters of formamide/water:
- Soret coefficient
- density
- viscosity
- heat capacity
- thermal conductivity

simulation model: porous mineral at hydrothermal vents
pore sizes L_x ~ 50 - 200 µm
L_y ~ 1 - 20 mm
combination of thermodiffusion and convection leads to accumulation of formamide in cold bottom corner

Mitglied der Helmholtz-Gemeinschaft

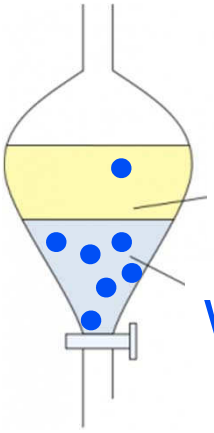
A way to achieve sufficiently high formamide concentrations to form prebiotic nucleobases under early earth conditions

by

Doreen Niether

„log *P*“ a „Scale bar“ for hydrogen bonding strength?

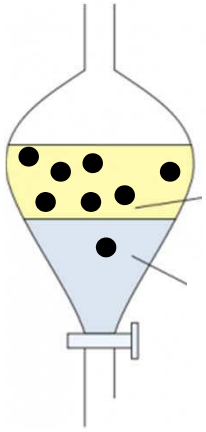
$$\log P = \log\left(\frac{[solute]_{octanol}}{[solute]^{unionized}_{water}}\right)$$



octanol

water

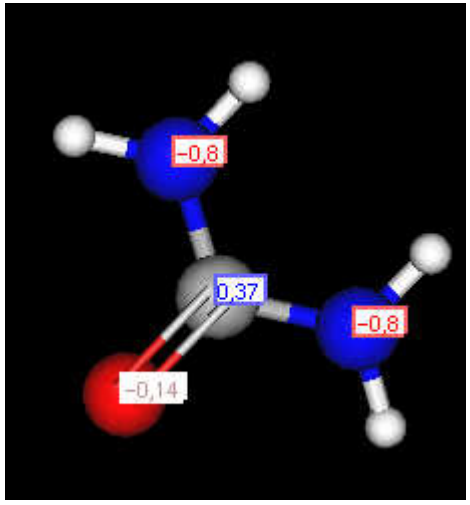
Hydrophilic compound: log $P < 0$

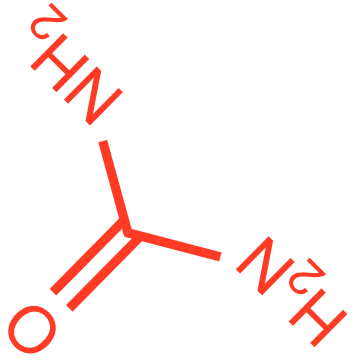


Hydrophobic compound: log $P > 0$

octanol

water





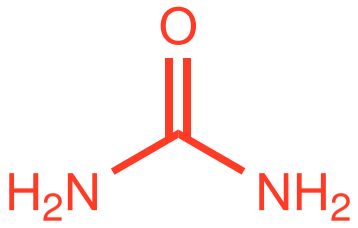
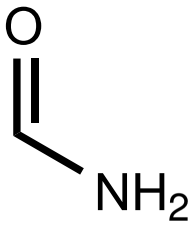
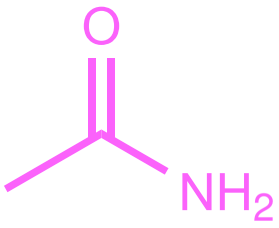
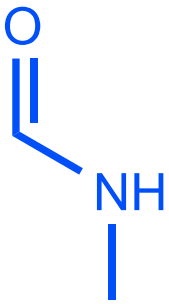
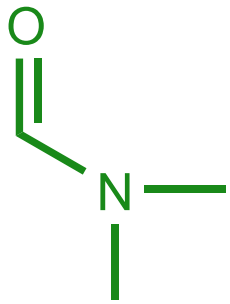
urea

Marvin 16.5.2.0, 2016, ChemAxon (http://www.chemaxon.com)

G. Klopman *et al.* J Chem Inf Comp Sci, **34** (1994) 752-781.

V. N. Viswanadhan et al. J Chem Inf Comp Sci, **29** (1989) 163-172.

„log *P*“ a „Scale bar“ for hydrogen bonding strength?

Urea	Formamide	Acetamide	N-Methyl-formamide	N,N-Dimethyl-formamide
				
Log *P* =				
-1.30	-1.13	-1.03	-0.89	-0.64

Marvin 16.5.2.0, 2016, ChemAxon (http://www.chemaxon.com)

„log *P*“ a „Scale bar“ for polar solvents ?

