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JÜLICH
FORSCHUNGSZENTRUM

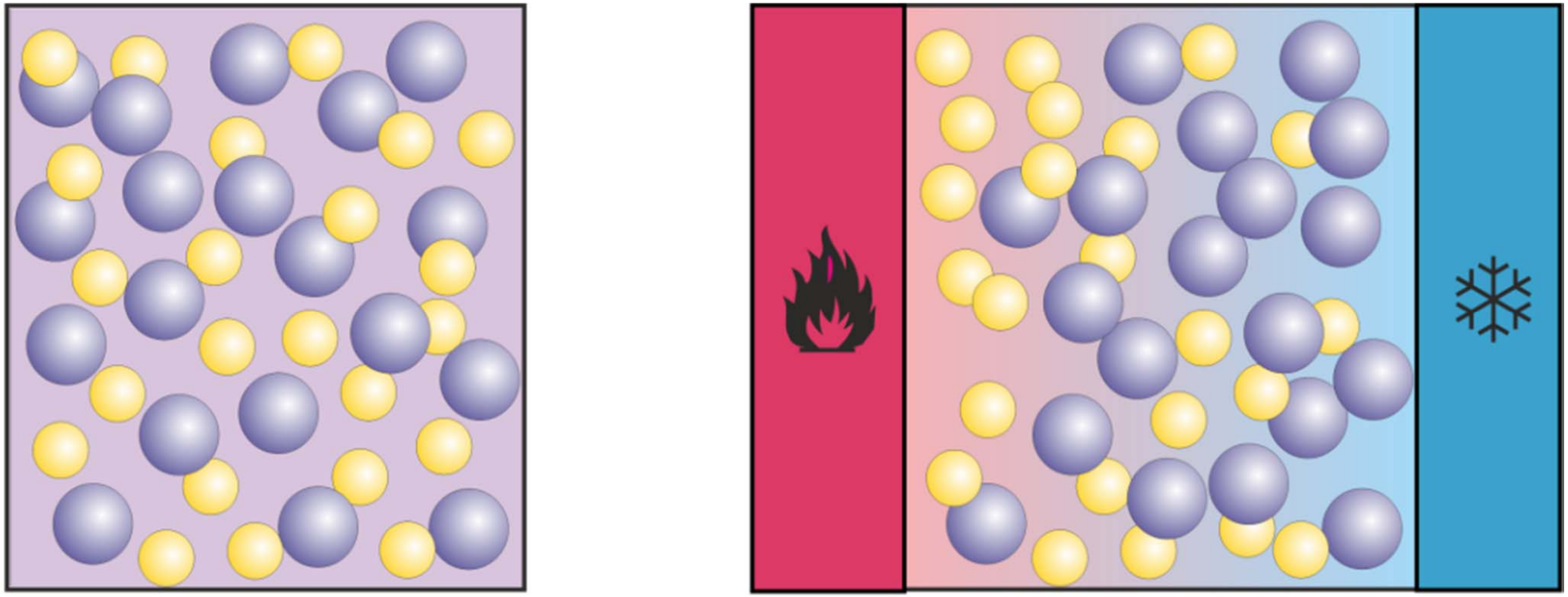
How do hydrogen bonds influence thermophoresis?

21. September 2016| **Simone Wiegand**,

Doreen Niether, Jan K.G. Dhont

Thermophoresis – the effect

(…, thermodiffusion, Soret effect)



