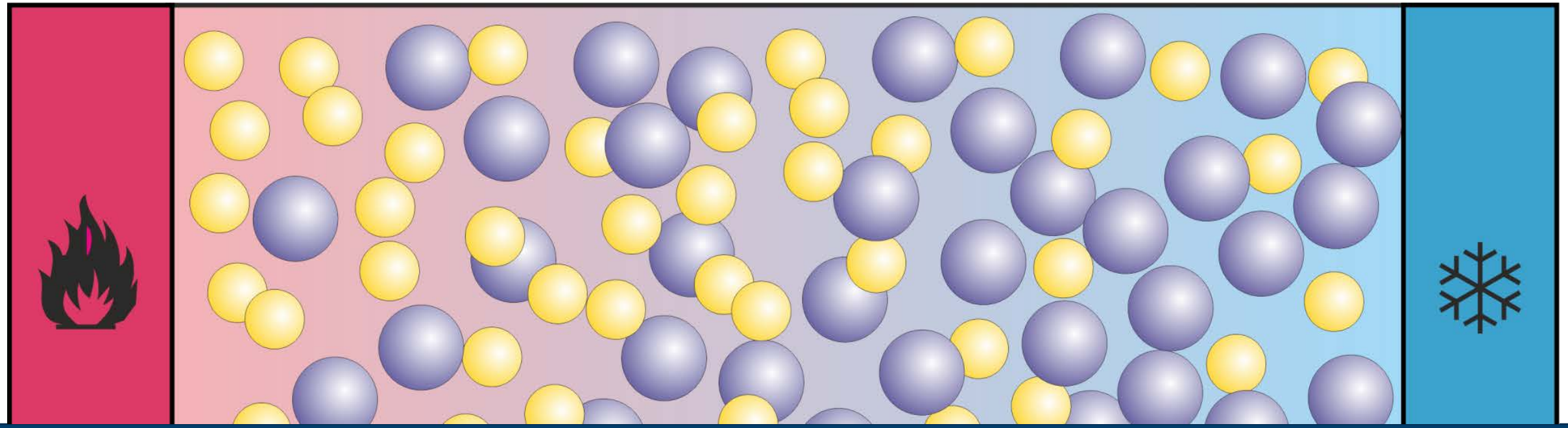


WHEN DOES THE SORET COEFFICIENT SHOW A MINIMUM WITH CONCENTRATION IN AQUEOUS ALKALI HALIDE SOLUTIONS?

26.05.2020 I SHILPA MOHANAKUMAR

Member of the Helmholtz Association

JÜLICH Forschungszentrum

MOTIVATION

Thermophoresis

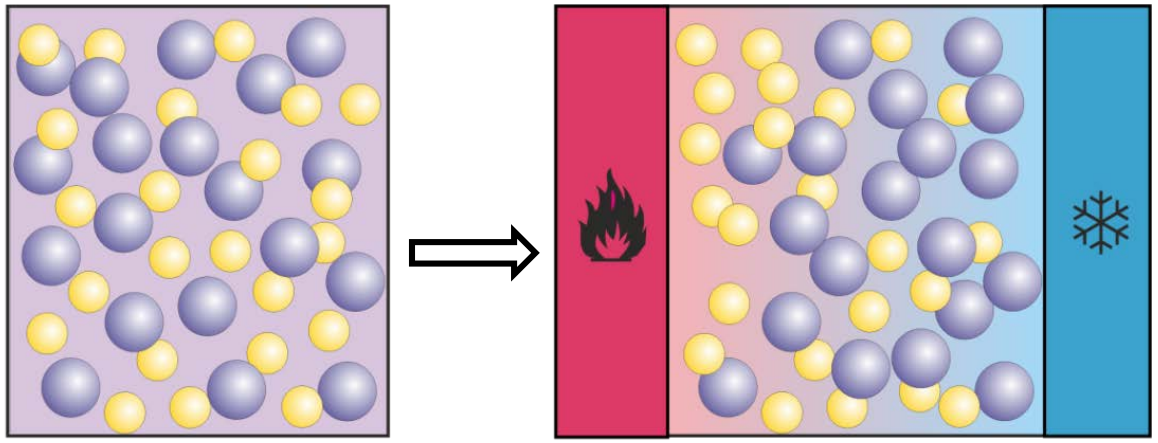
- Motion of solute particles induced by thermal gradient.
- Sensitive tool for probing molecular interactions.

Steady state:
concentration difference/temperature difference is quantified by *Soret coefficient* S_T.

$$\frac{D_T}{D} = -\frac{\Delta c}{c(1-c)\Delta T}$$

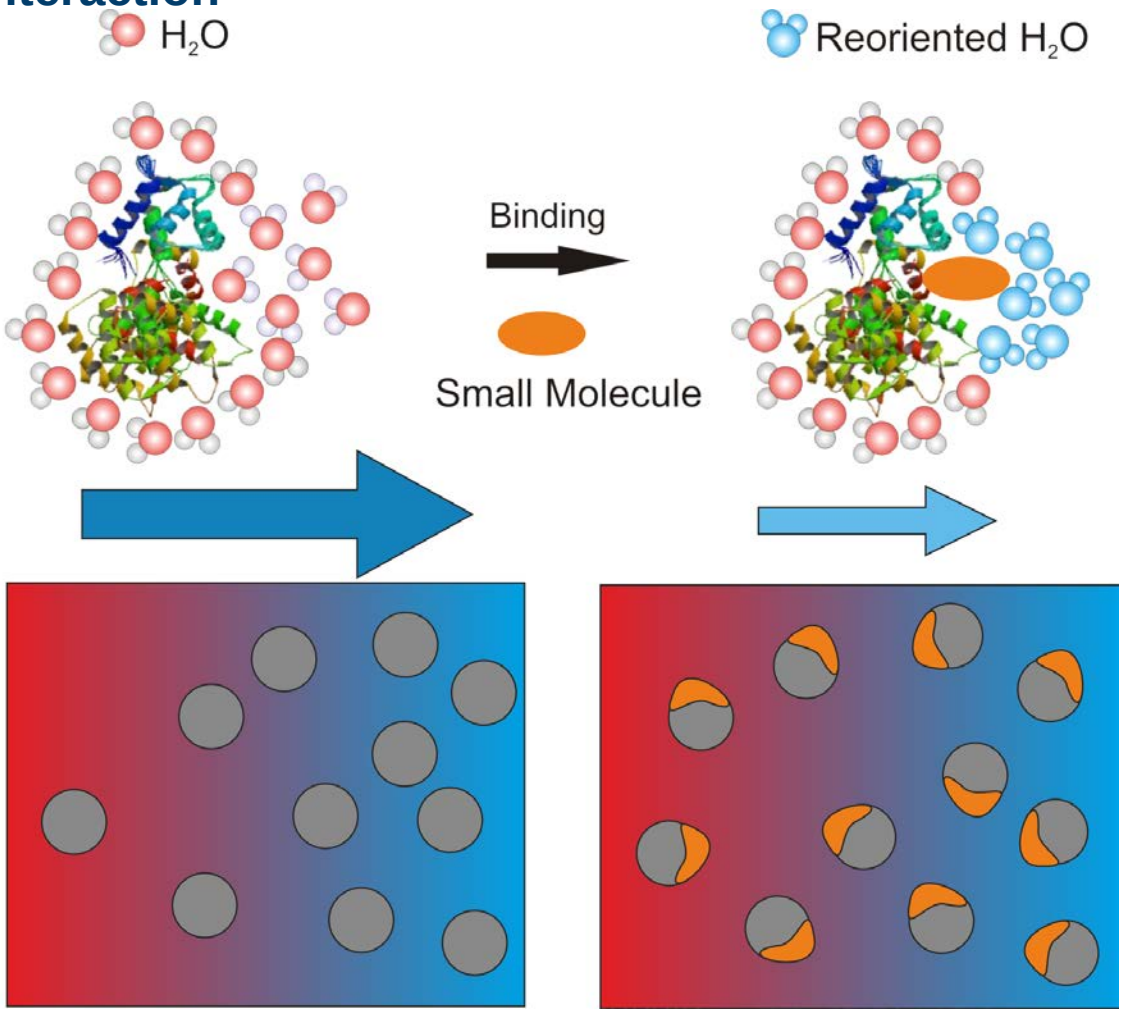
$$S_T = \frac{D_T}{D} \propto \frac{\Delta c}{\Delta T}$$

$\vec{j}$	mass flux
c	concentration
D	diffusion coefficient
D_T	thermodiffusion coefficient
T	temperature
S_T	Soret coefficient



THERMOPHORESIS

Monitors protein-ligand interaction



LONGTERM GOAL: PROTEIN-LIGAND BINDING

Step 1 – Simple salts

- Systematic study of various components:
  - Simple salts
  - Drugs
  - Proteins

In order to separate contributions stemming from

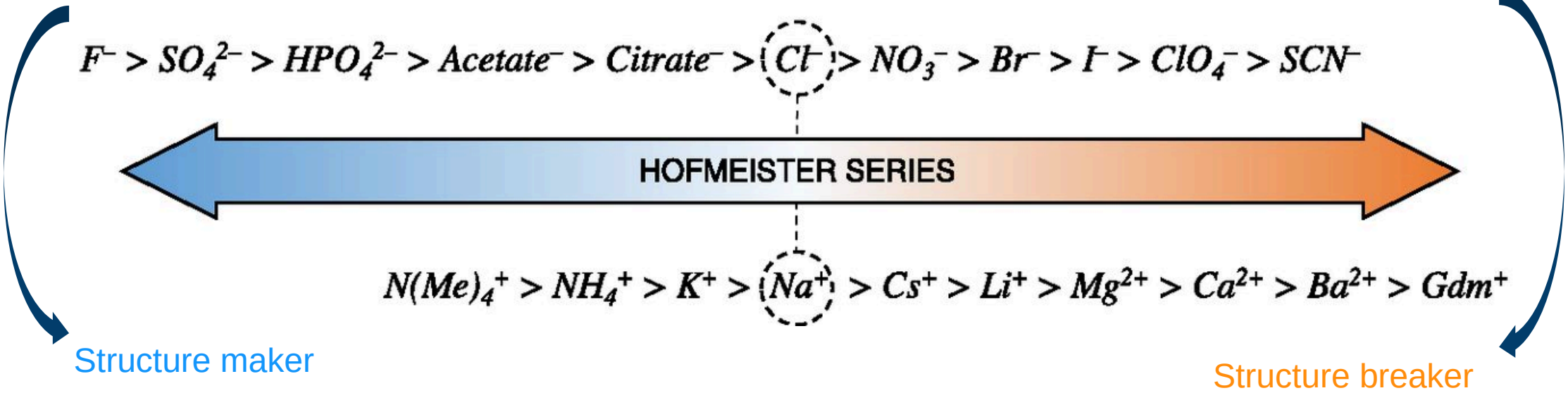
- Ionic
- Hydrophobic
- Hydrogen bonds
- Van der Waals force

HOFMEISTER SERIES

Different ions behave different…..