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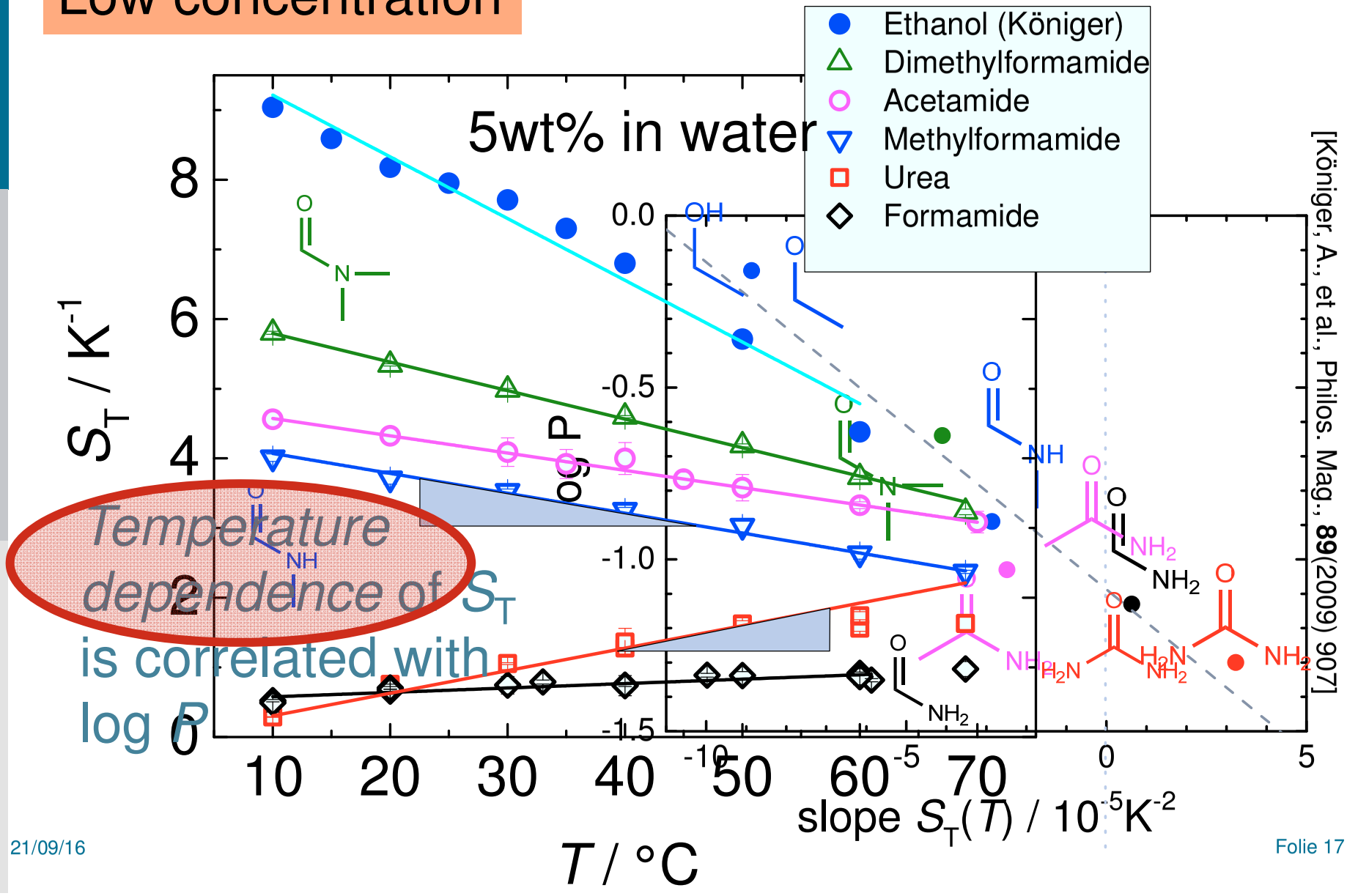
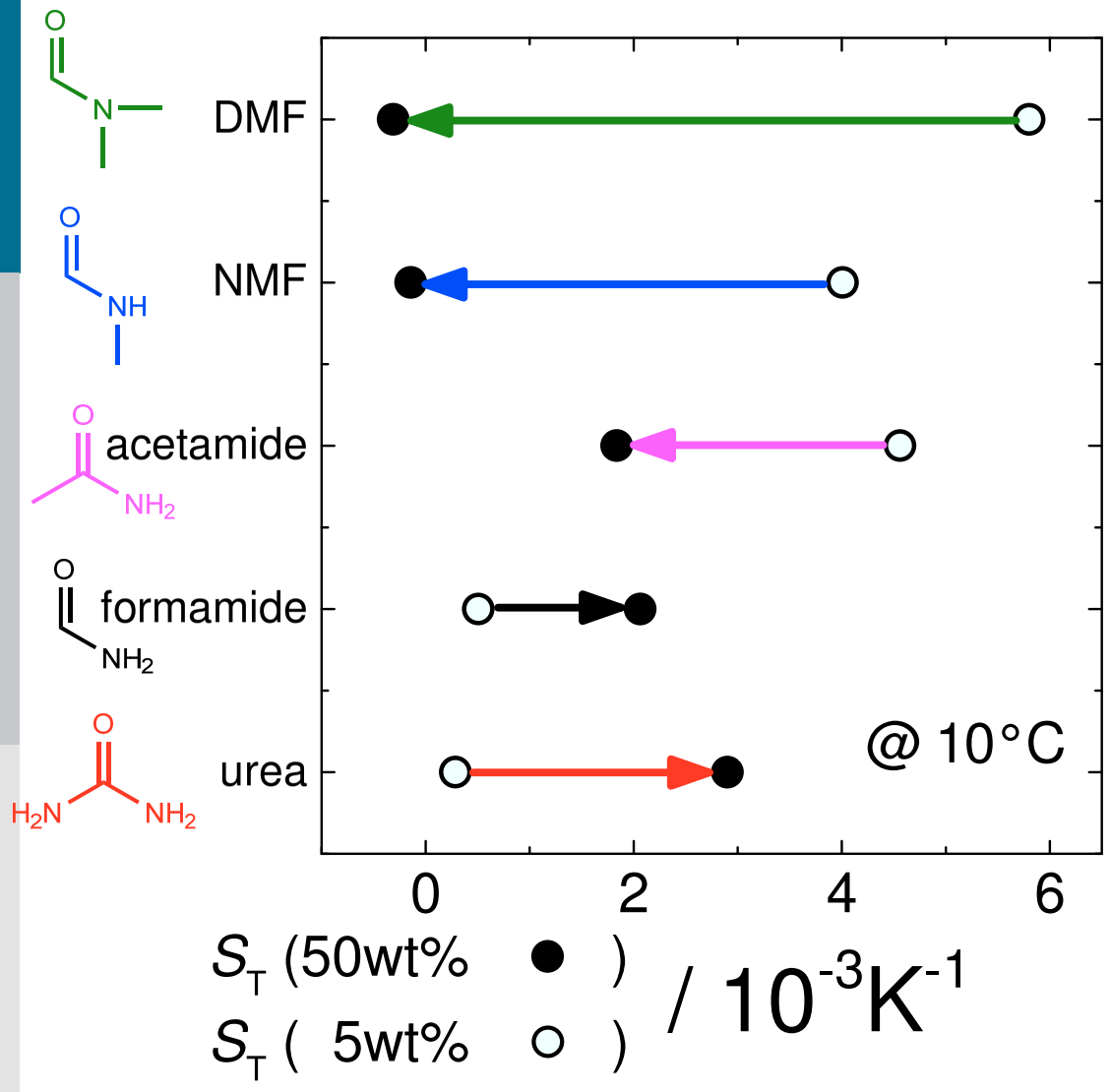
Low concentration