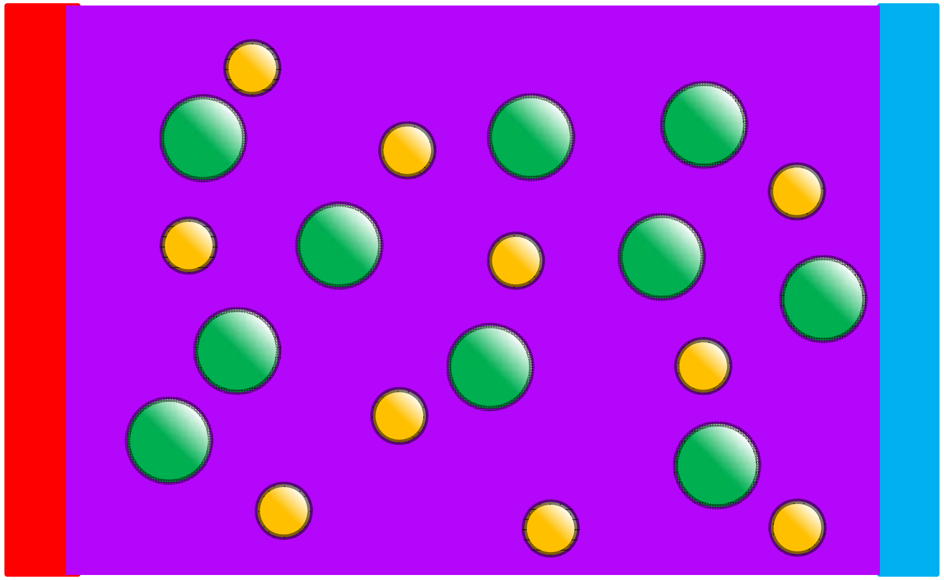
⇨ **No microscopic understanding**

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,

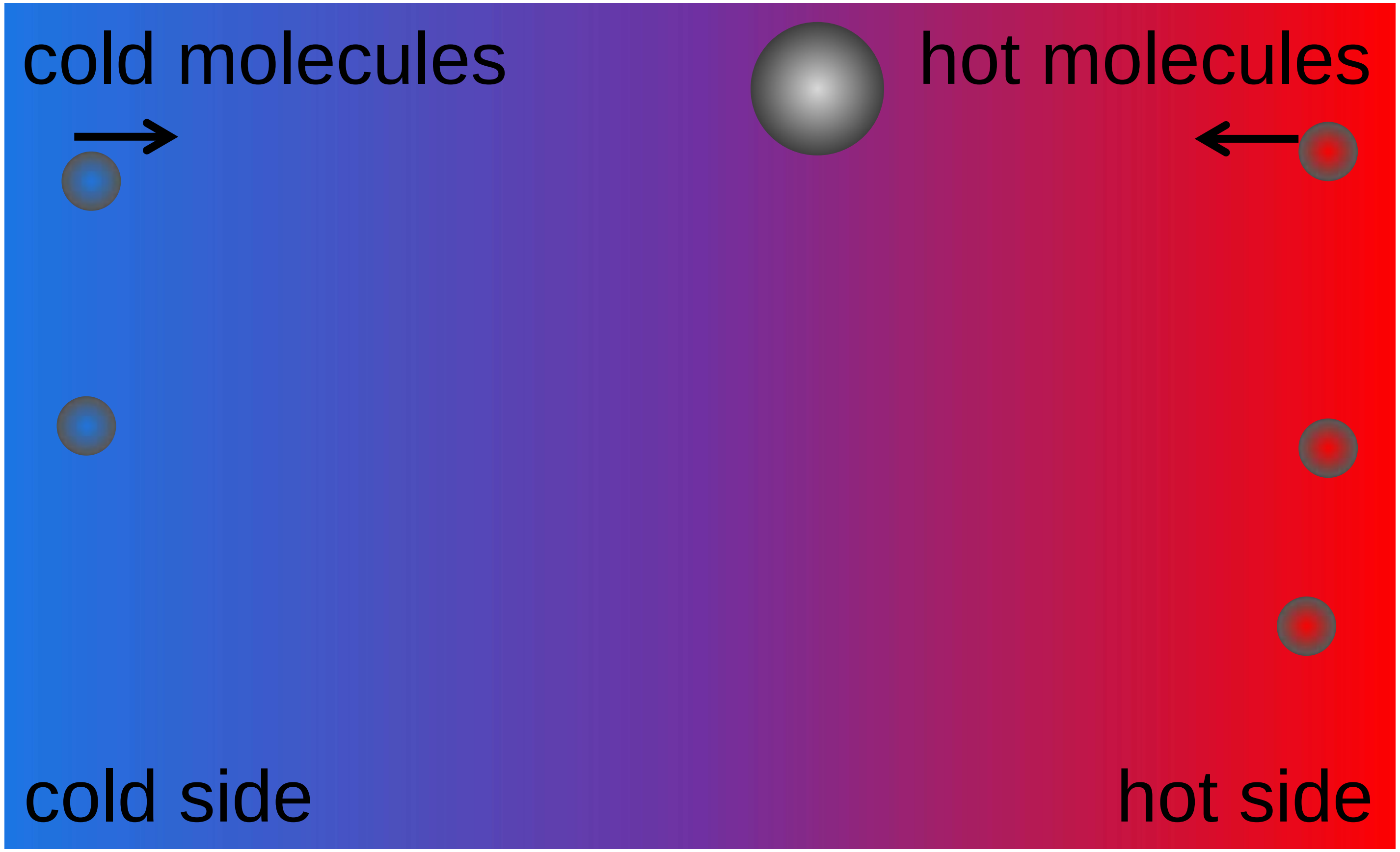
D_T - thermodiffusion coeff.,

$\vec{j}$ – flux,

T – temperature,

S_T –Soret coefficient

Mass effect: animation



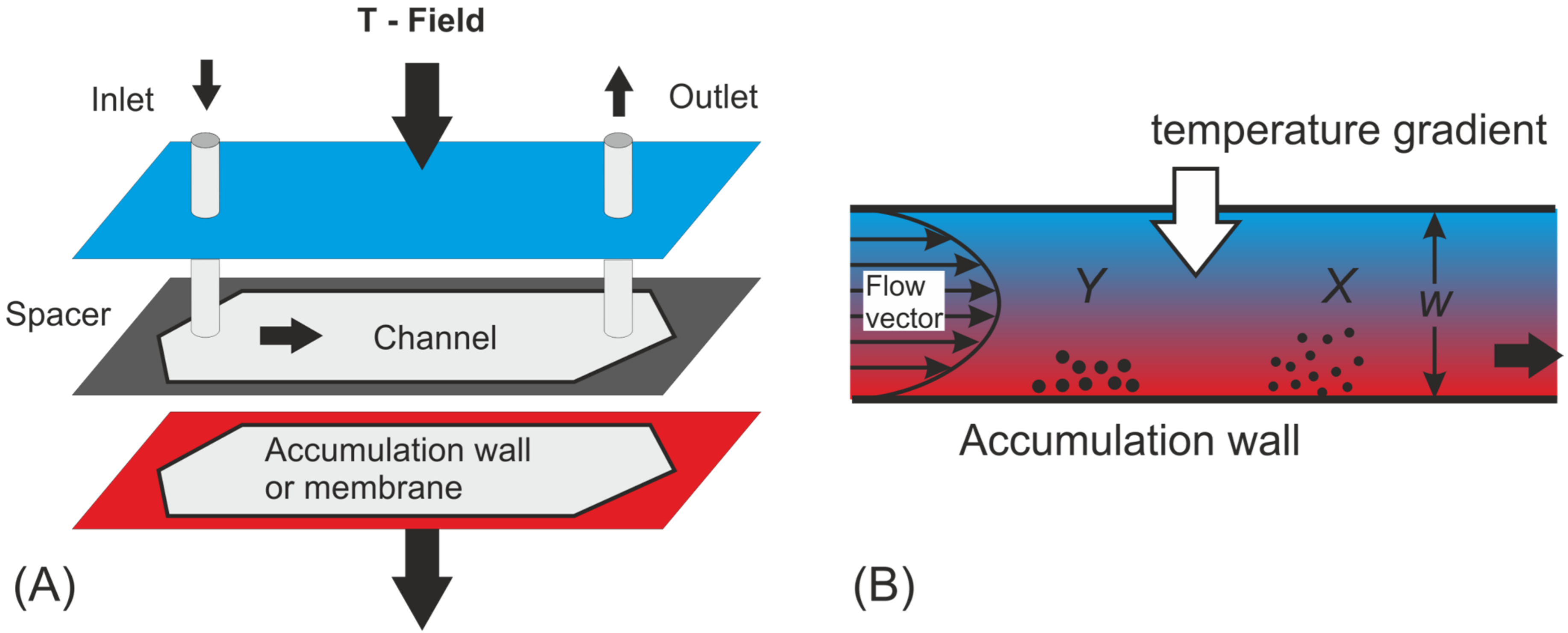
"kinetic gas model"
higher momentum transfer from the warm side

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

Thermophoresis: Where is it used?

Application examples: "Characterization of Soft Matter"

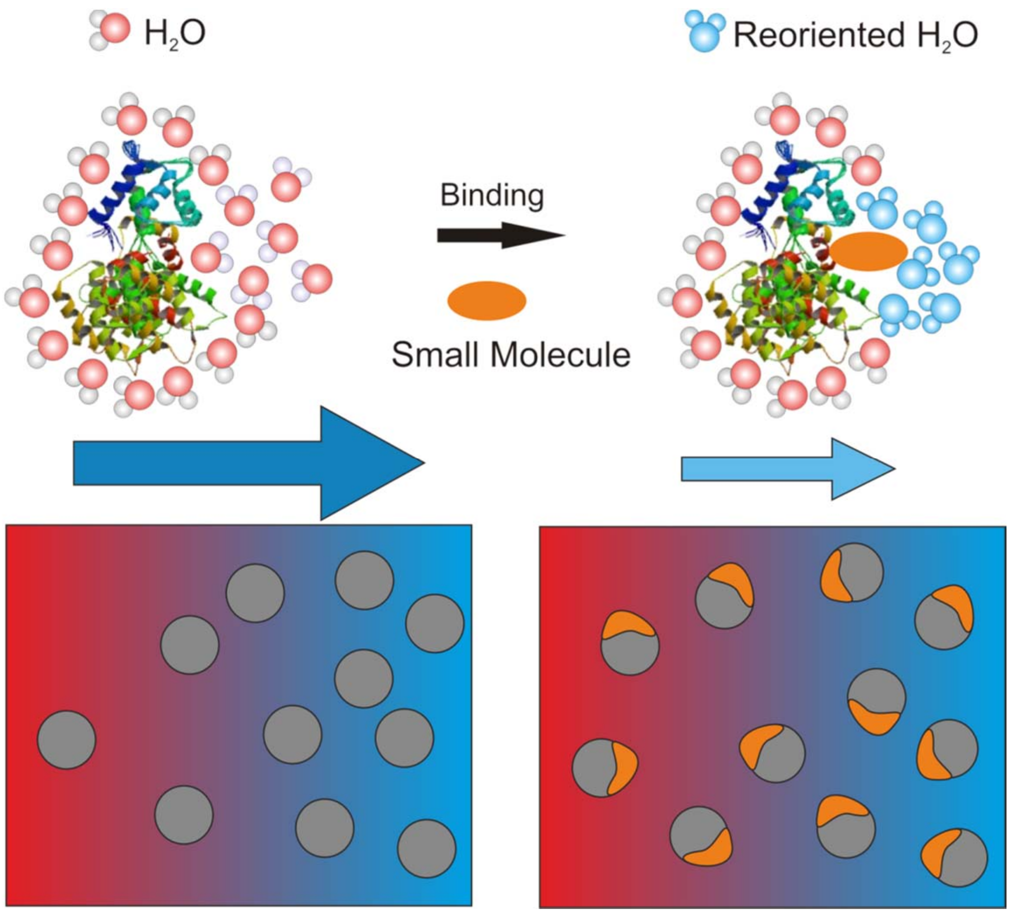
Thermal field flow fractionation



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?

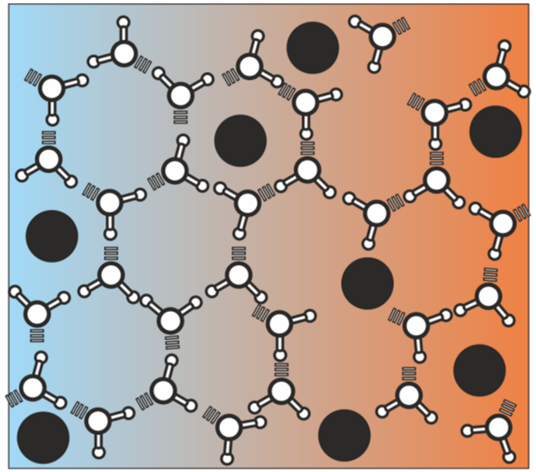
Application examples: "Biochemical reactions"
Microscale thermophoresis



Microscale Thermophoresis: Technology and Applications //NanoTemper GMBH

Hydrogen bonds: temperature effect

Assuming local thermodynamic equilibrium



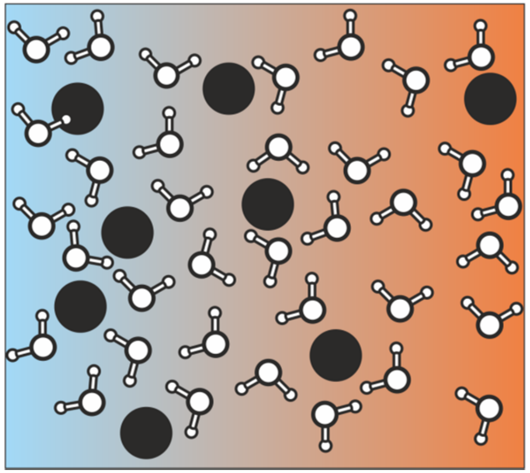
At low temperatures:

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

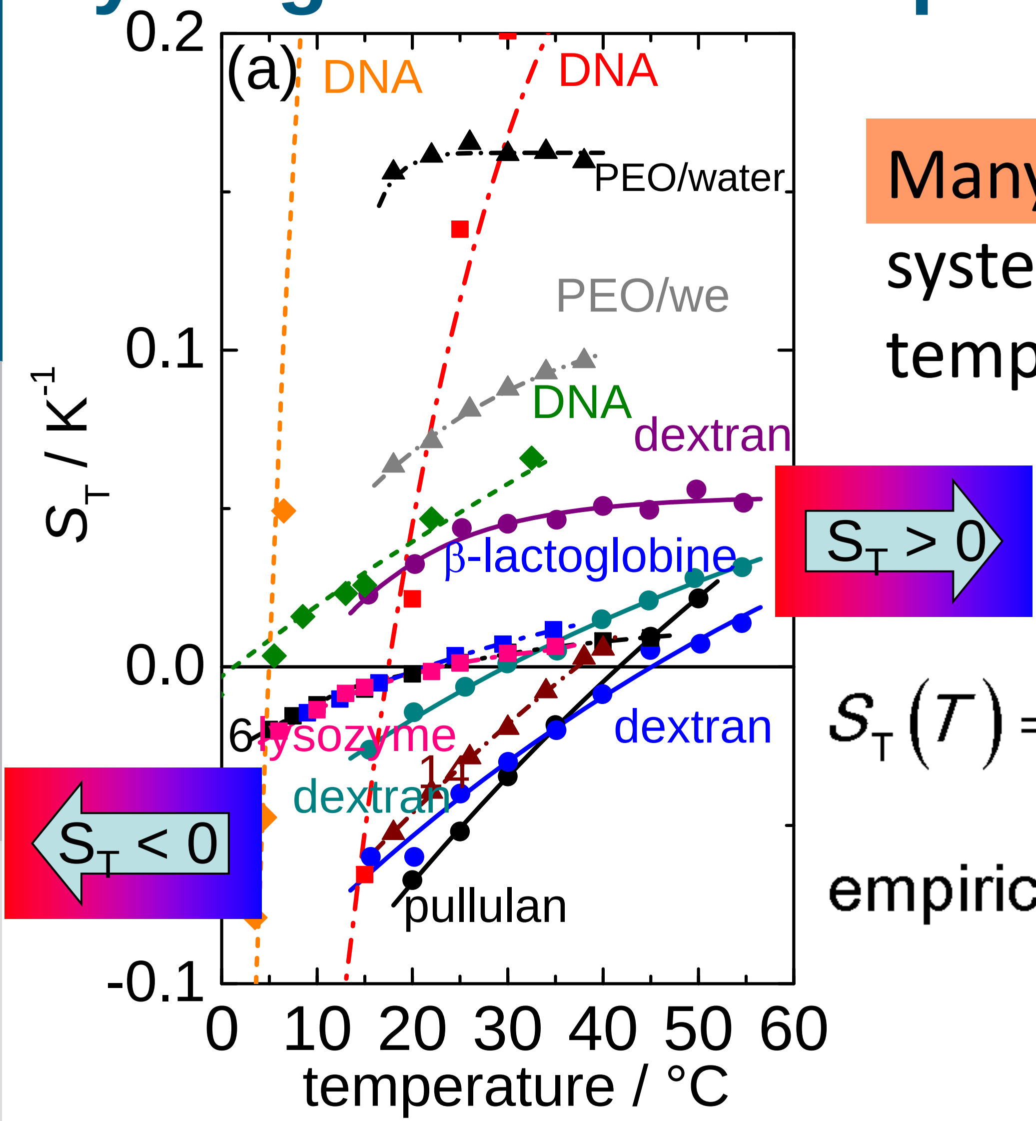
$$F = U - TS$$

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

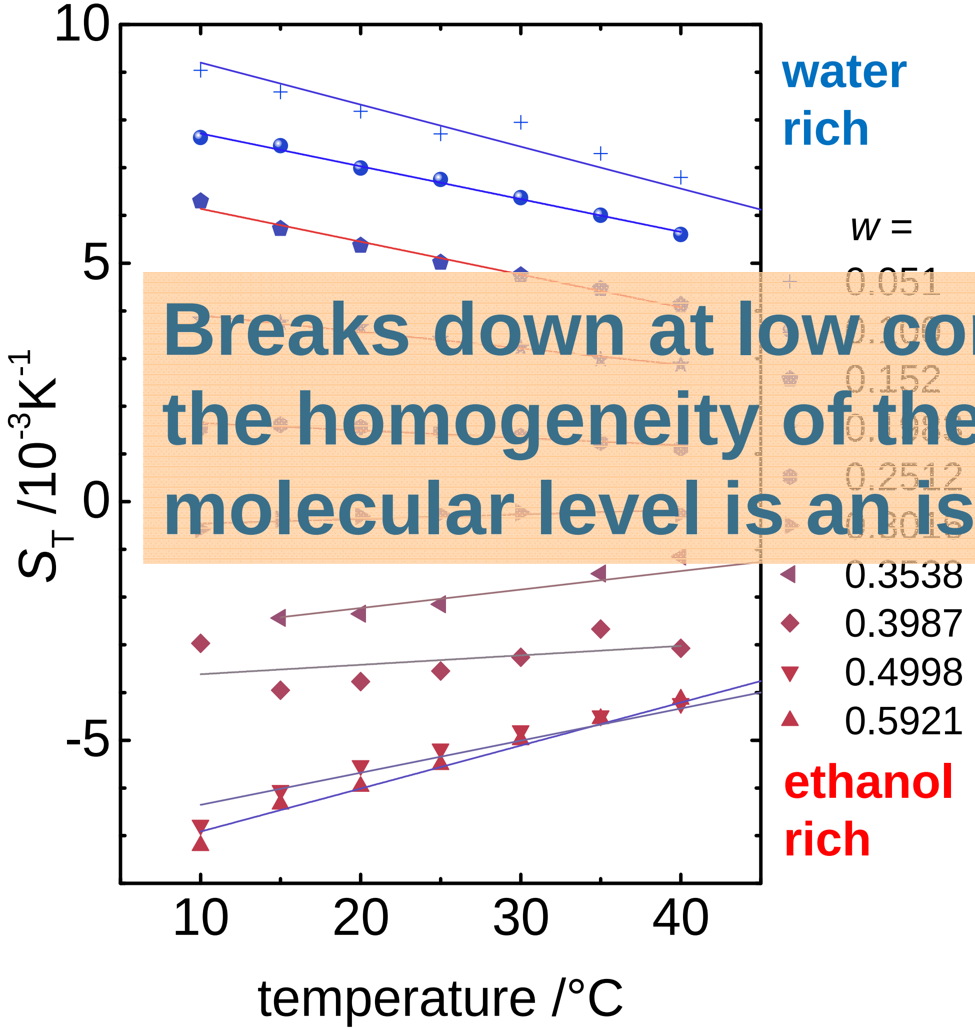
[Iacopini et al., Eur. Phys. J. E, **19**(2006) 59]

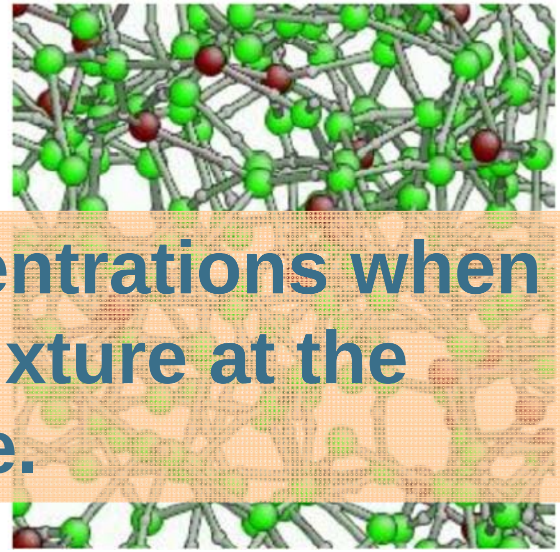
[Kishikawa, Y., SW, and R. Kita, Biomacromolecules, **11** (2010) 740]

Validity of the empirical formula?

ethanol/water

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





20 mol % ethanol

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

- “pure water rings are formed”
- **clumping** of like molecules

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

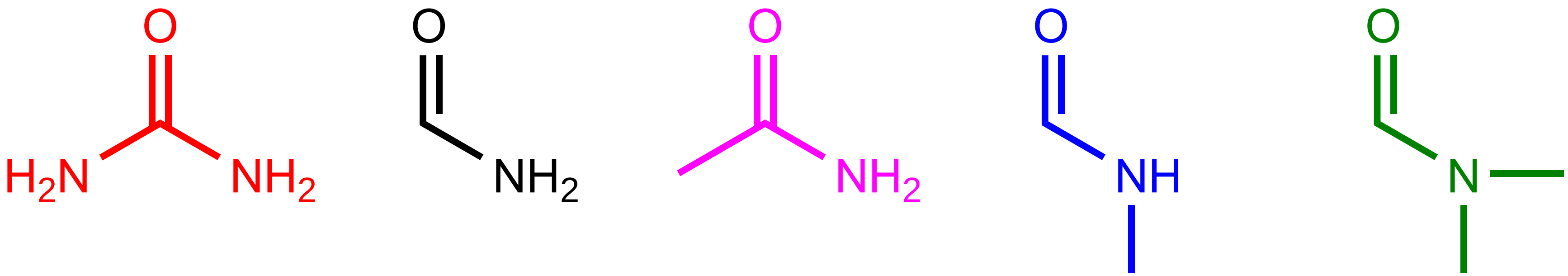
[O. Gereben, Journal of Molecular Liquids, 211 (2015) 812-820]

Systematic study of amides

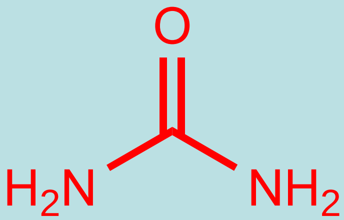
Why amides? *".. serve as model of the peptide bond "*

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

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



Temperature dependence



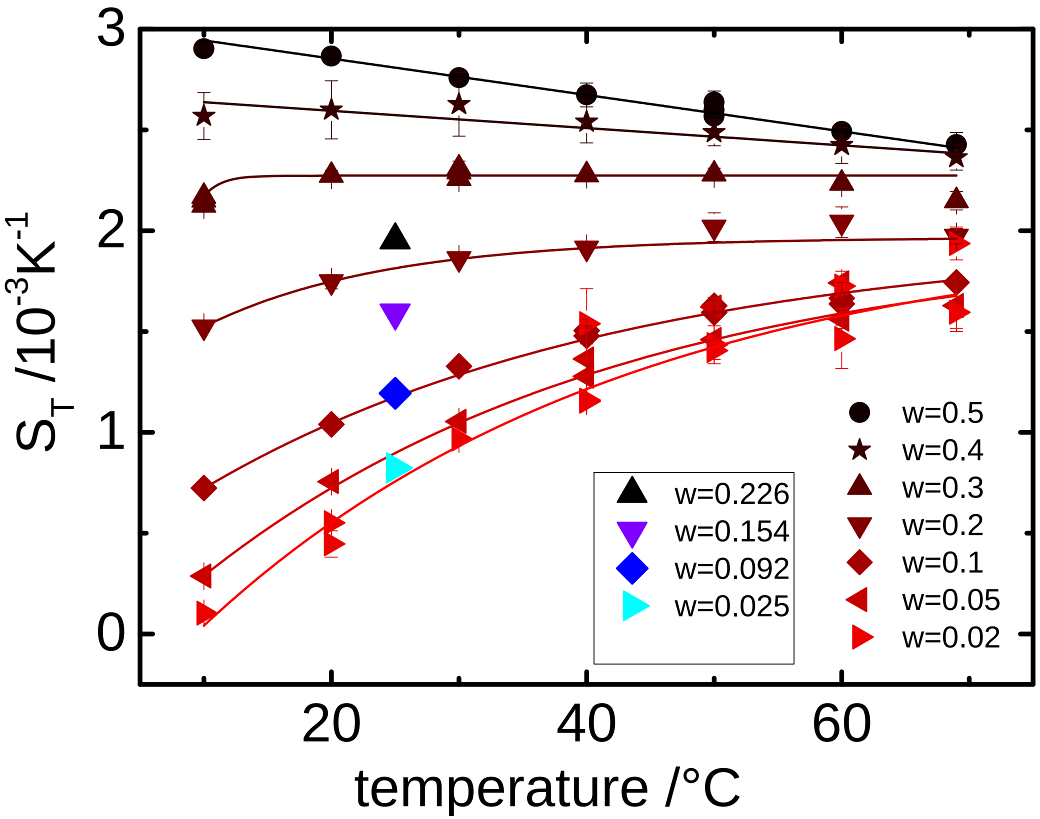
urea in water

- at low concentrations (***w* ≤0.3**):