- Increase protein stability
- Less denaturing
- Salting out (aggregates)
- Kosmotropic

- Decrease protein stability
- More denaturing
- Salting in (solubilizes)
- Chaotropic

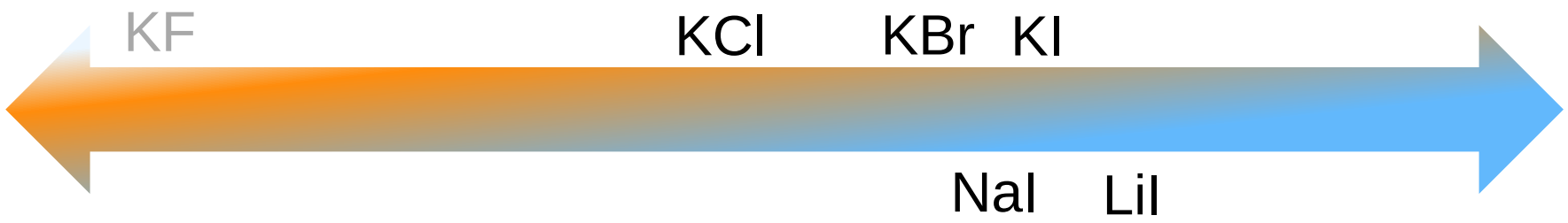


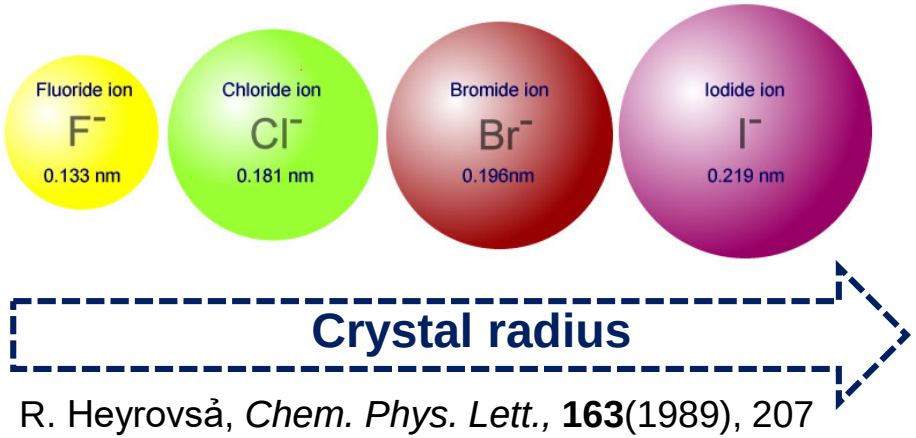
Structure maker

Structure breaker

Y. Zhang et al., *Curr. Opin. Chem. Biol.*, **10**(2006), 658

CHOICE OF THE SYSTEMS



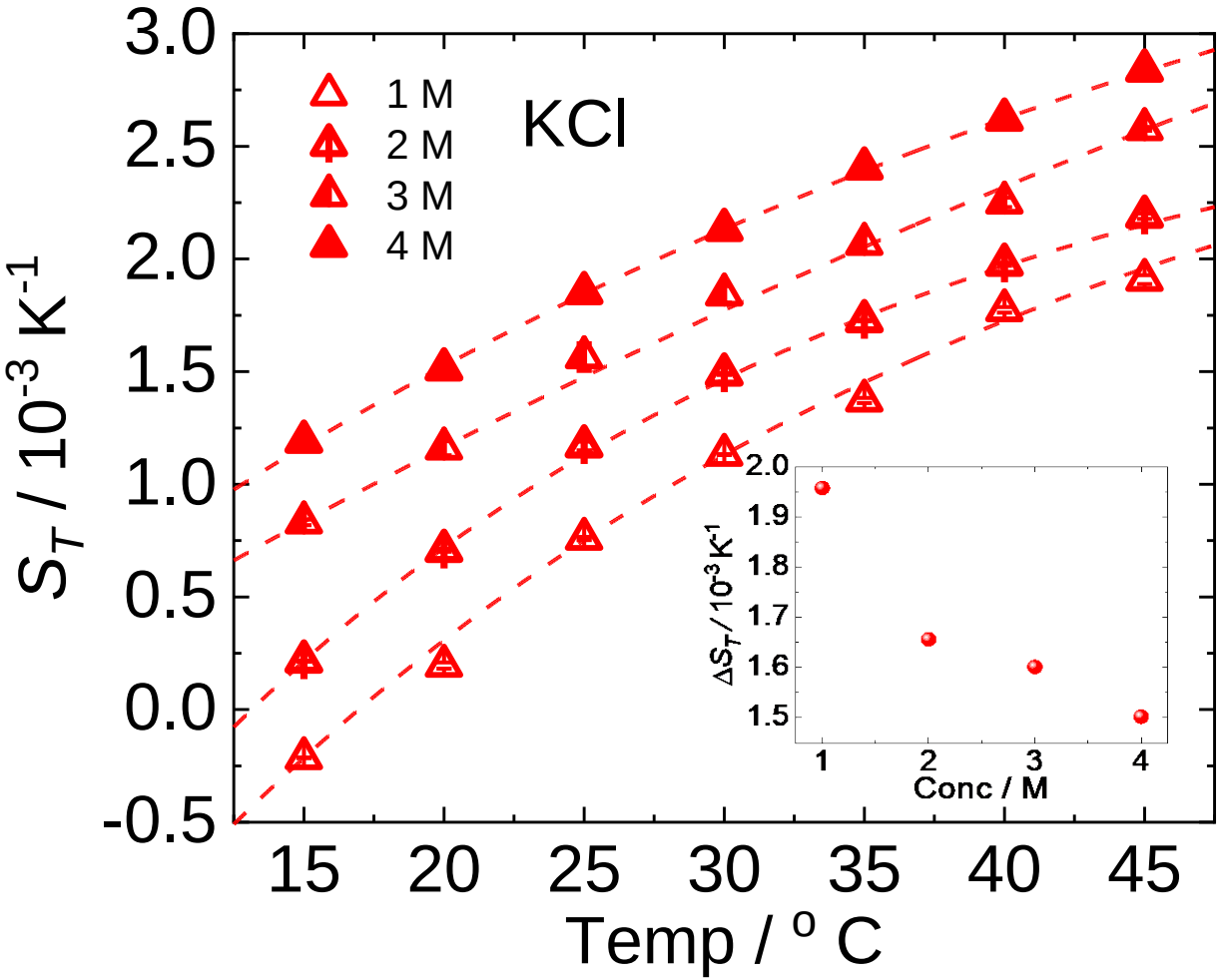


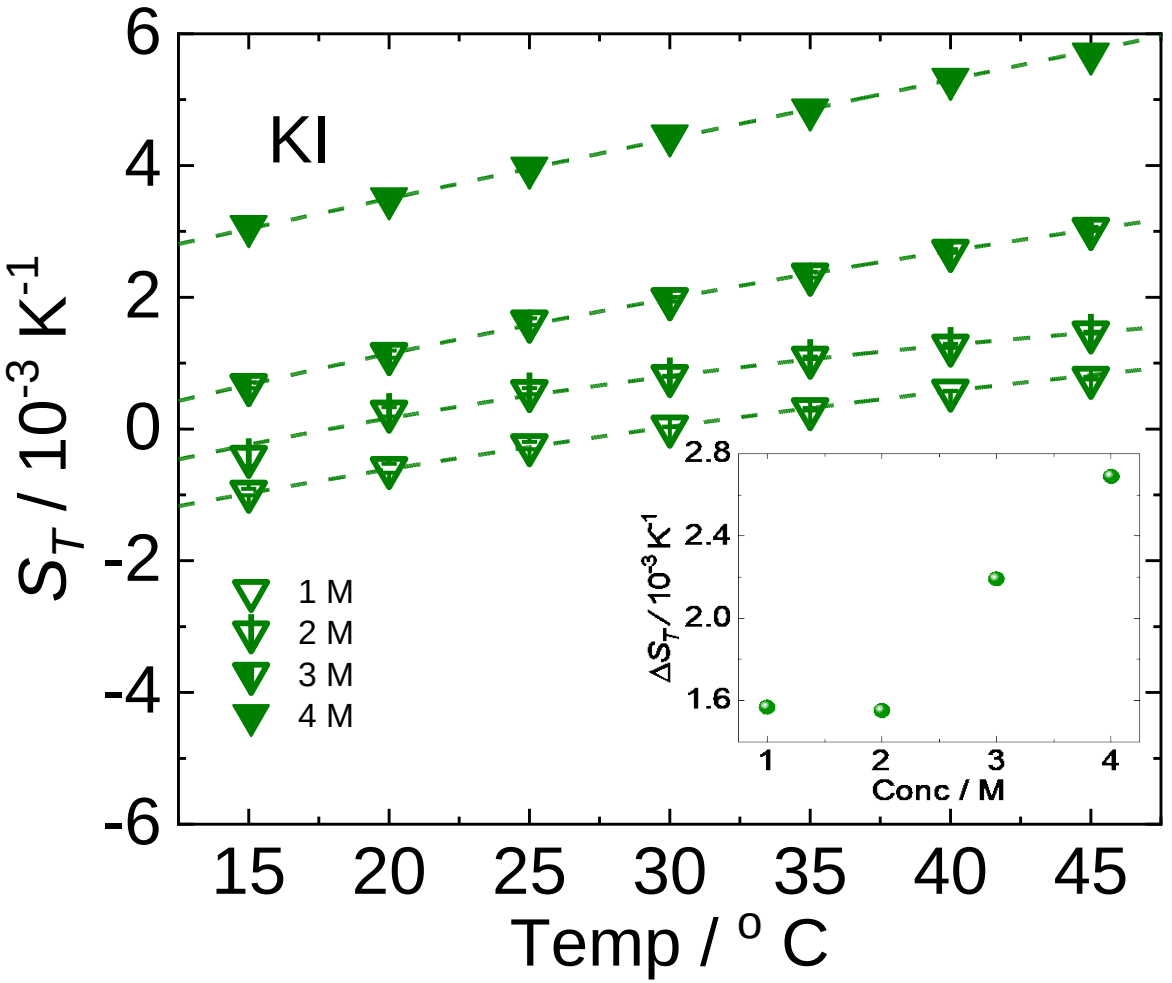
R. Heyrovså, *Chem. Phys. Lett.*, **163**(1989), 207

- Is it enough to consider the charge of the salt?
- Won't the effect of hydration layer vary depending upon the salt ?