Temperature dependence of S_T is correlated with log *P*

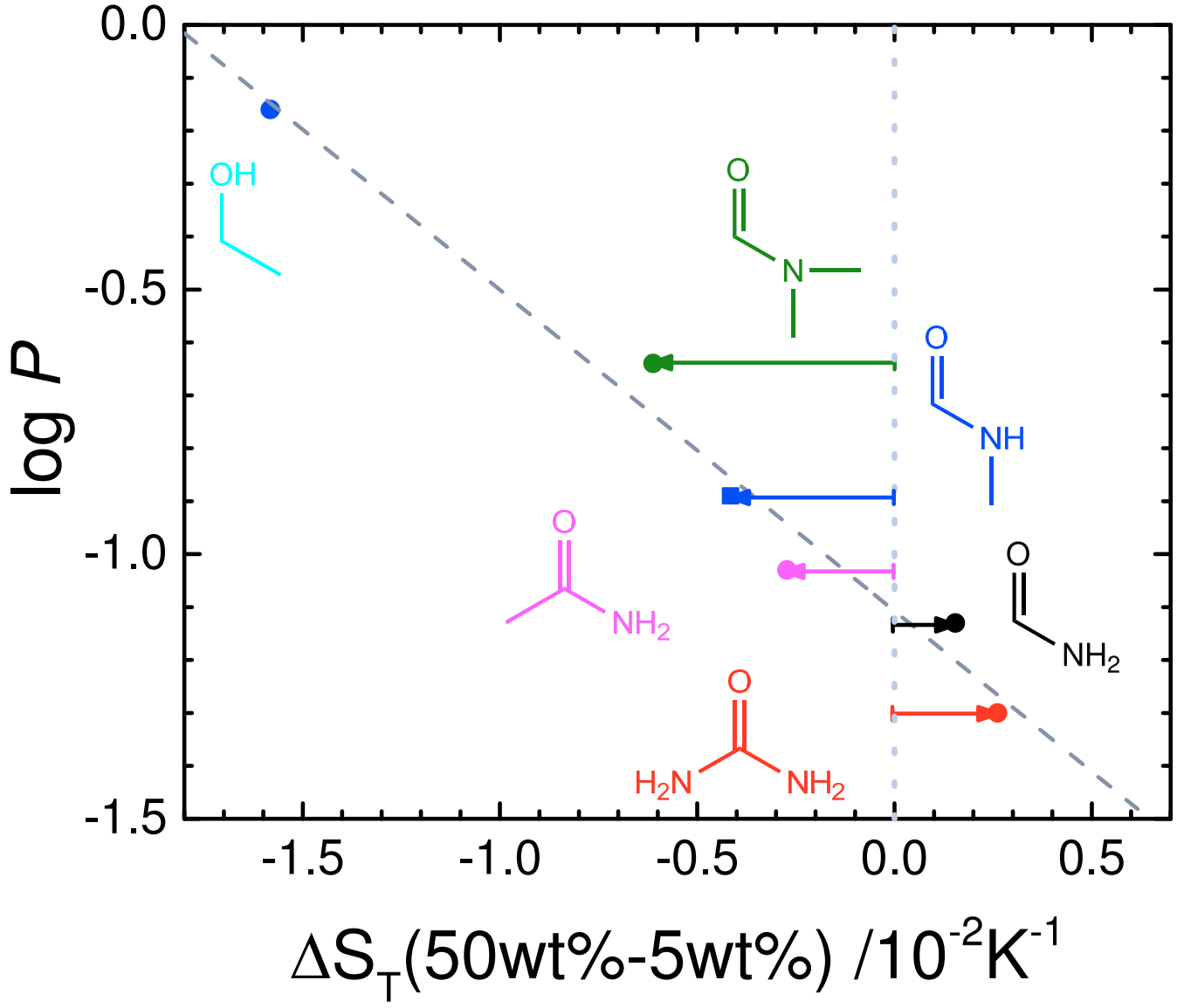
Comparison: low and high concentration



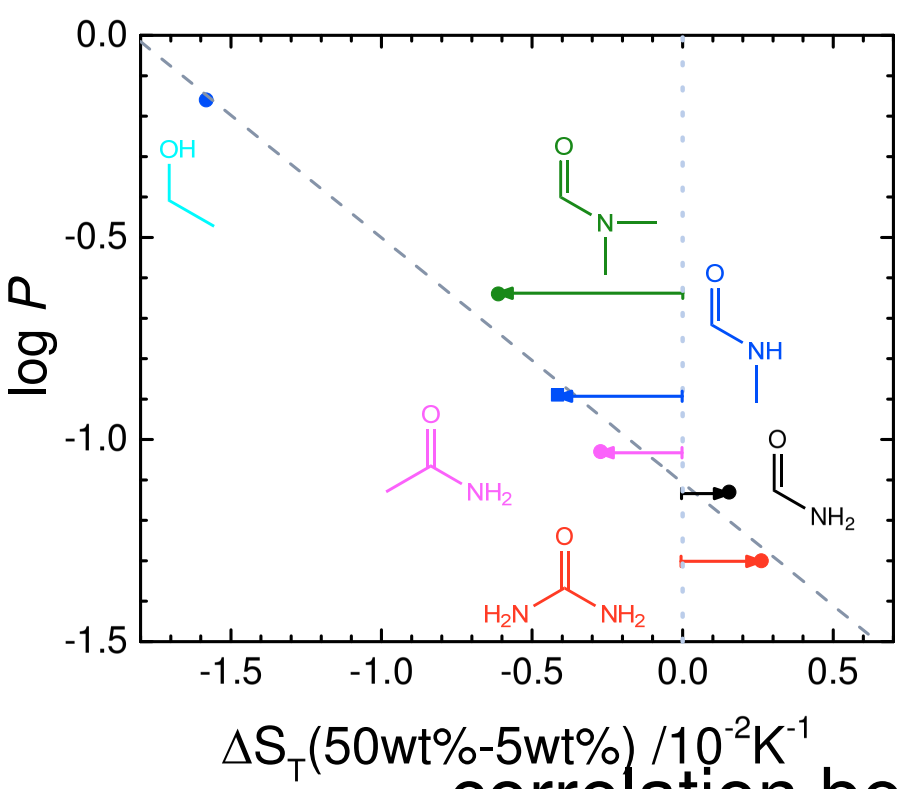