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

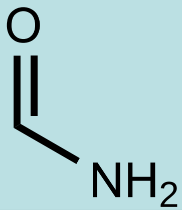
- more flexible fit function needed to describe T-dependence at higher concentrations:

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



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

Temperature dependence



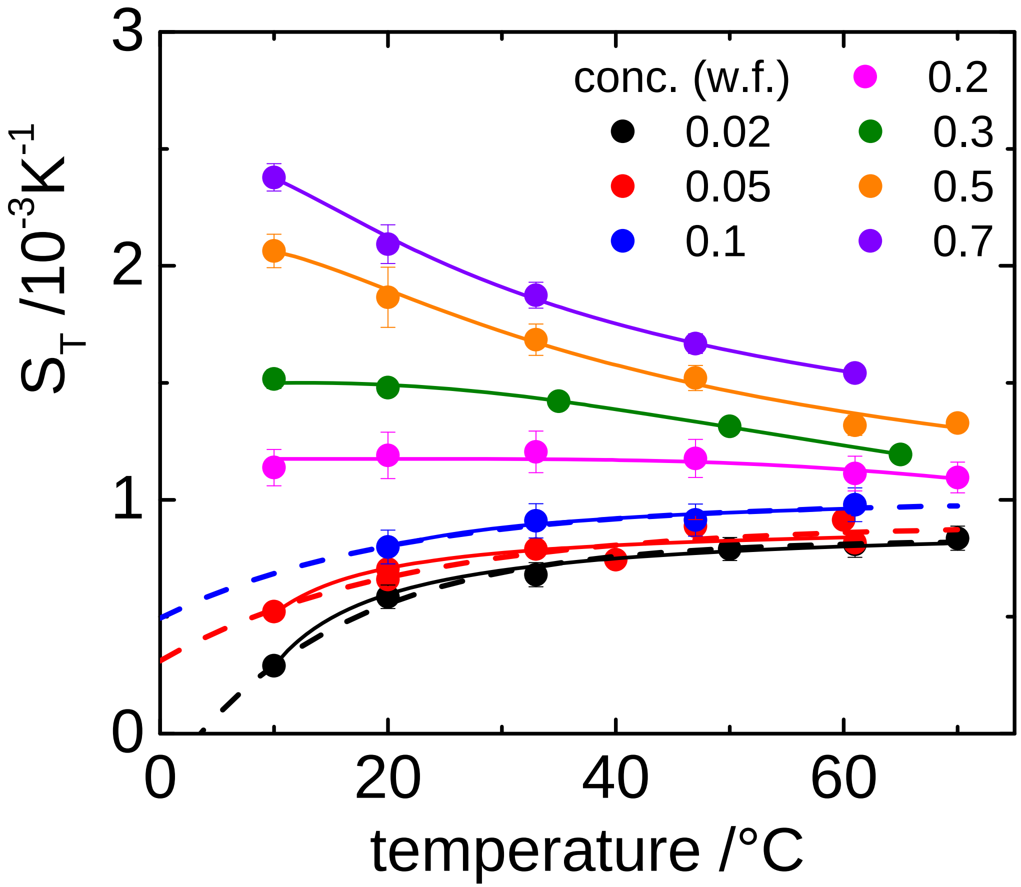
formamide in water

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

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

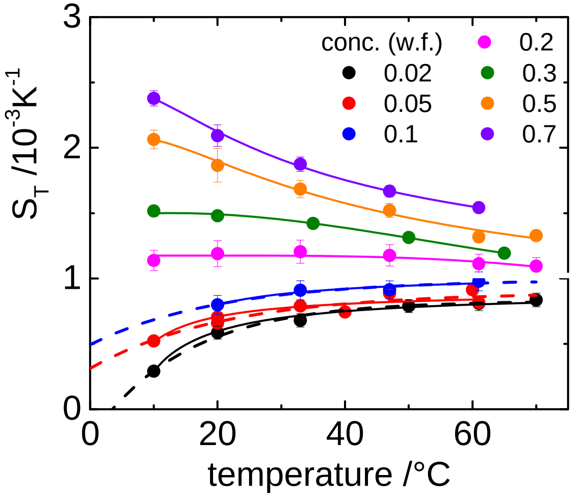
- more flexible fit function needed to describe T-dependence at higher concentrations:

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



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

Structural explanation



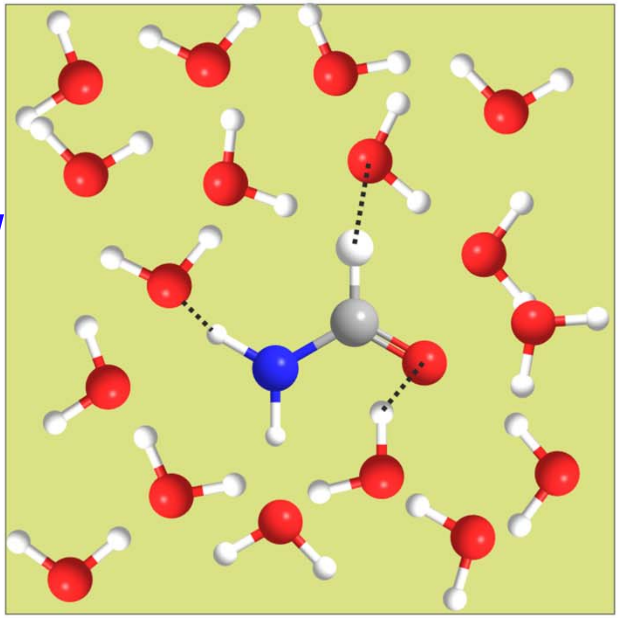
Molecular dynamic simulations
[Elola & Ladanyi, JCP 125,(2006) 184506]

conc. = ?

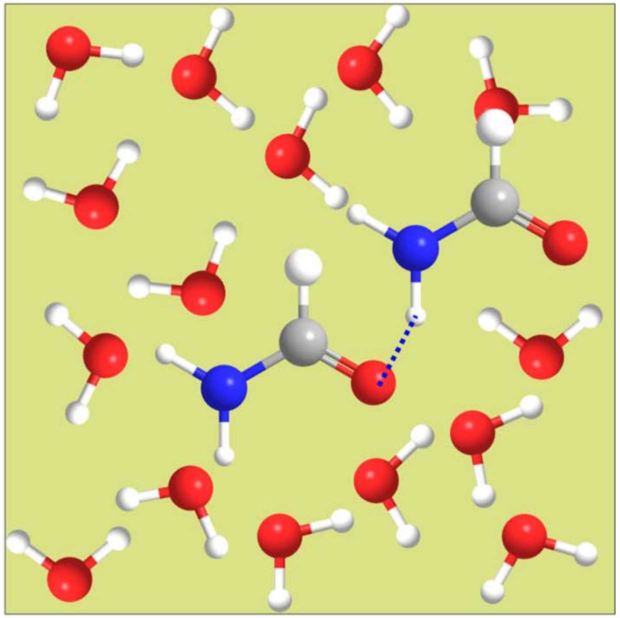
suggest the following picture:

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

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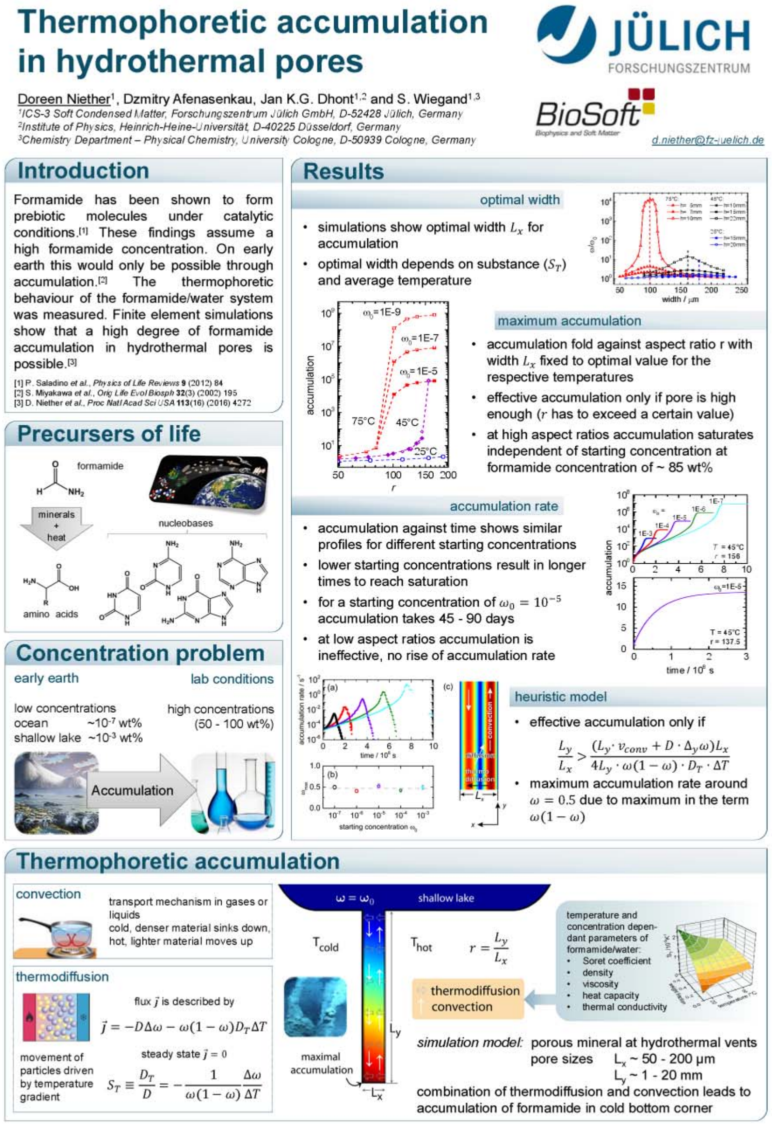