Temperature dependence:

$$\Delta S_T = S_T(50\,^{\circ}C) - S_T(20\,^{\circ}C)$$

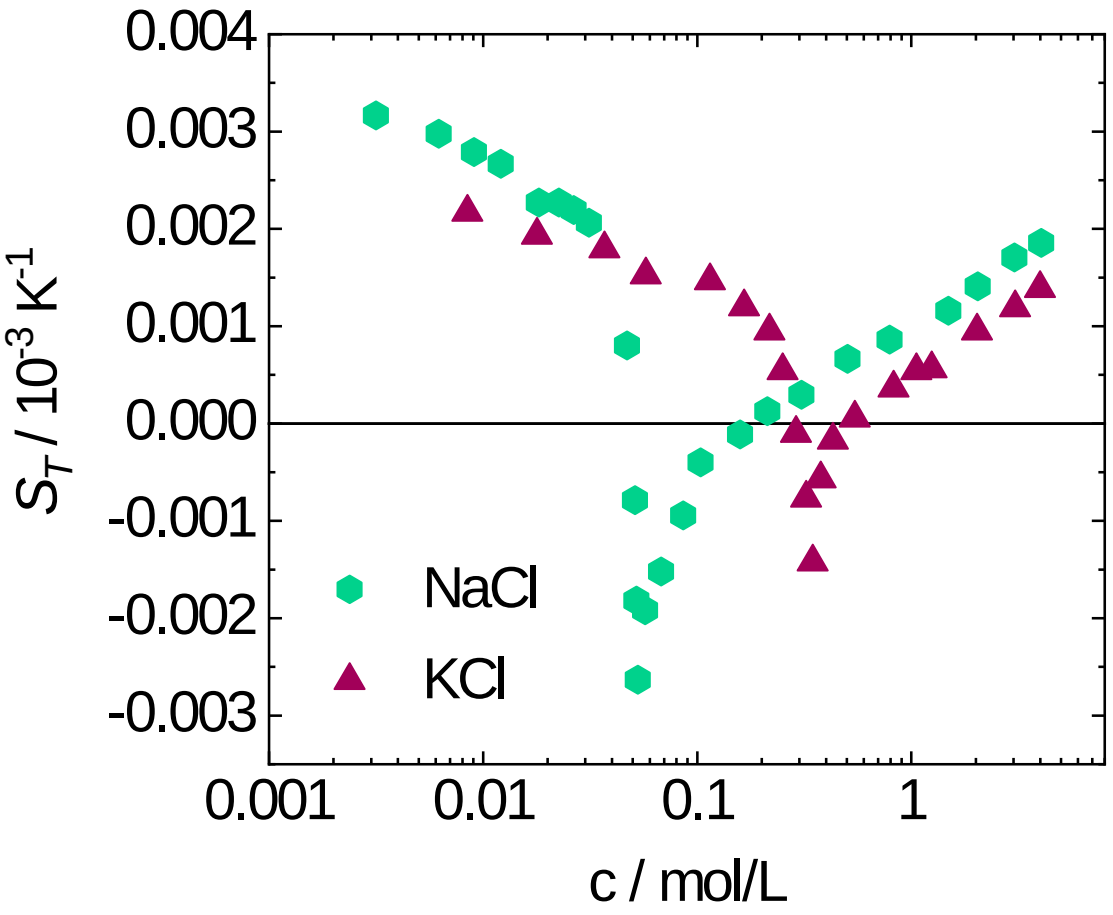




$$S_T(T) = S_T^{\infty}\left[1 - \exp\left(\frac{T^* - T}{T_0}\right)\right]$$

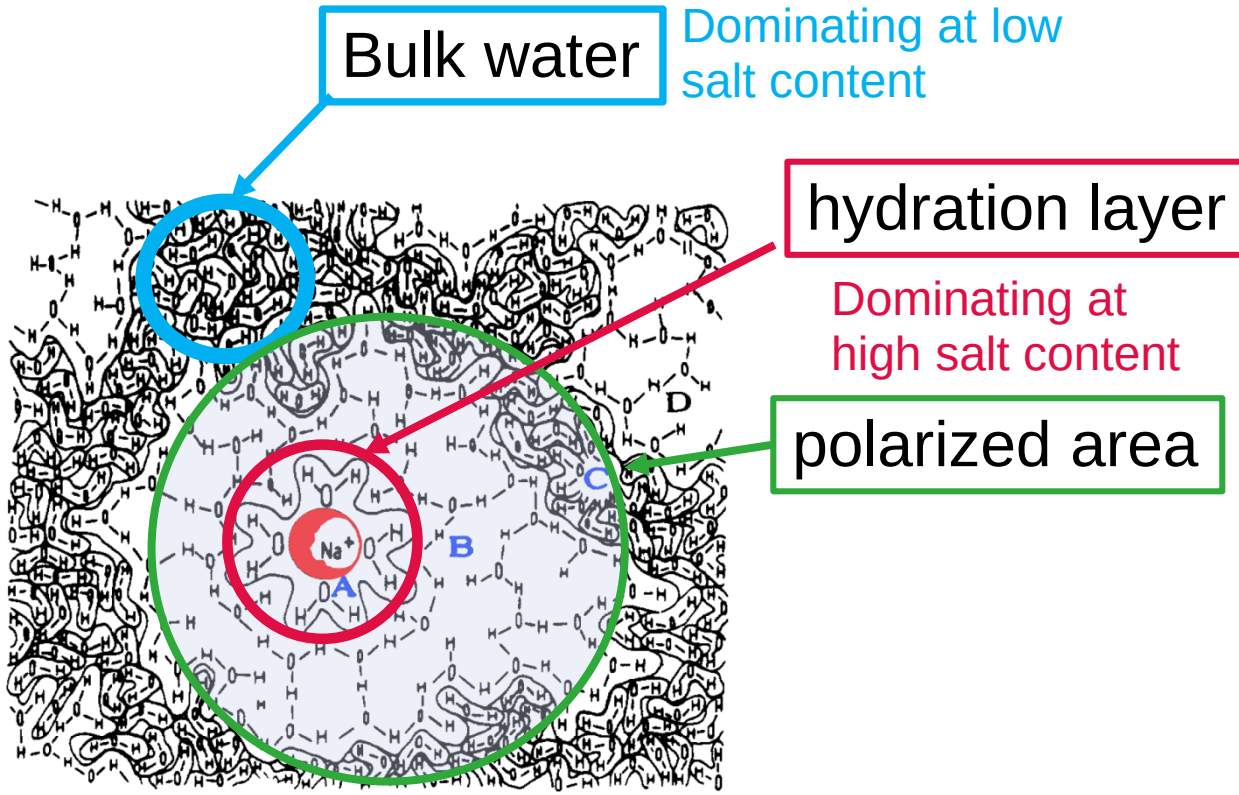
CONCENTRATION DEPENDENCE

Literature results: experiments



Gaeta et al., J. Phys. Chem., **15** (1982) 2967

Chanu-Gaeta Model

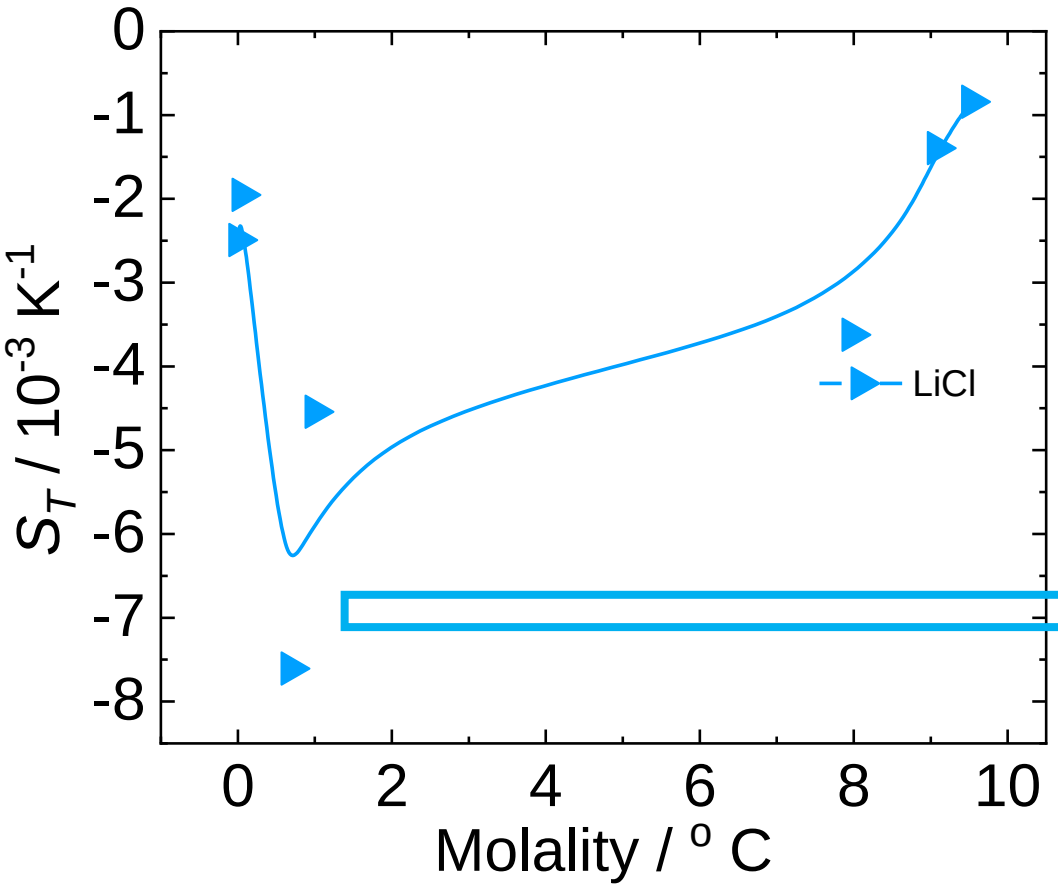


$$S_T = \frac{\delta Q}{c_1 T \left(\partial \mu_1 / \partial c_1\right)_{p,T}}$$