hydrophobic systems: increasing concentration: solute becomes more thermophilic

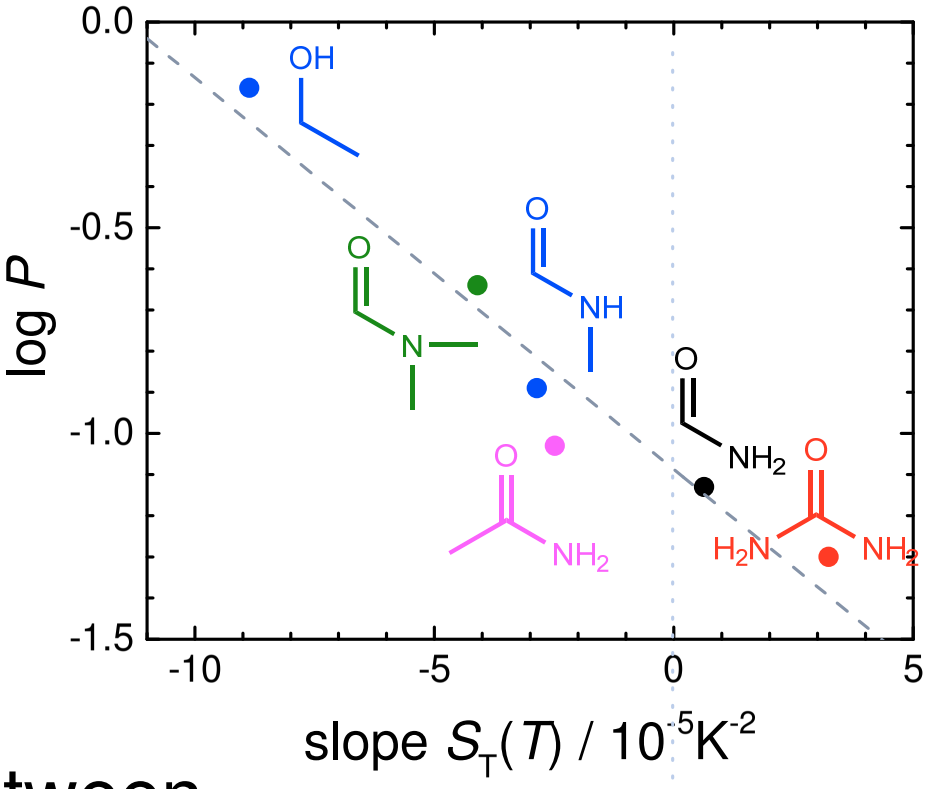
hydrophilic systems: increasing concentration: solute becomes more thermophobic