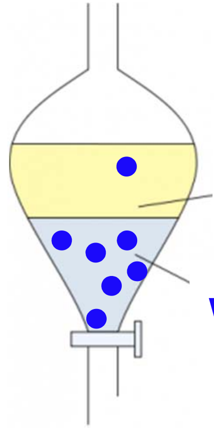
A way to achieve sufficiently high formamide concentrations to form prebiotic nucleobases under early earth conditions

by

Doreen Niether

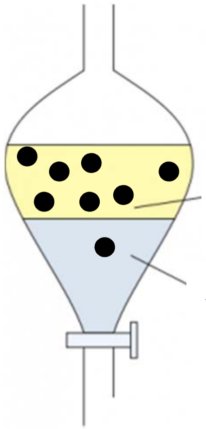
„log *P*“ a „Scale bar“ for hydrogen bonding strength?

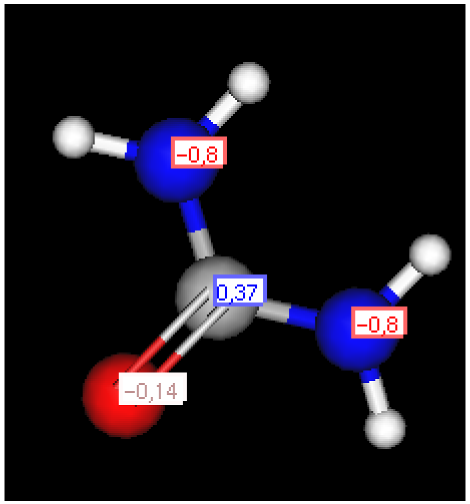
$$\log P = \log\left(\frac{[\mathit{solute}]_{\mathrm{octanol}}}{[\mathit{solute}]_{\mathrm{water}}^{\mathrm{unionized}}}\right)$$