μ chemical potential

CONCENTRATION DEPENDENCE

Literature results: experiments



Uses Chanu-Gaeta model

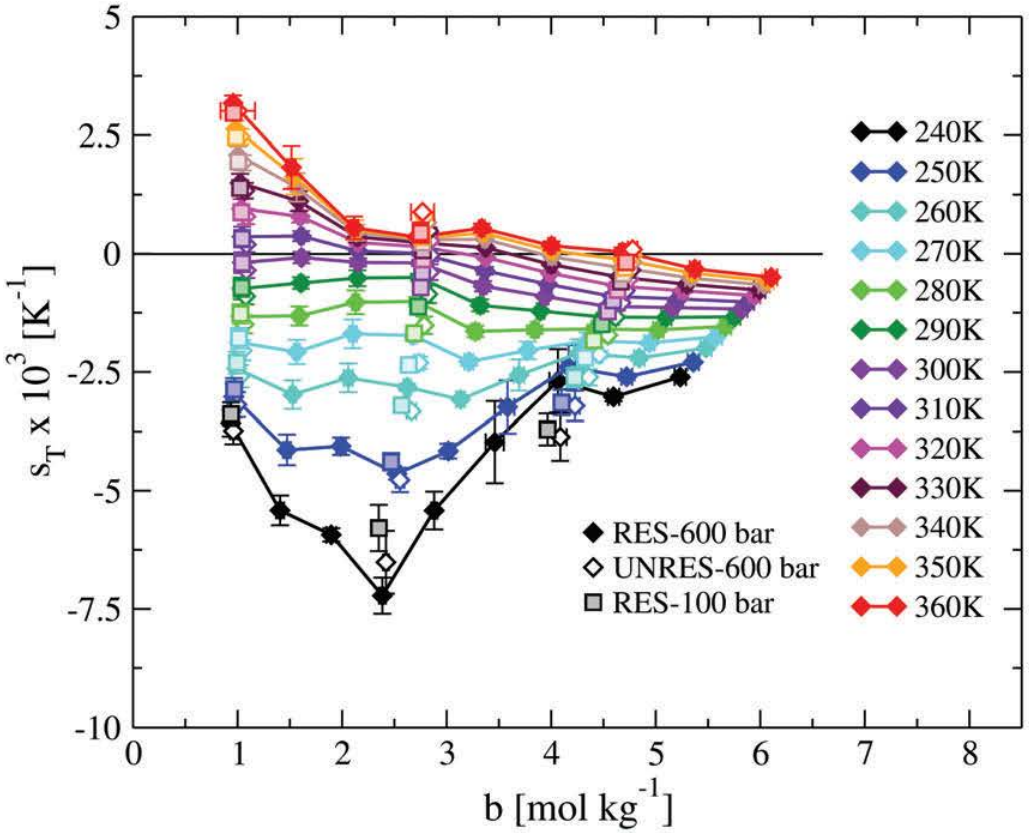
High amount of order exist in high concentration and high dilution → This order corresponds to 2 different structures

Associated with the structure breaking mechanism(Assumption!)

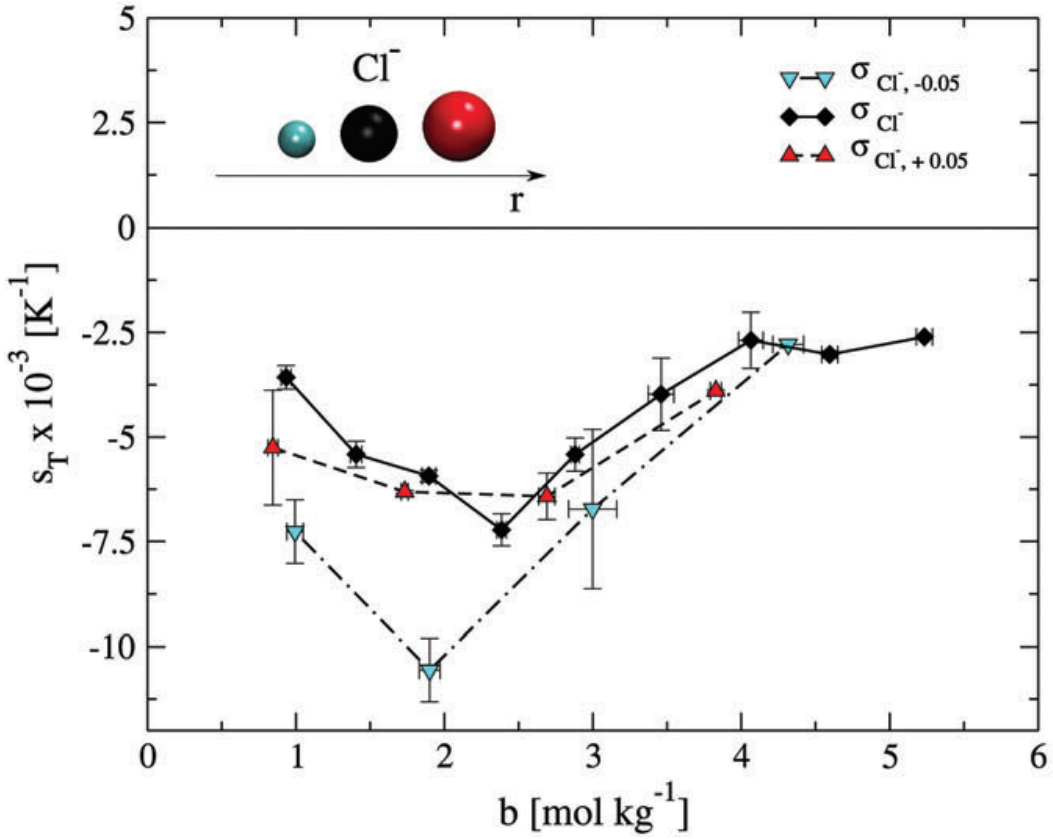
Colombani et al., J. Chem. Phys., **110** (1999) 8622

CONCENTRATION DEPENDENCE

Literature results: Simulations



S. Di Lecce et al, *Phys Chem Chem Phys*, **19** (2017), 9575

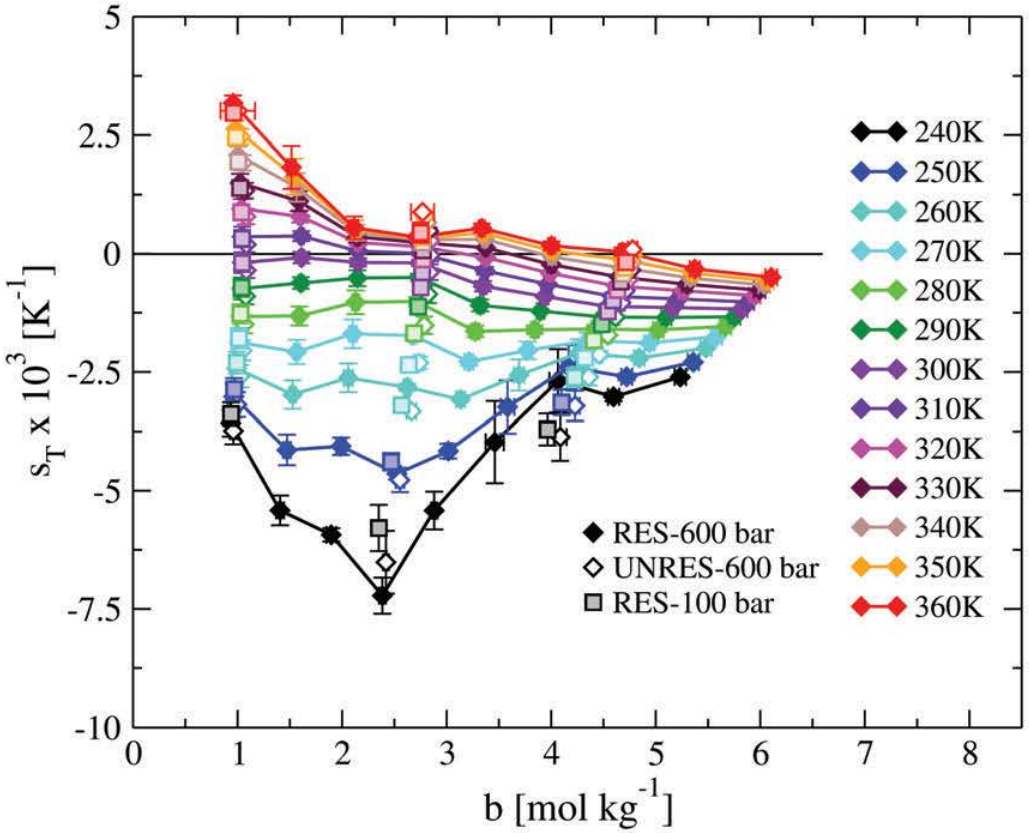


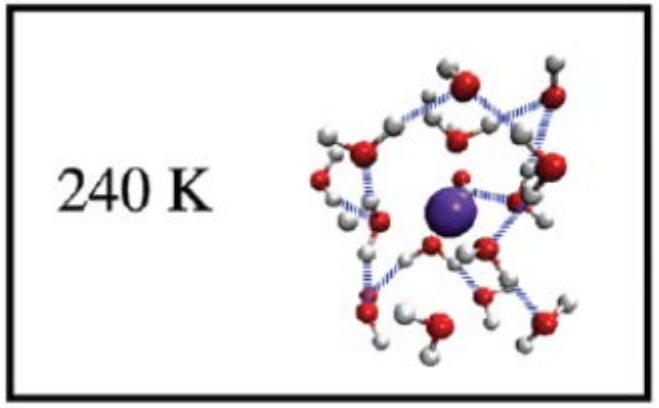
Minimum is enhanced by …

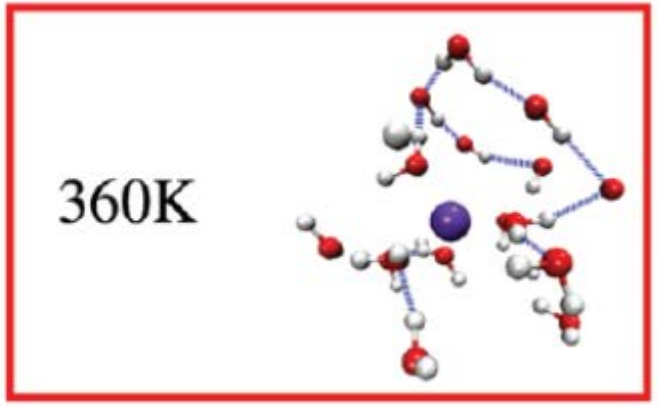
- artificially decreasing the size of the Cl-