„log p“ scales S_T change with concentration



„log p“ scales ΔS_T inrespect to *c* and *T*





correlation between

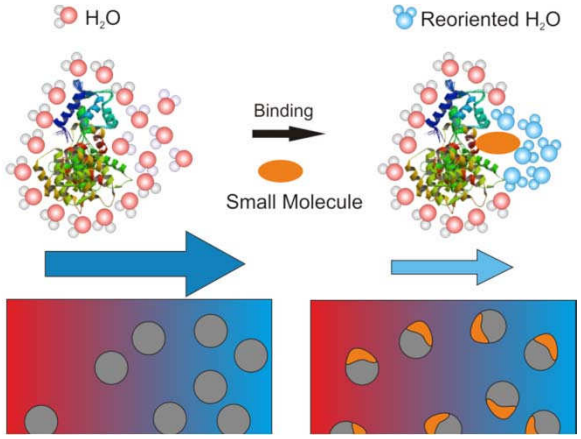
log *P* and the **change of S_T** with

… **concentration**

… **temperature**

Take home message

Thermophoresis is sensitive to changes of the hydration layer

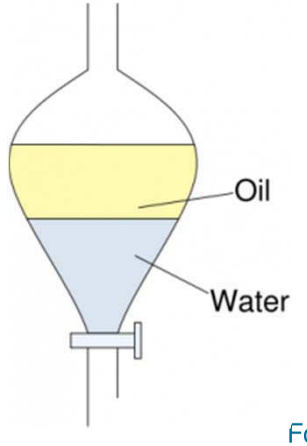


$$S_T(T) = S_{\infty}\left[1 - \exp\left(\frac{T_{\pm} - T}{T_0}\right)\right]$$

- breaks down at high ***w***
- breaks down at low ***w***
- due to inhomogeneities

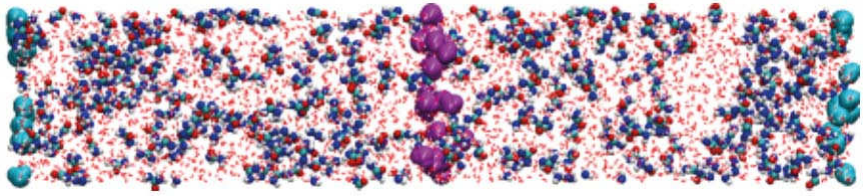
Log *P* correlates with temperature dependence of S_T

Log *P* correlates with concentration change of S_T

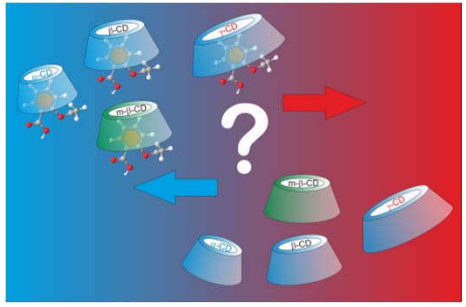


Thanks to many people and …

FZ Jülich
Jan Dhont‘s group
(ICS-3)



Fernando Bresme‘s group
Silvia di Lecce
Imperial College London, GB

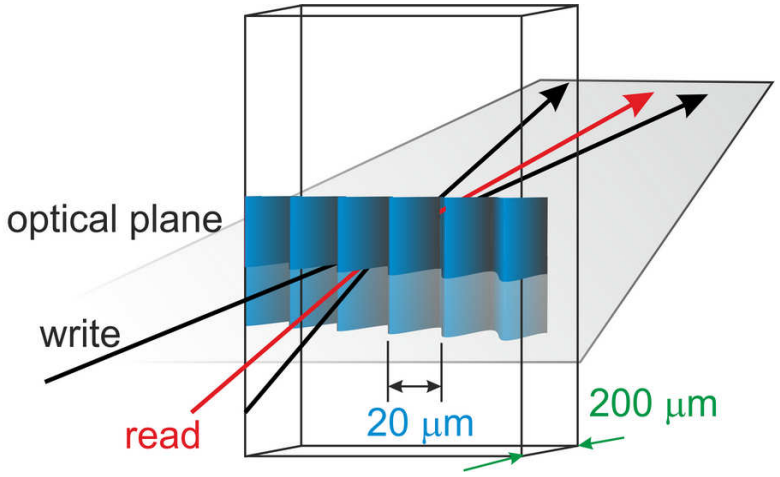


Rio Kita‘s lab
Kazuya Eguchi
Tokai University, Japan

EUROPEAN SOFT MATTER INFRASTRUCTURE

… thank you for your attention

How do we measure?