Hydrophilic compound: log $P < 0$

Hydrophobic compound: log $P > 0$



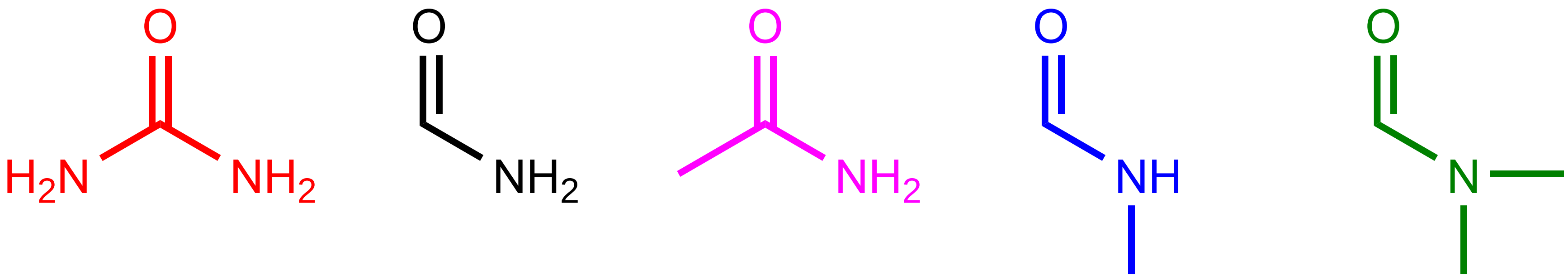


urea

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



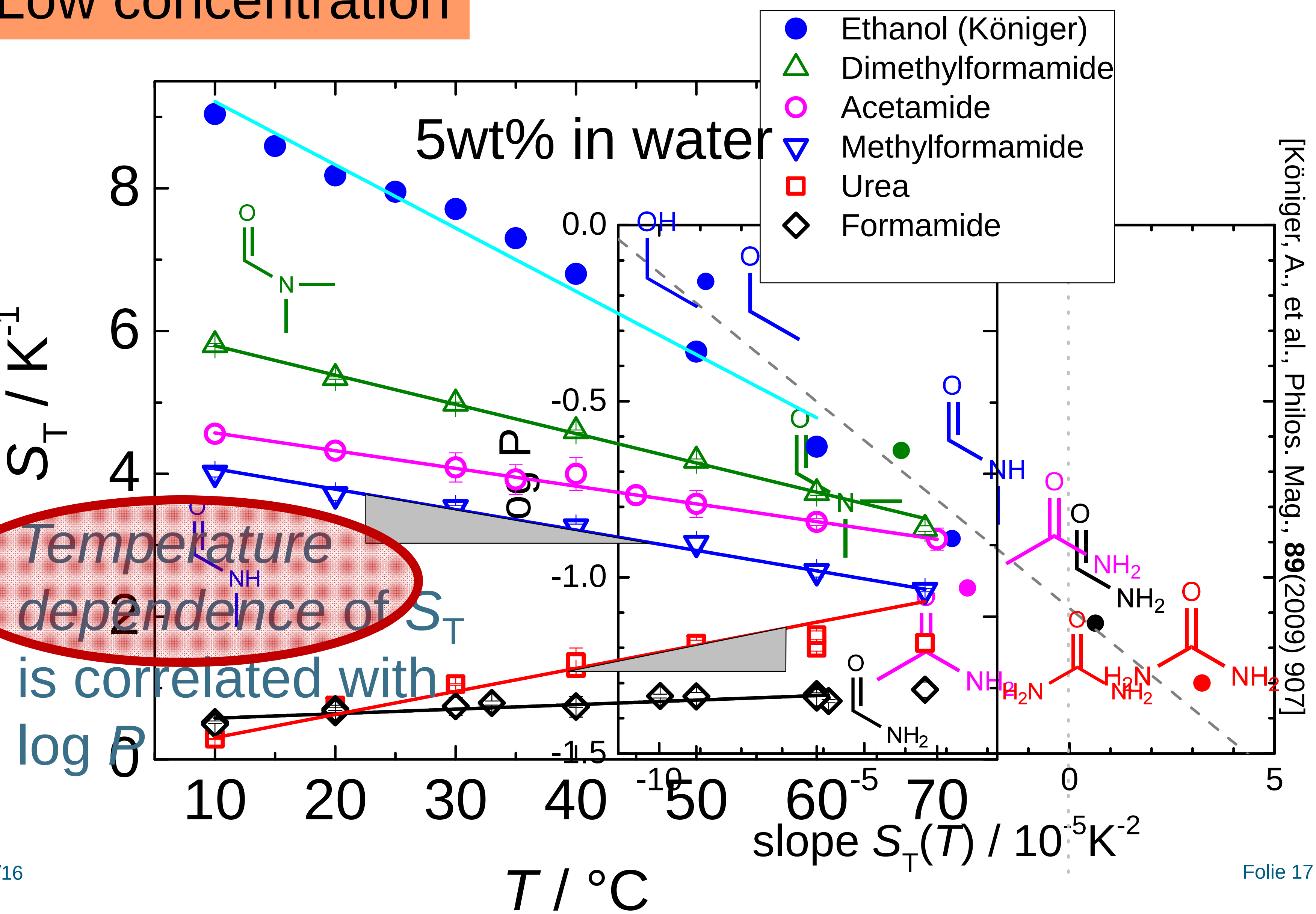
Log *P* =

-1.30	-1.13	-1.03	-0.89	-0.64

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

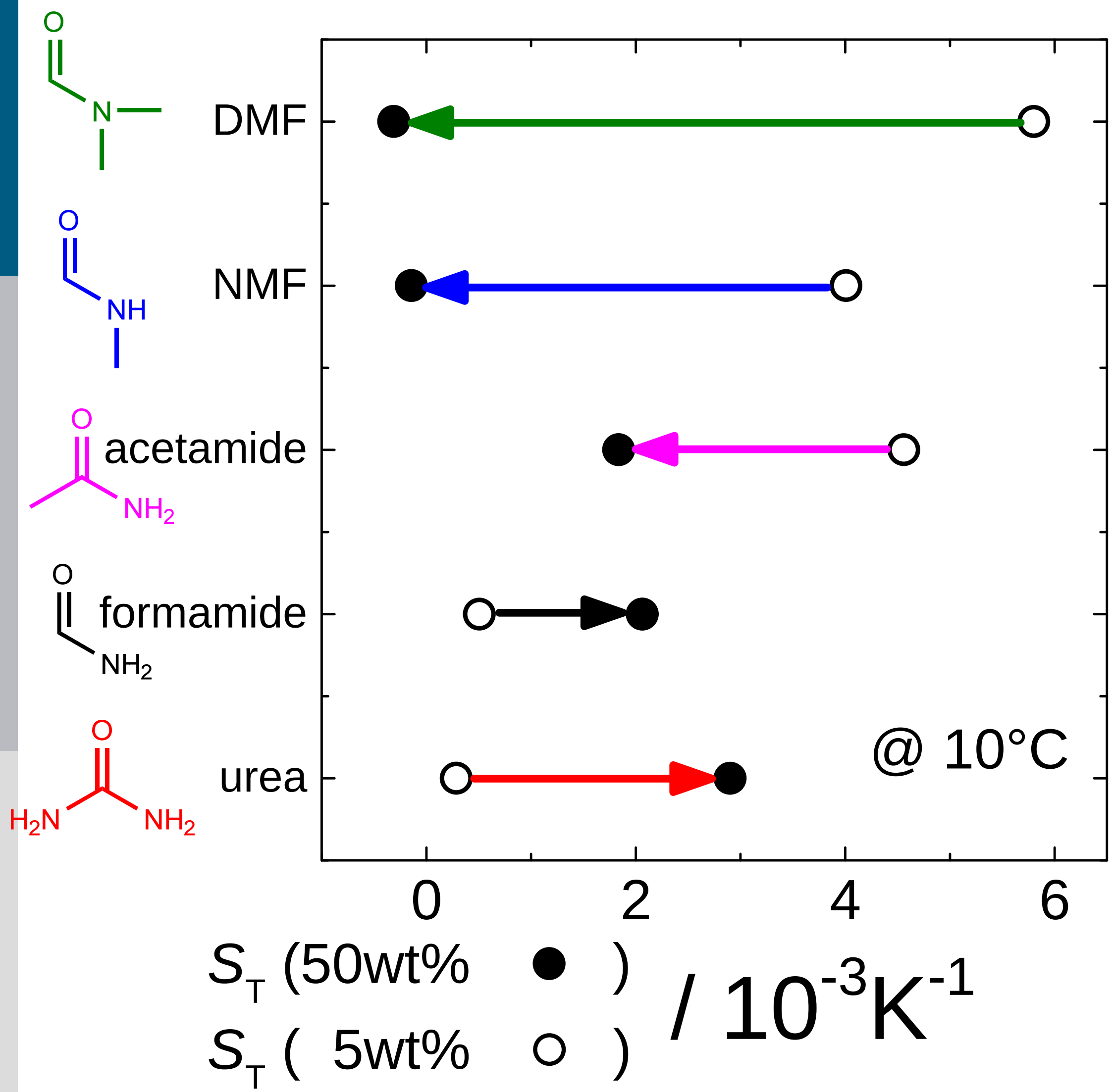
„log *P*“ a „Scale bar“ for polar solvents ?

Low concentration



Temperature dependence of S_T is correlated with log *P*

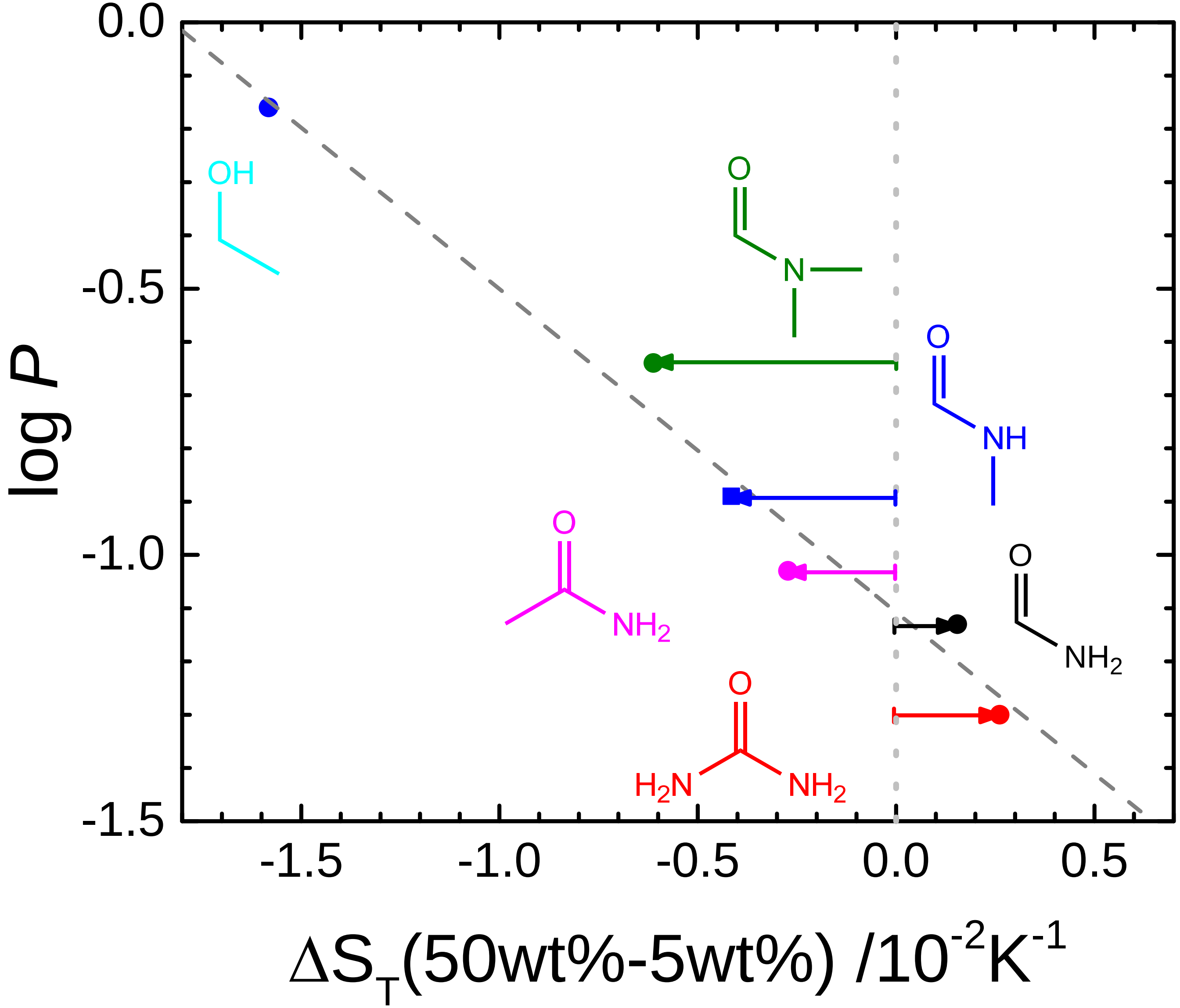
Comparison: low and high concentration



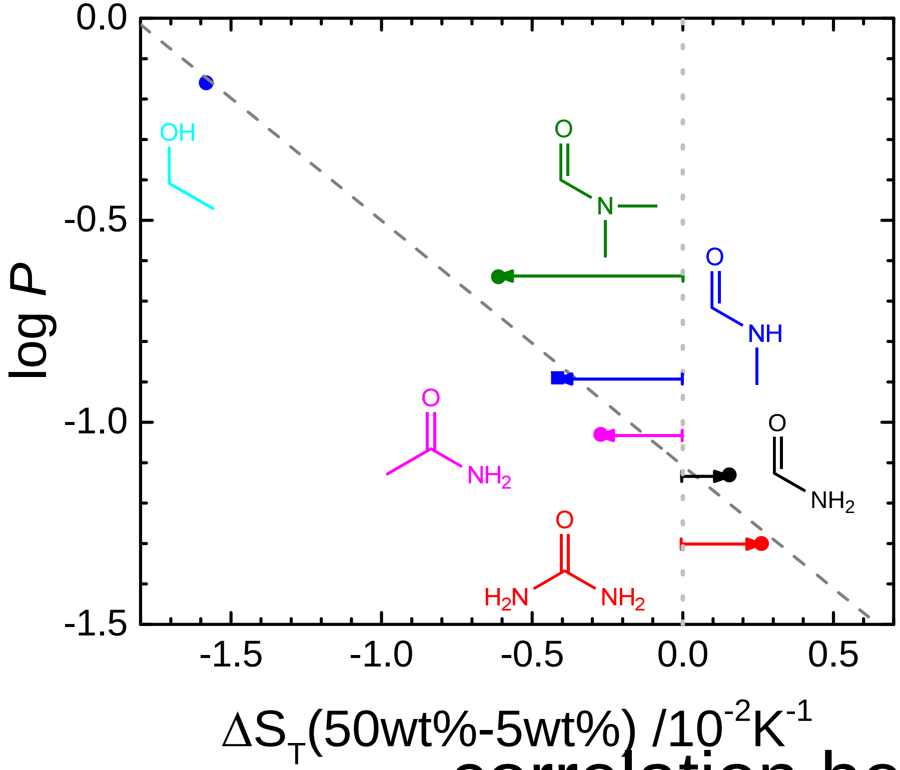
hydrophobic systems:
increasing concentration:
solute becomes more thermophilic