CONCENTRATION DEPENDENCE

Literature results: Simulations







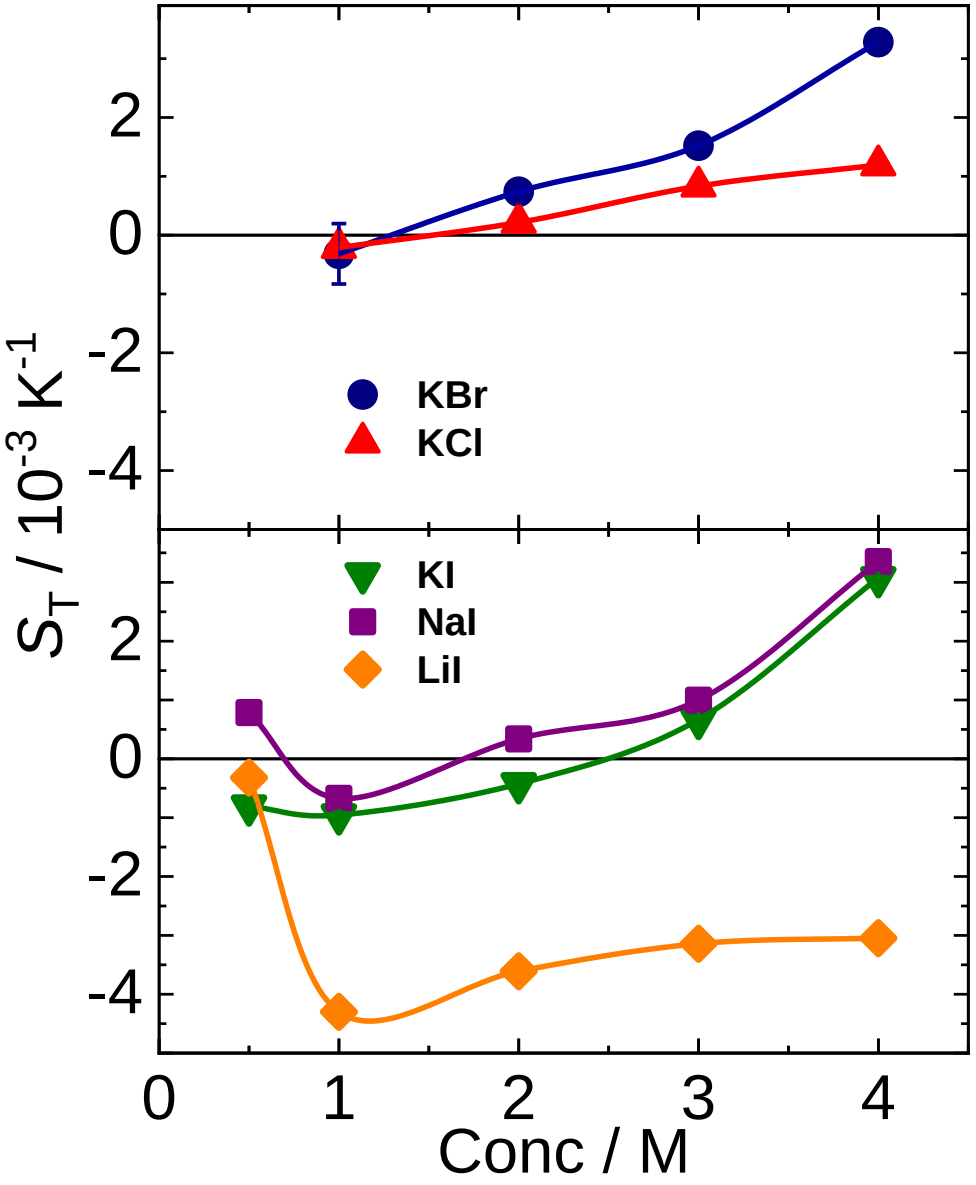
- Higher ordering at lower temperature
- At the temperature corresponding to the minimum, the co-ordination shell features a stronger structure

S. Di Lecce et al, *Phys Chem Chem Phys*, **19** (2017), 9575

Concentration dependence:

TDFRS experiments

- Minimum is observed for KI, NaI and LiI.
- Minimum is absent for KCl and KBr
- All salts except NaI shows thermophilic behavior at low concentrations



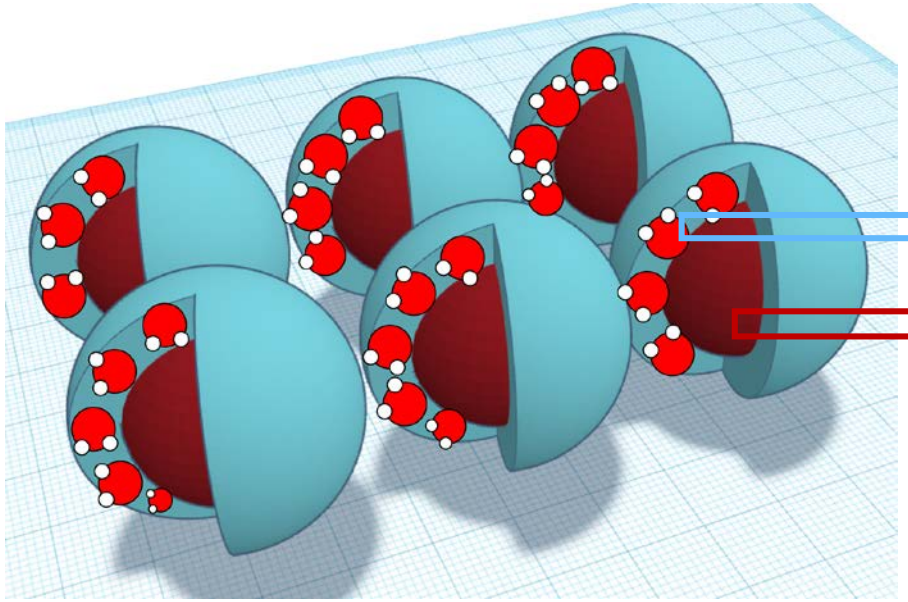
ATTEMPTS TO UNDERSTAND THE MINIMUM

Considering one layer of water molecule around one ion

$$\frac{4}{3}\pi R_{ion}^3 + N_{ion} * \frac{4}{3}\pi R_{water}^3 = \frac{4}{3}\pi(R_{ion} + 2R_{water})^3$$

N_{ion} is the number of water molecules surrounding the ion in first water shell

$$\phi_{salt} = \frac{Volume_{cation} + Volume_{anion}}{Volume_{cation} + Volume_{anion} + (N_{cation} + N_{anion}) * Vol_{water}}$$

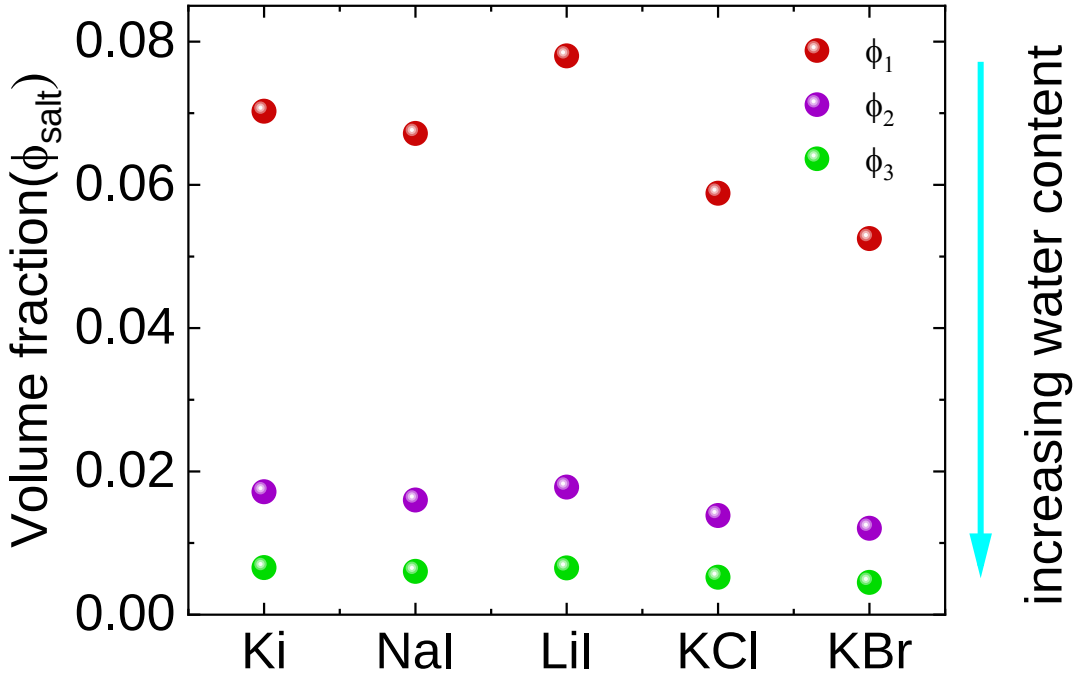


First layer of water molecules

Ion

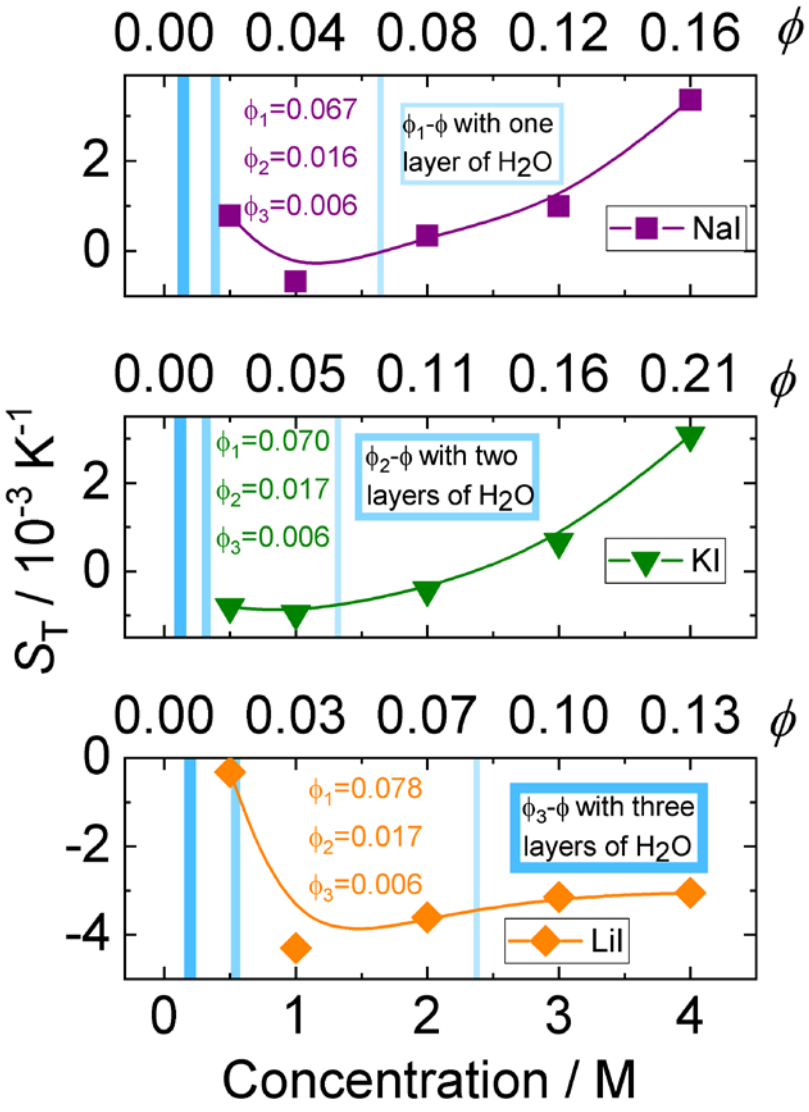
ATTEMPTS TO UNDERSTAND THE MINIMUM

Considering one-, two-, three layers of water molecules around one ion



- Φ_1- Volume fraction with one layer of water molecule surrounding the ion
- Φ_2- Volume fraction with two layers of water molecules surrounding the ion
- Φ_3- Volume fraction with three layers of water molecules surrounding the ion