IR-TDFRS – **I**nfra**R**ed -**T**hermal **D**iffusion **F**orced **R**ayleigh **S**cattering

Advantages:

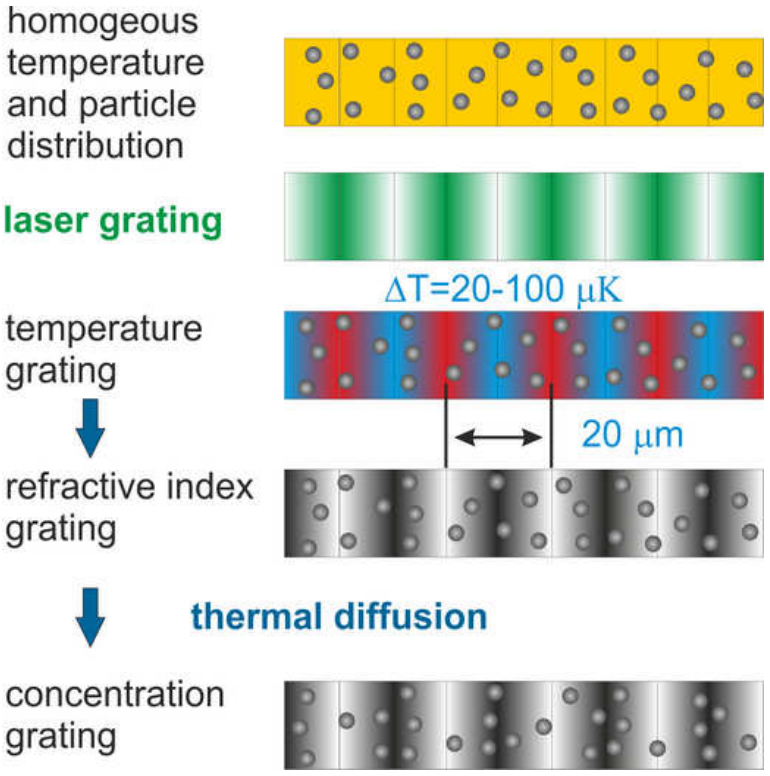
- small ΔT
- no fluorescent labeling required
- wide molecular range

Disadvantages:

- buffer solutions: difficult
- colloids >100 nm: difficult.

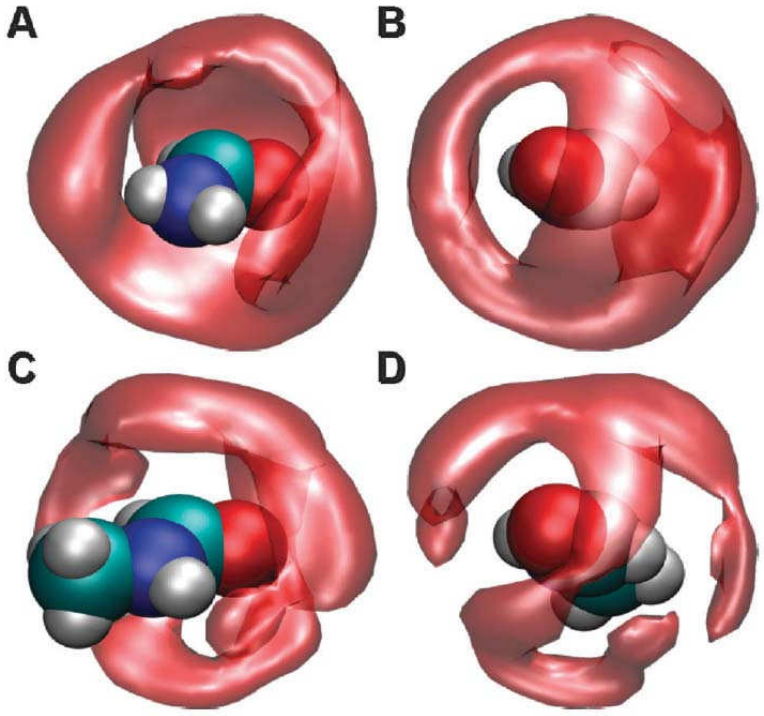
Typical gradients: 1K/m

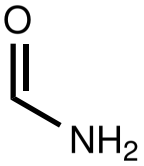
Measured quantity: Intensity of the diffracted beam



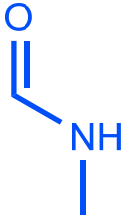
[SW *et al.*, J. Phys. Chem. B, **111**(2007) 14169]