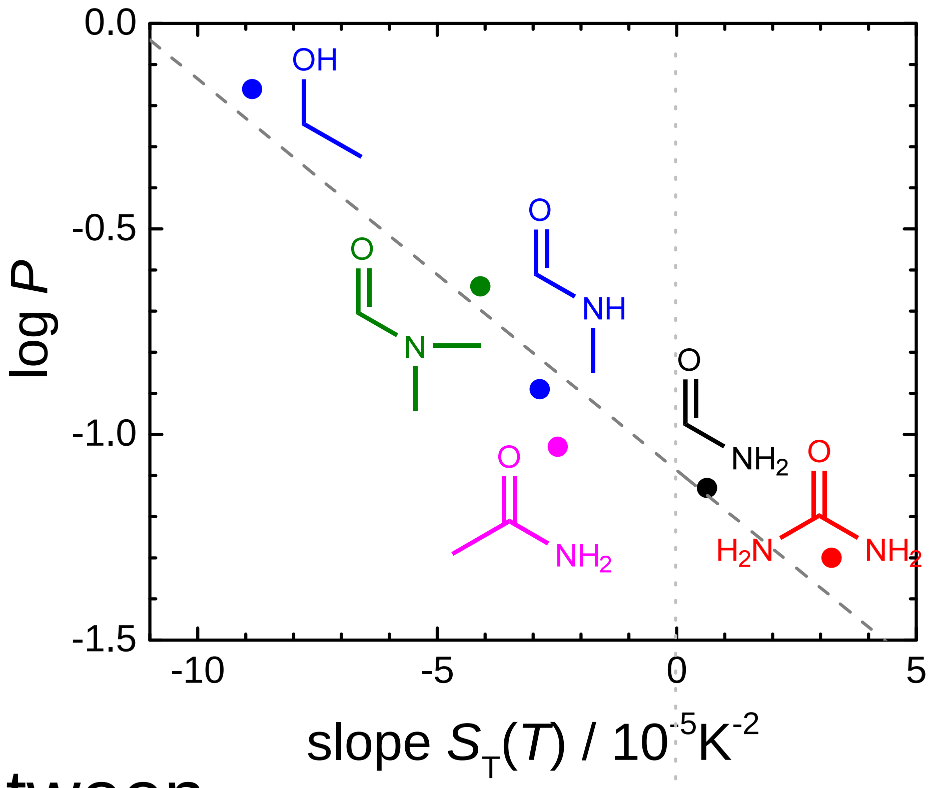
hydrophilic systems:
increasing concentration:
solute becomes more thermophobic

„log p“ scales S_T change with concentration



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





correlation between

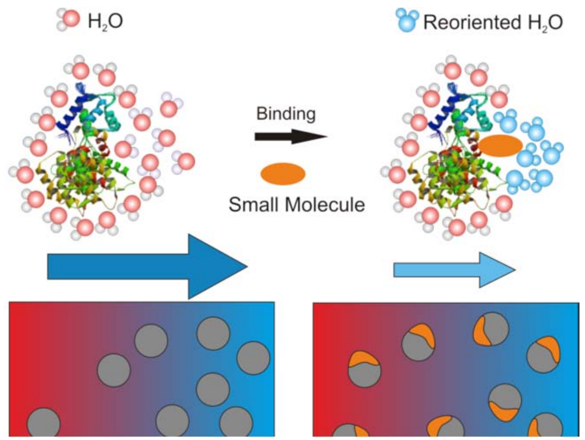
log *P* and the **change of S_T** with

… **concentration**

… **temperature**

Take home message

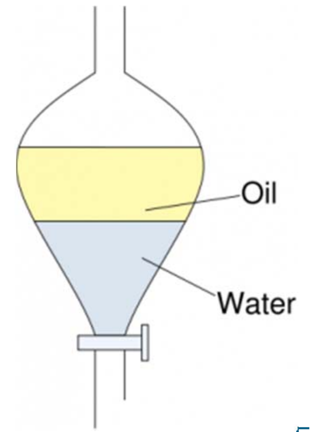
Thermophoresis is sensitive to changes of the hydration layer



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

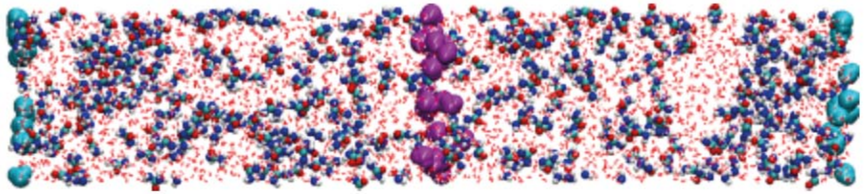
breaks down at high ***w***
breaks down at low ***w***
due to inhomogeneities

Log *P* correlates with temperature dependence of S_T
Log *P* correlates with concentration change of S_T

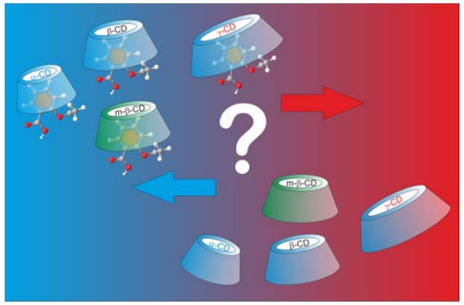


Thanks to many people and …

FZ Jülich
Jan Dhont's group
(ICS-3)



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

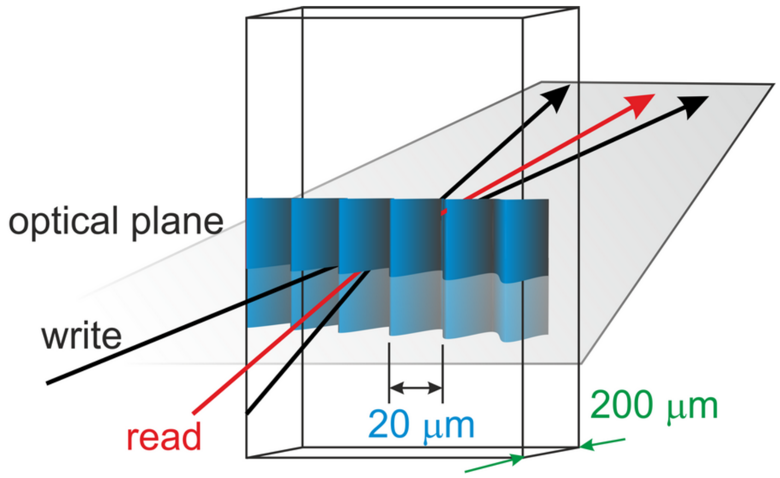


Rio Kita's lab
Kazuya Eguchi
Tokai University, Japan

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:

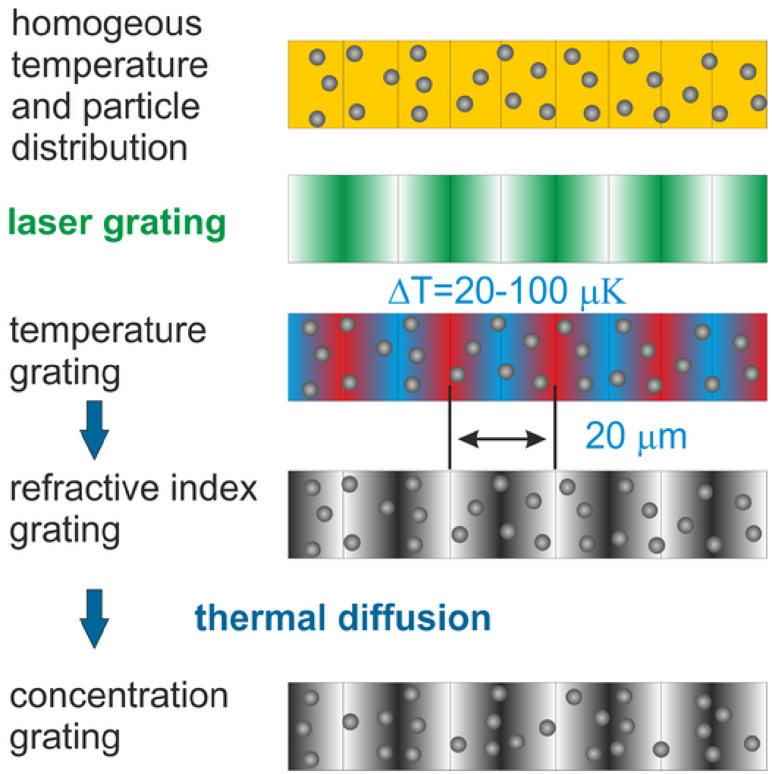
- small ΔT
- no fluorescent labeling required
- wide molecular range

Disadvantages:

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

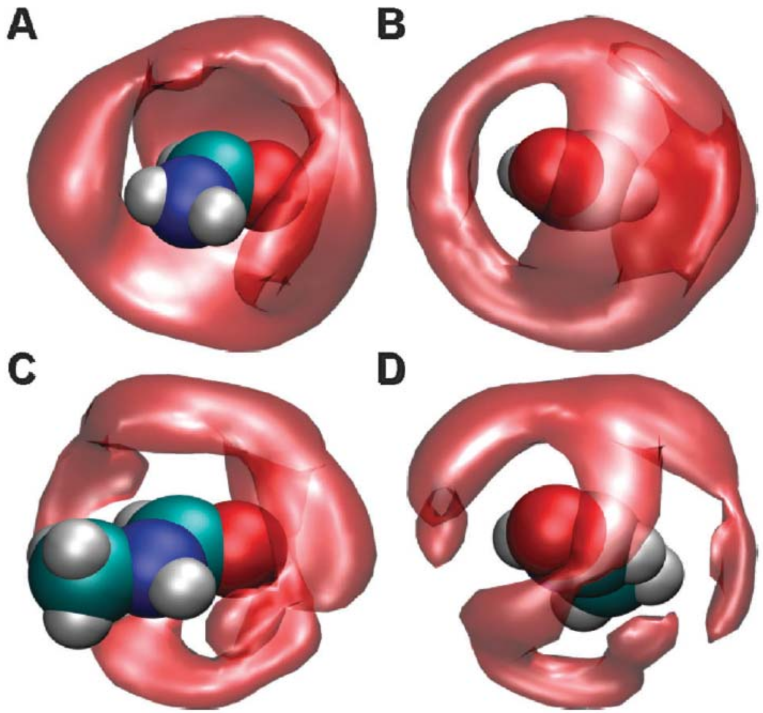
Typical gradients: 1K/m

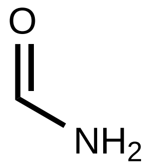
Measured quantity: Intensity of the diffracted beam



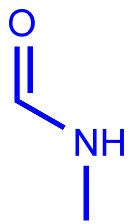
[SW *et al.*, J. Phys. Chem. B, **111**(2007) 14169]