ATTEMPTS TO UNDERSTAND THE MINIMUM

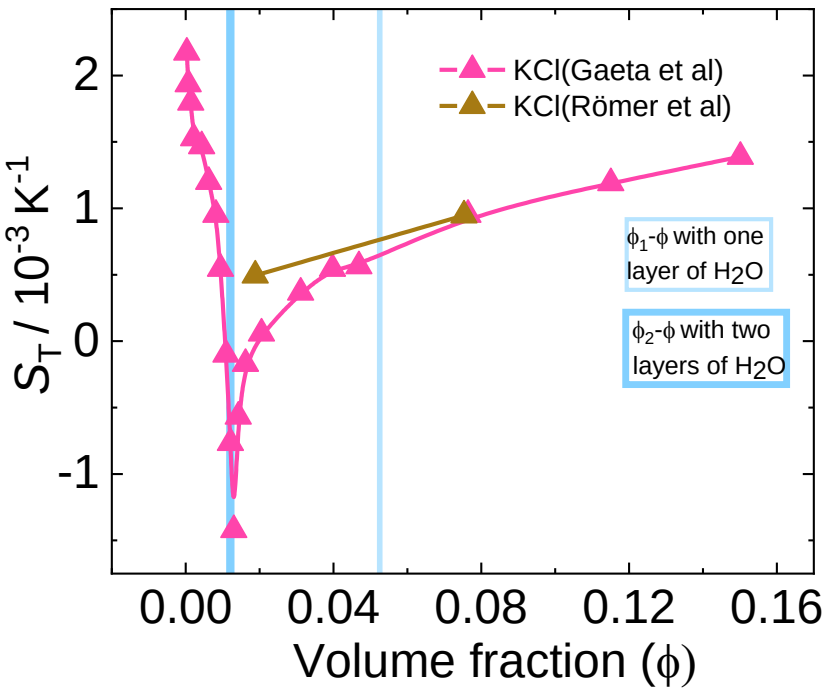


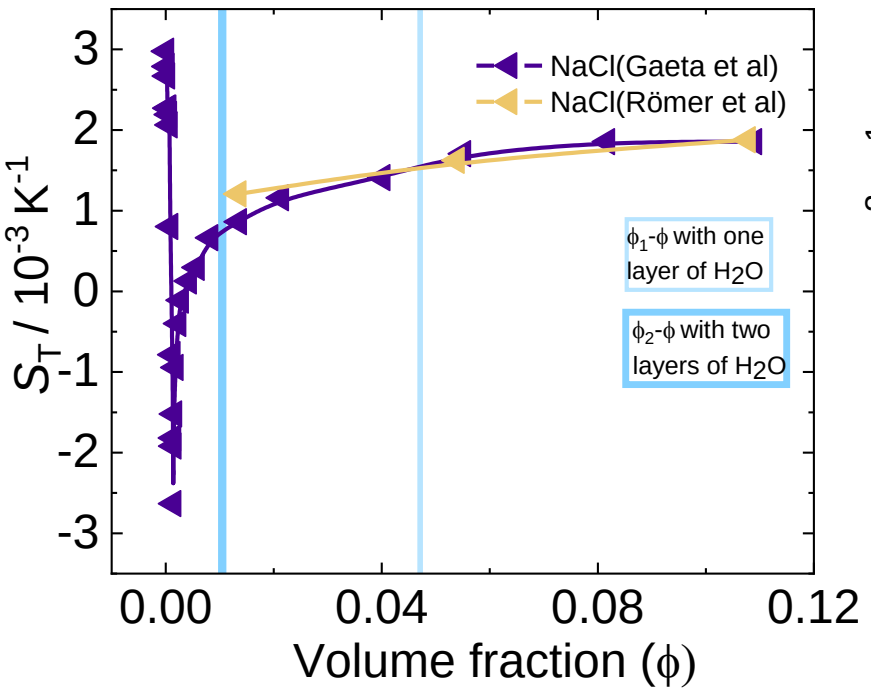
- Minimum for these salts was falling in between ϕ_2 and ϕ_1
- Hypothesis: Minimum occurs at the concentration in which a change in the hydration shell surrounding the ions occur.

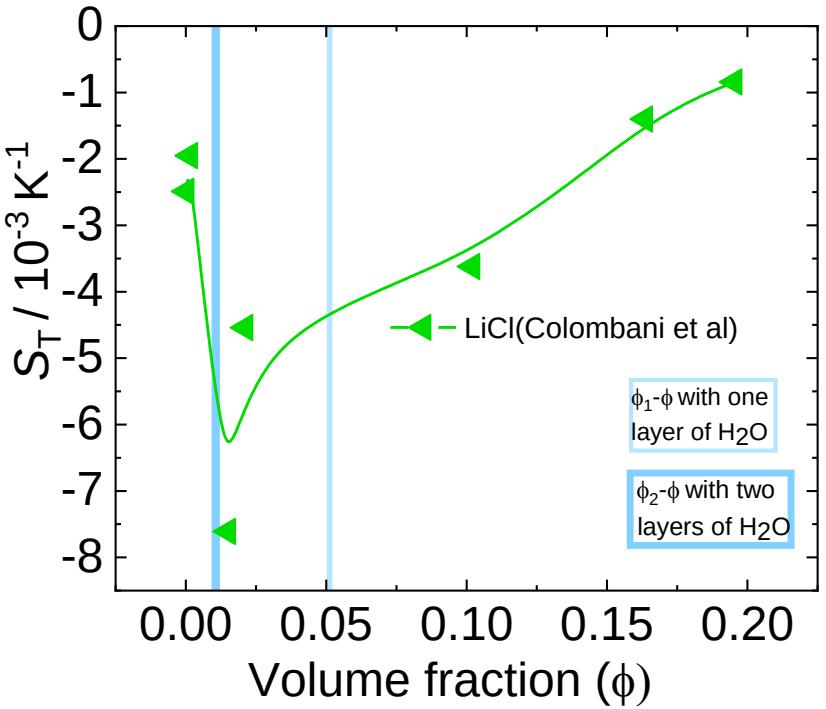
Is this being followed for the literature data of KCl, NaCl and LiCl?

JÜLICH Forschungszentrum

ATTEMPTS TO UNDERSTAND THE MINIMUM







KCl, LiCl: Follows our assumption

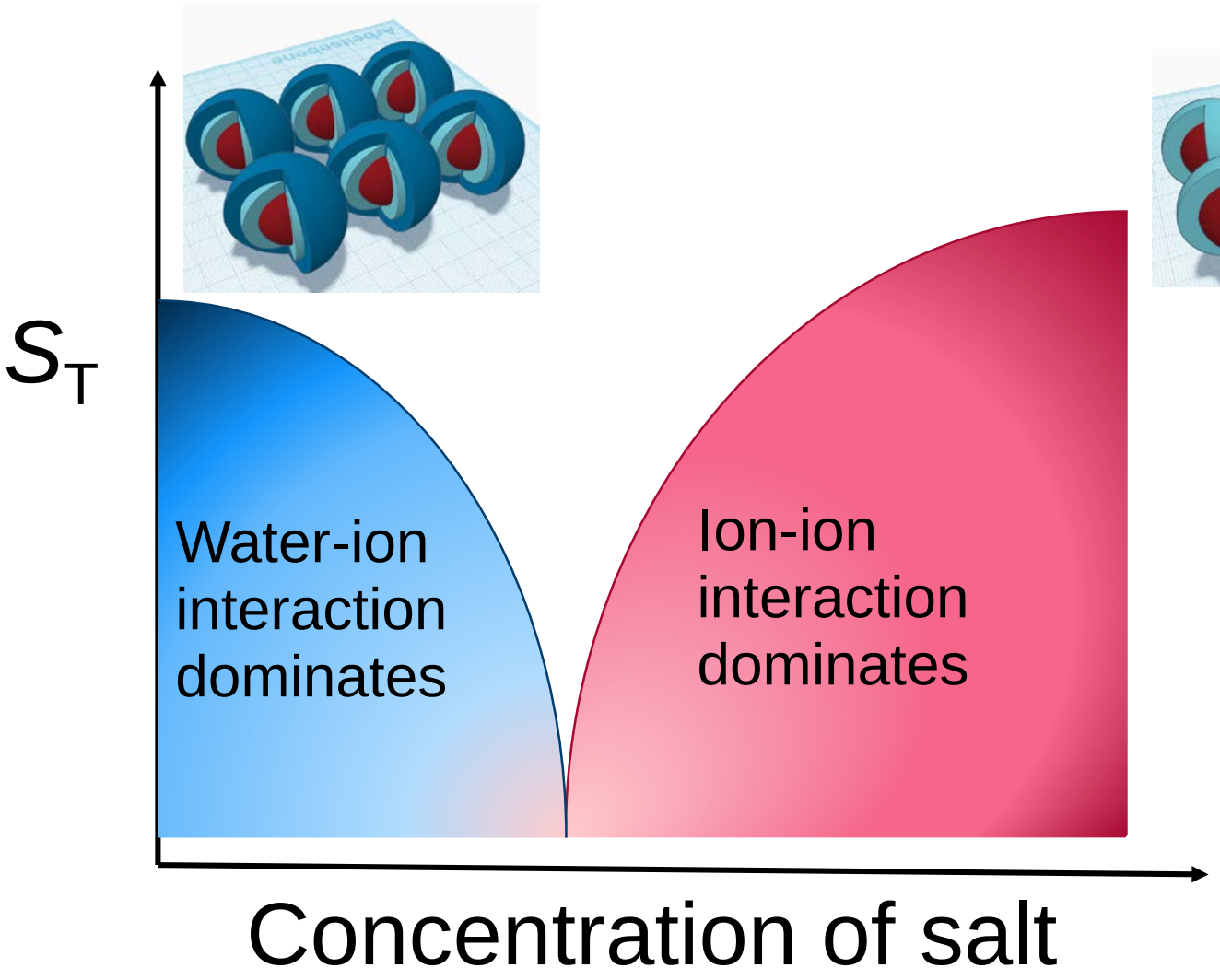
NaCl: Deviates from our assumption (problem with the data?)