Formamide vs. *N*-methylformamide





formamide

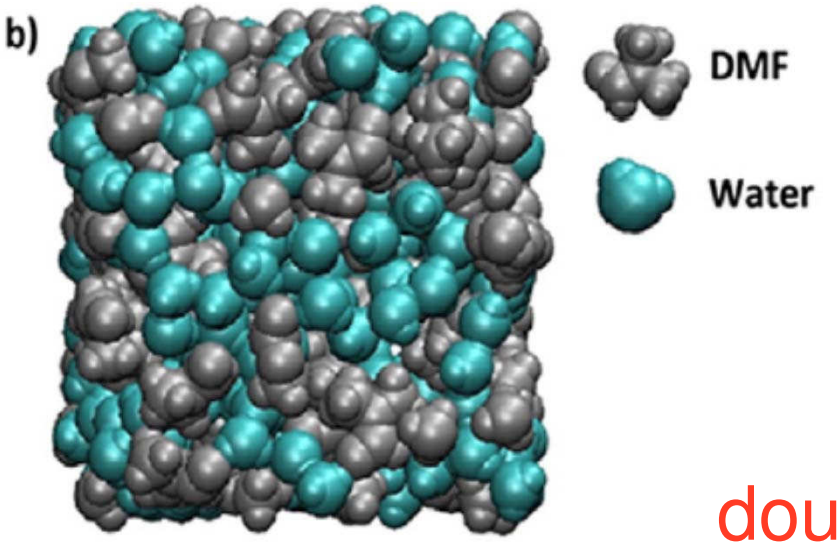


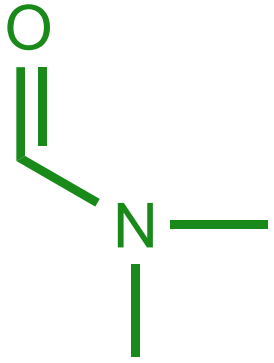
methyl-
formamide

"Whereas formamide is almost encaged by the oxygen density, the influence of the methyl group disrupts this pattern rigorously"

[A. K. H. Weiss, et al. PCCP, **13** (2011) 12173]

Dimethylformamide/water





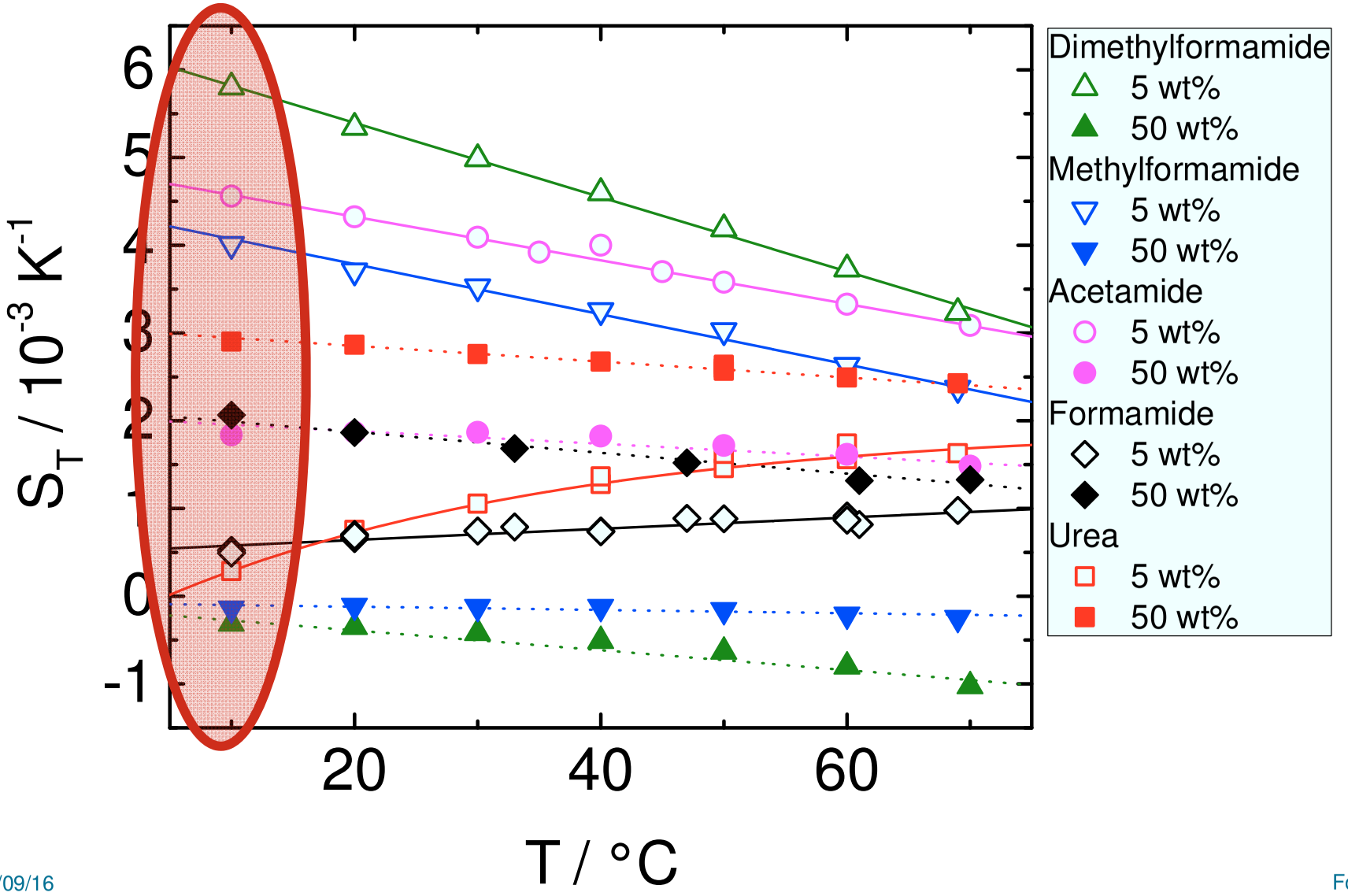
dimethyl-
formamide

doubts about the Force field ?