Formamide vs. *N*-methylformamide





formamide

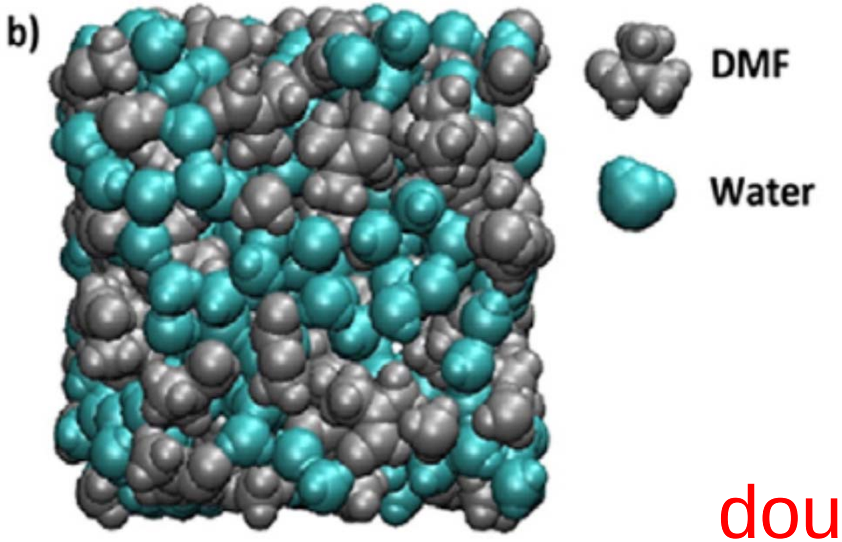


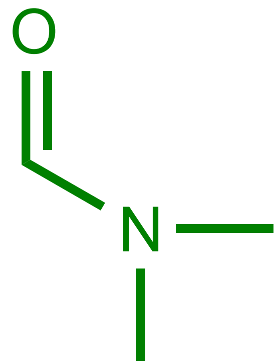
methyl-
formamide

"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





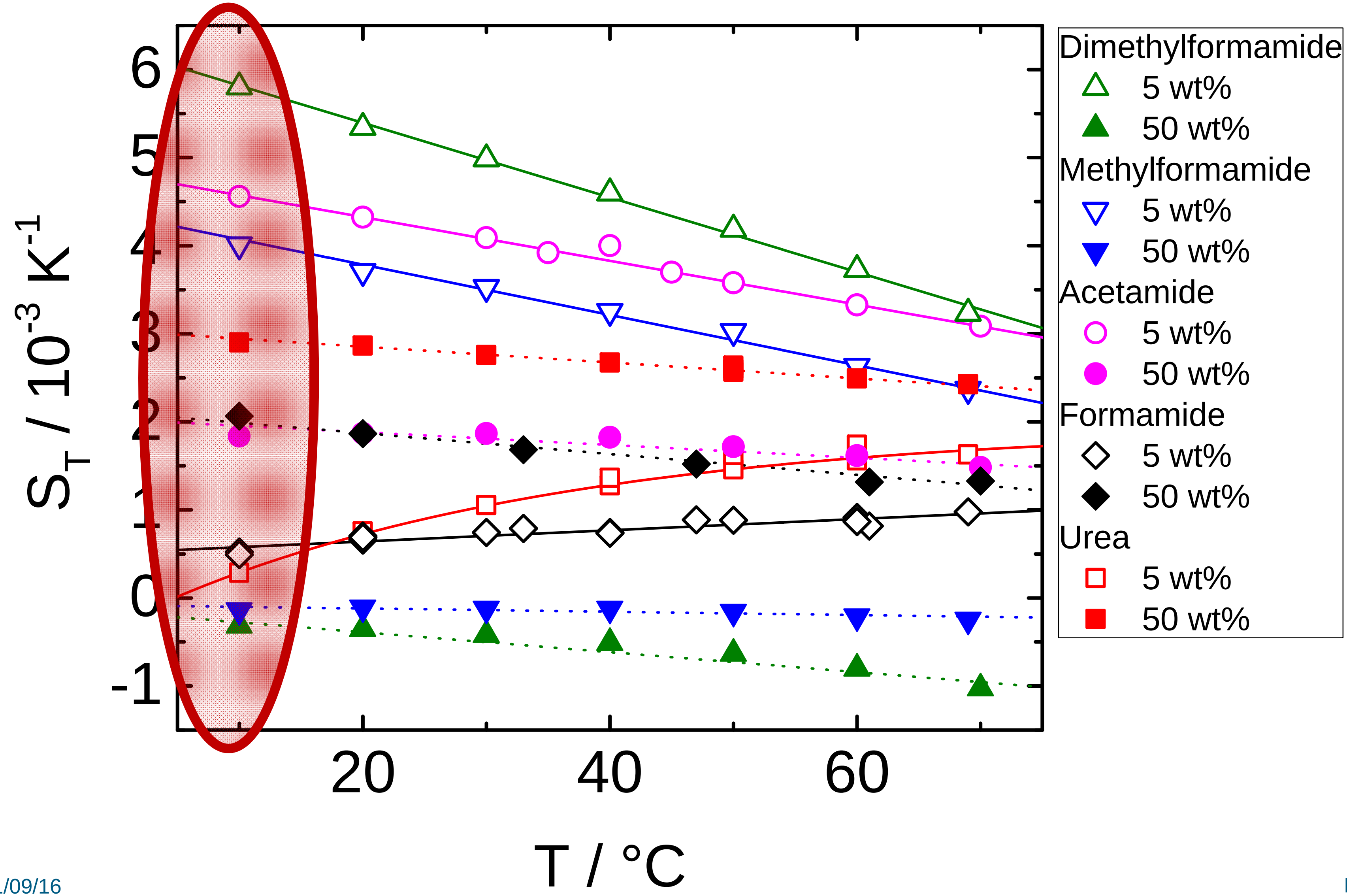
dimethyl-
formamide

doubts about the Force field ?

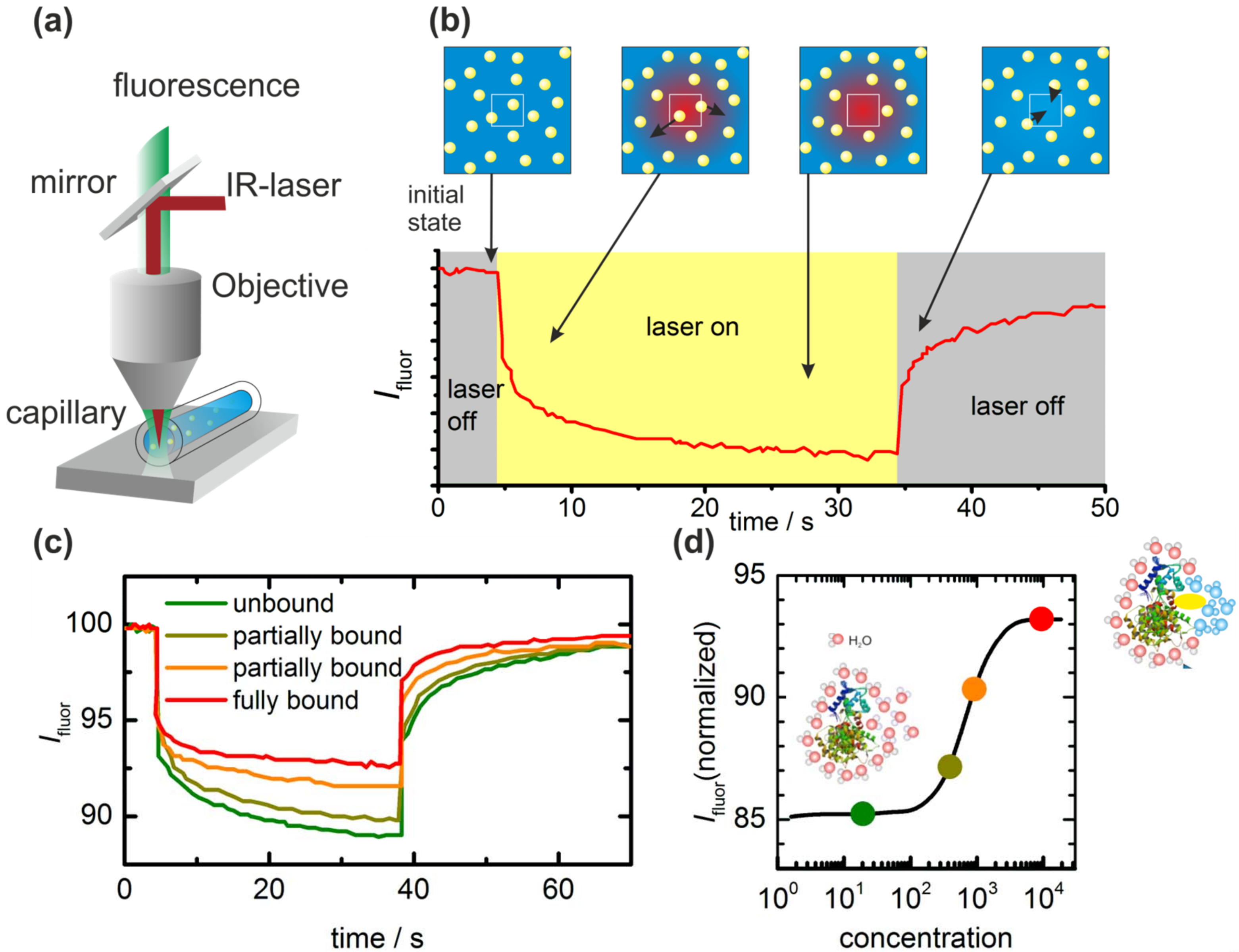
"The increases in the peaks of RDFs between water molecules are not so much caused by an increase in the structure of water as they are by the tendency of water to remain in aggregates in the mixtures."

[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.