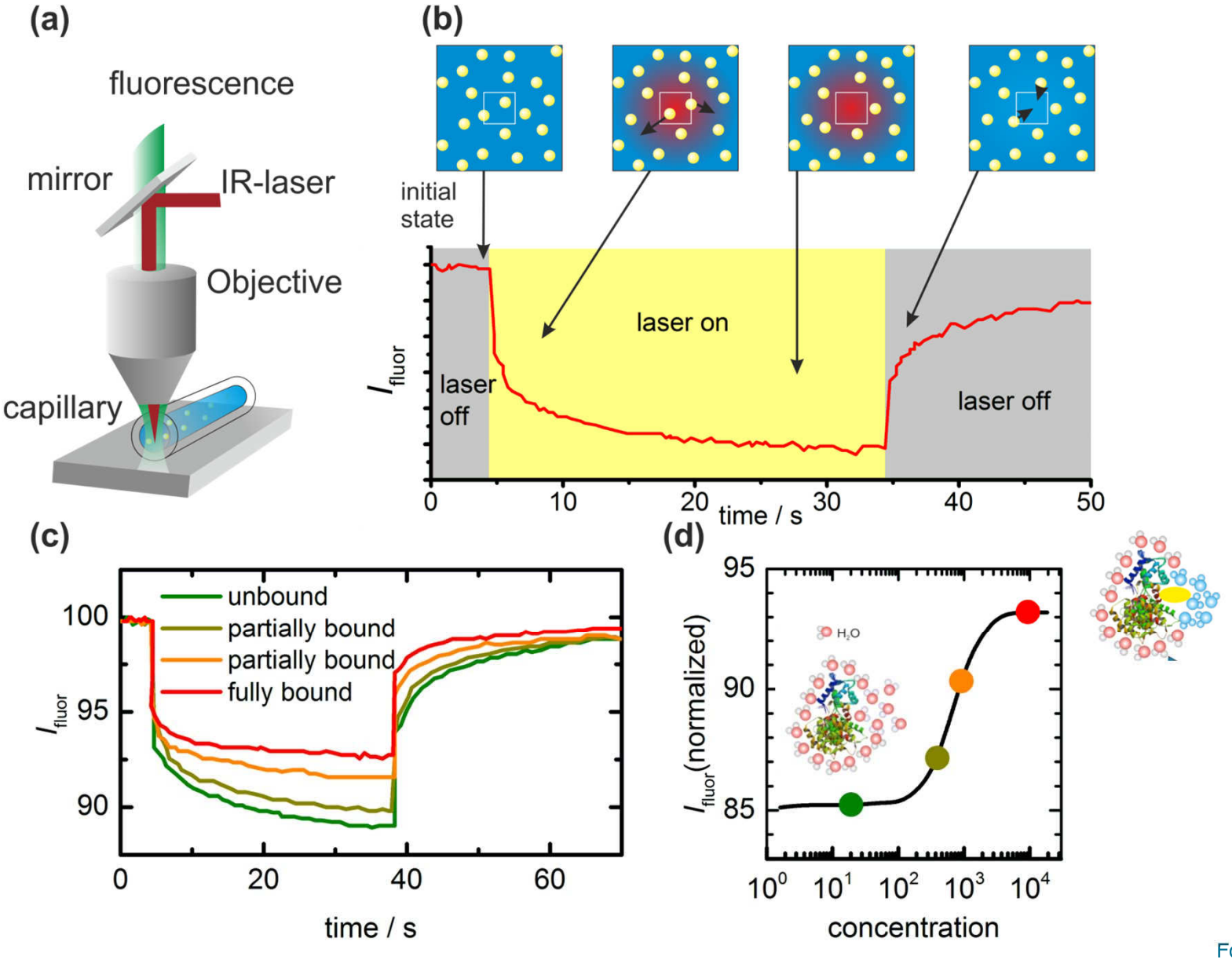
"The increases in the peaks of RDFs between water molecules are not so much caused by an increase in the structure of water as they are by the tendency of water to remain in aggregates in the mixtures."

[Lei, Y., et al., JPC A, **107**(2003) 1574
Vasudevan, V. and S.H. Mushrif, J. Mol. Liq., **206**(2015) 338]

Comparison: low and high concentration



Principle Microscale thermophoresis



SW., *Introduction to thermal gradient related effects*, in *Functional Soft Matter*, J.K.G. Dhont, et al., Editors. 2015, Forschungszentrum Jülich: Jülich. p. F4.1-F4.24.