Colombani et al., J. Chem. Phys., **110** (1999) 8622

Gaeta et al., J. Phys. Chem., **15** (1982) 2967

Römer, et al., J. Phys. Chem. B, **117** (2013) 8209

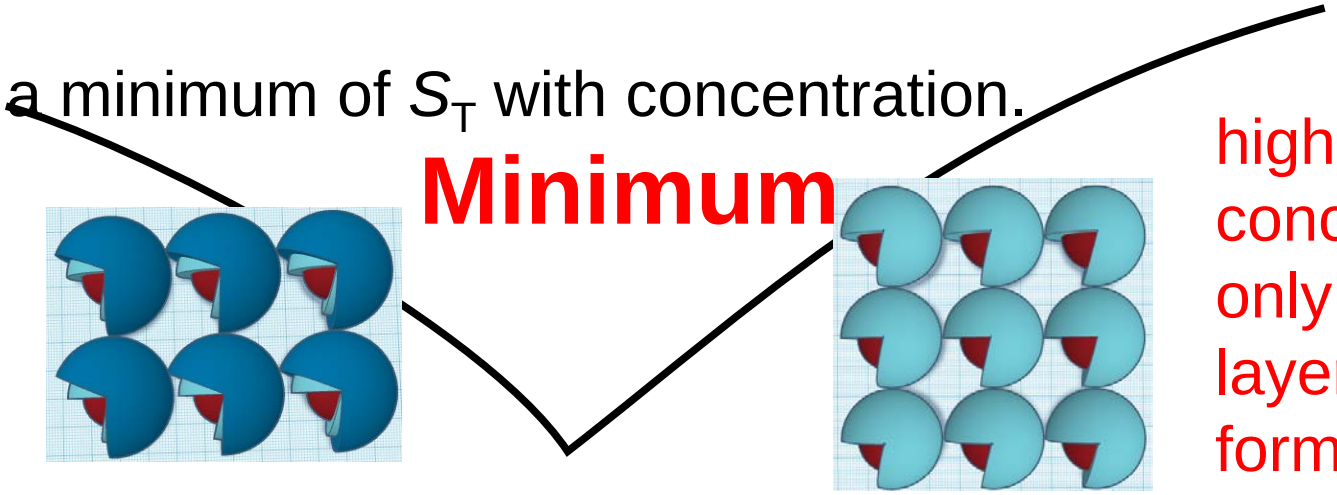
ASSUMPTION BASED ON THE RESULTS



- Very high water content (=low salt concentration: ions sees only water
- Moderate salt content between two and one layers of water molecules
- Very high salt content (=low water content) ions see ions

CONCLUSIONS

- We performed systematic thermophoretic measurements of 5 Alkali halides
- S_T of salts KBr and KCl show the typical *T*- and *c*-dependence of non-ionic solutes
- Some salts showed a minimum of S_T with concentration.



- This observation is also valid for most literature systems

Long term goal: Quantitative understanding of protein-ligand binding. Impact of salts

CONCLUSIONS

- We carried out calculations assuming that the changes in hydration layer of water in presence of ion is the cause for the occurrence of minimum
- We calculated the volume fraction corresponding to each hydration layer
- Hypothesis : Minimum could be corresponding to the concentration at which a change from second hydration shell to first shell occurs
- This hypothesis was being validated for previous literature data

The first two statements are basically identical. And personally I do not think that this step needs to be mentioned in detail. It is included in the picture.

Long term goal:

Quantitative understanding of protein-ligand binding

ACKNOWLEDGEMENT

Simone Wiegand, Jan K.G. Dhont and the whole IBI-4

Doreen Niether, IEK-8

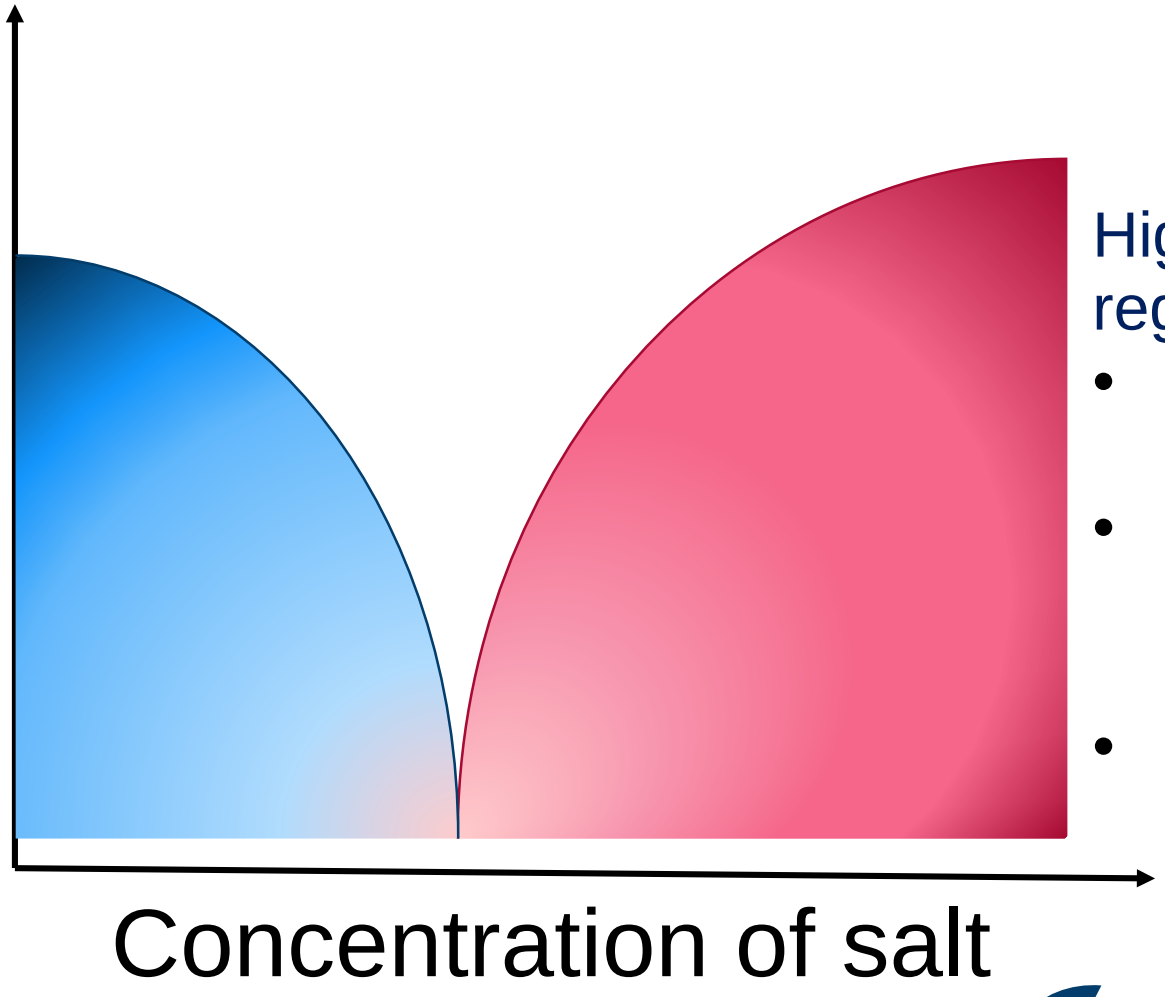
Thank you and Stay Healthy

CONCENTRATION DEPENDENCE

Literature results: experiments

Low concentration region:

- Migration of ion gives more ordering
- Results in decrease of entropy
- Results in heat liberation
- Ions diffuse towards the cold wall to contend with the heat flux due to thermal gradient(S_T>0)



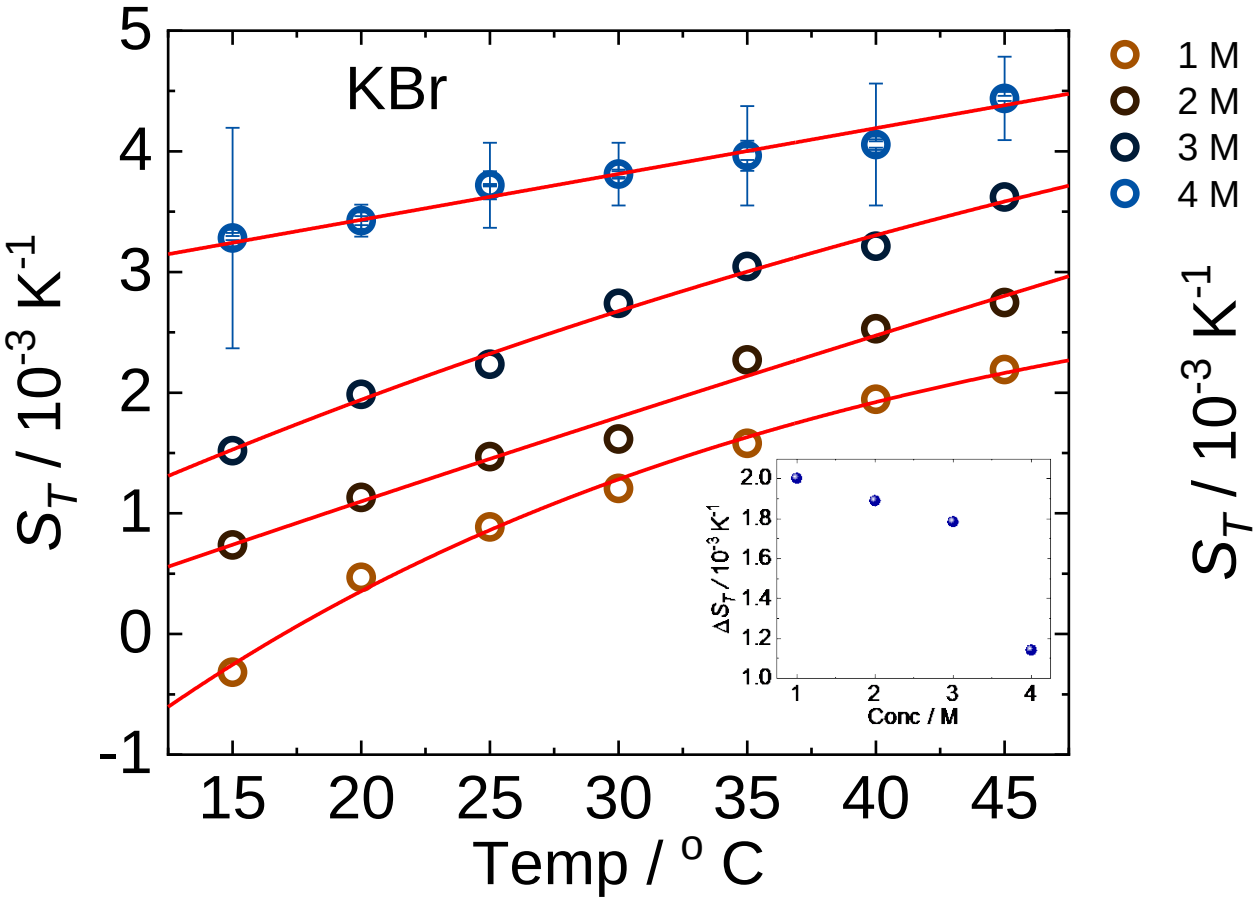
High concentration region:

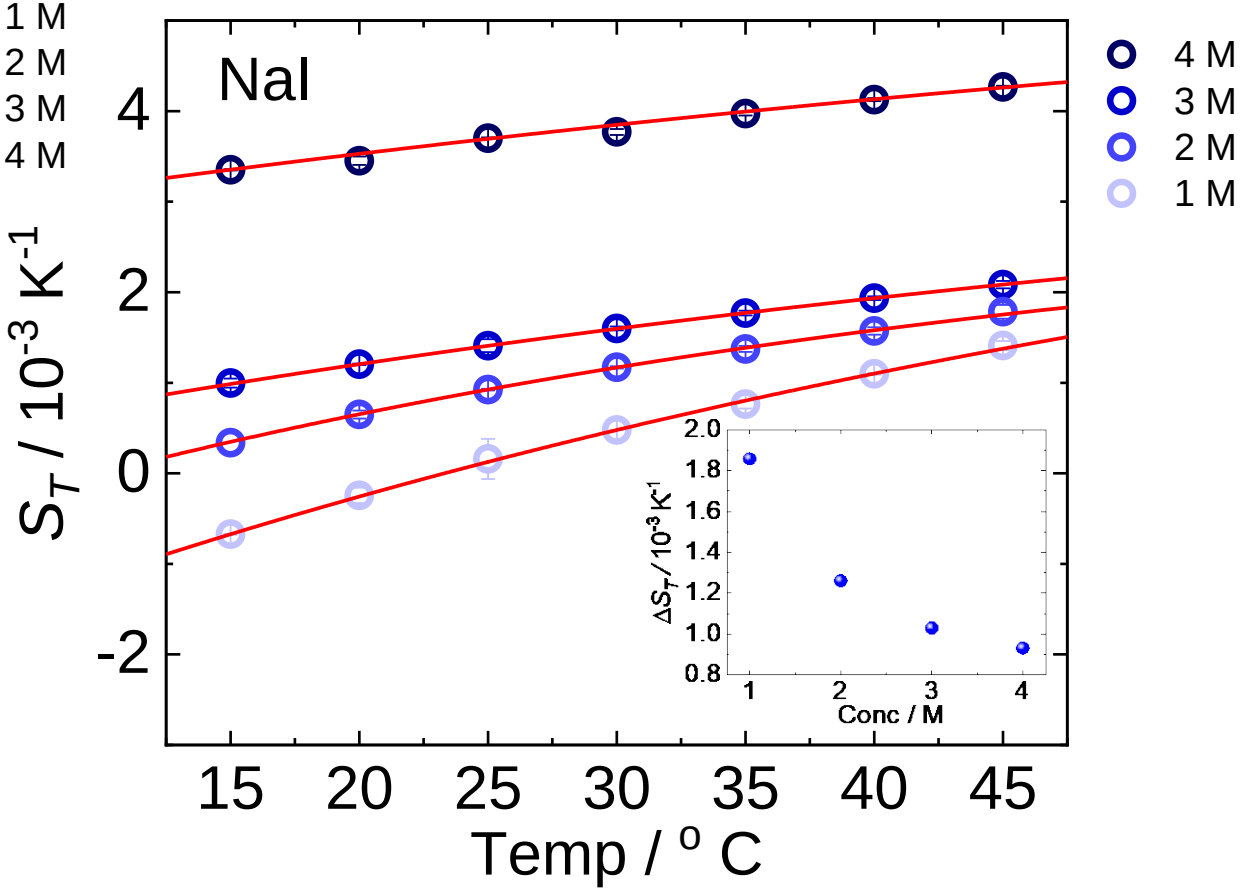
- More number of hydrogen bonds
- Results in decrease of entropy
- S_T is positive

Colombani et al., J. Chem. Phys., **110** (1999) 8622

Temperature dependence:

Could you please update the figures and include all concentrations also 0.5 M

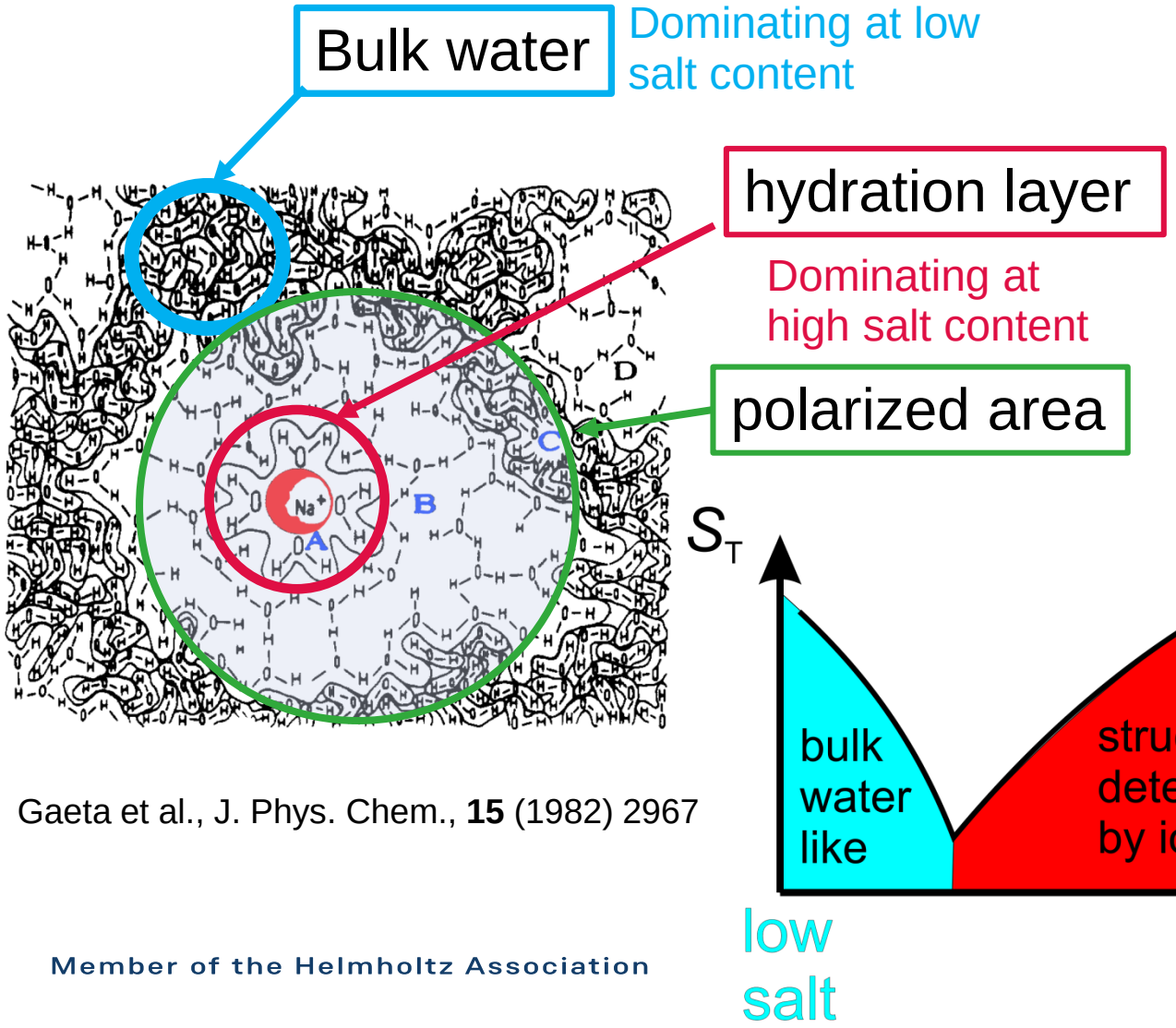




- Temperature dependent slope of S_T increases for KI, while NaI behaves as non-ionic solutes

ATTEMPT TO EXPLAIN THE MINIUMUM

Early work by Gaeta – argumentation considers only entropic effects



Gaeta et al., J. Phys. Chem., **15** (1982) 2967

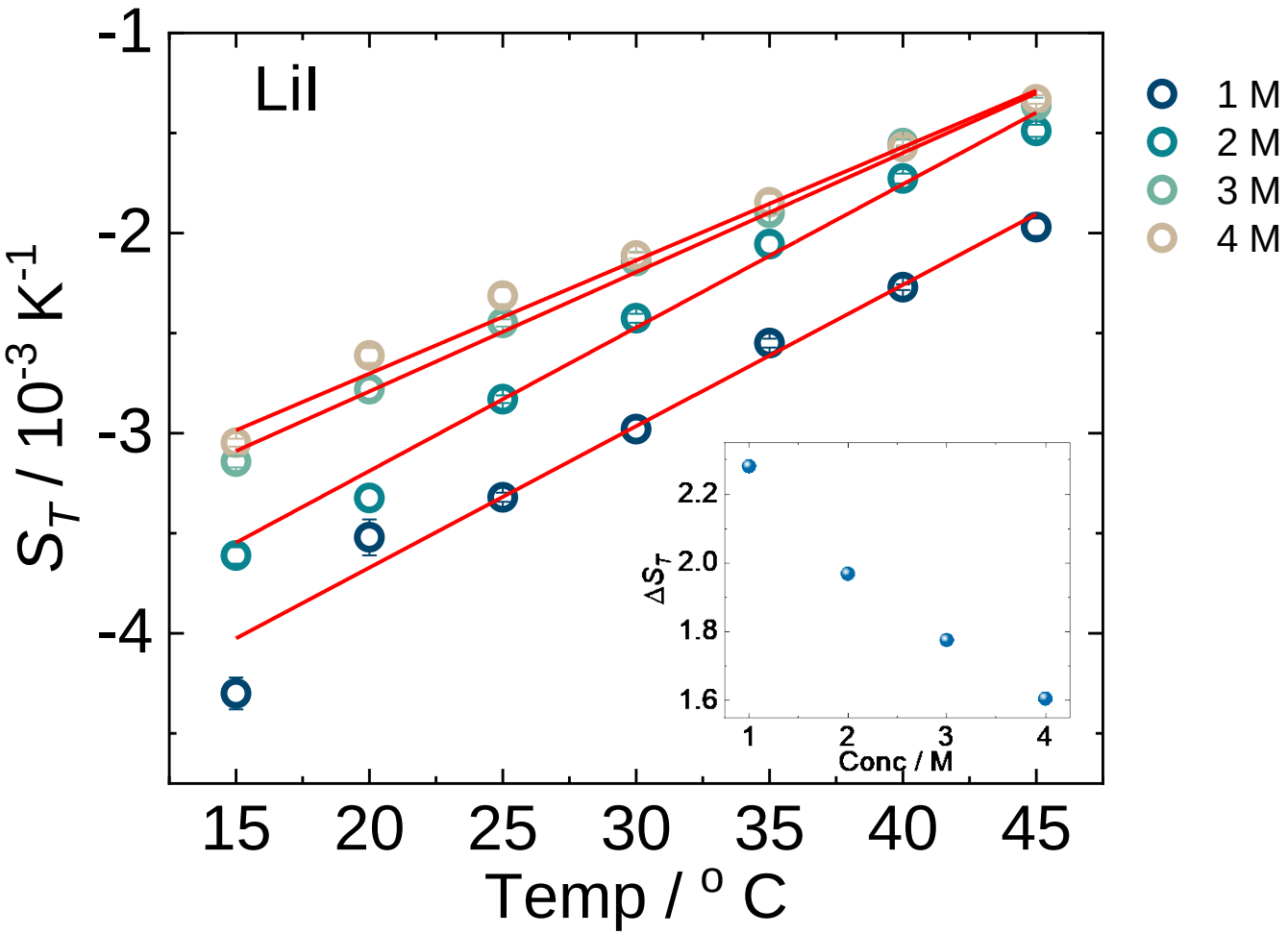
Bulk water less ordered
Hydrating water more ordered

Moving the ion into the area of bulk water leads to a higher order and an entropy loss and a local heat release $\delta Q > 0$

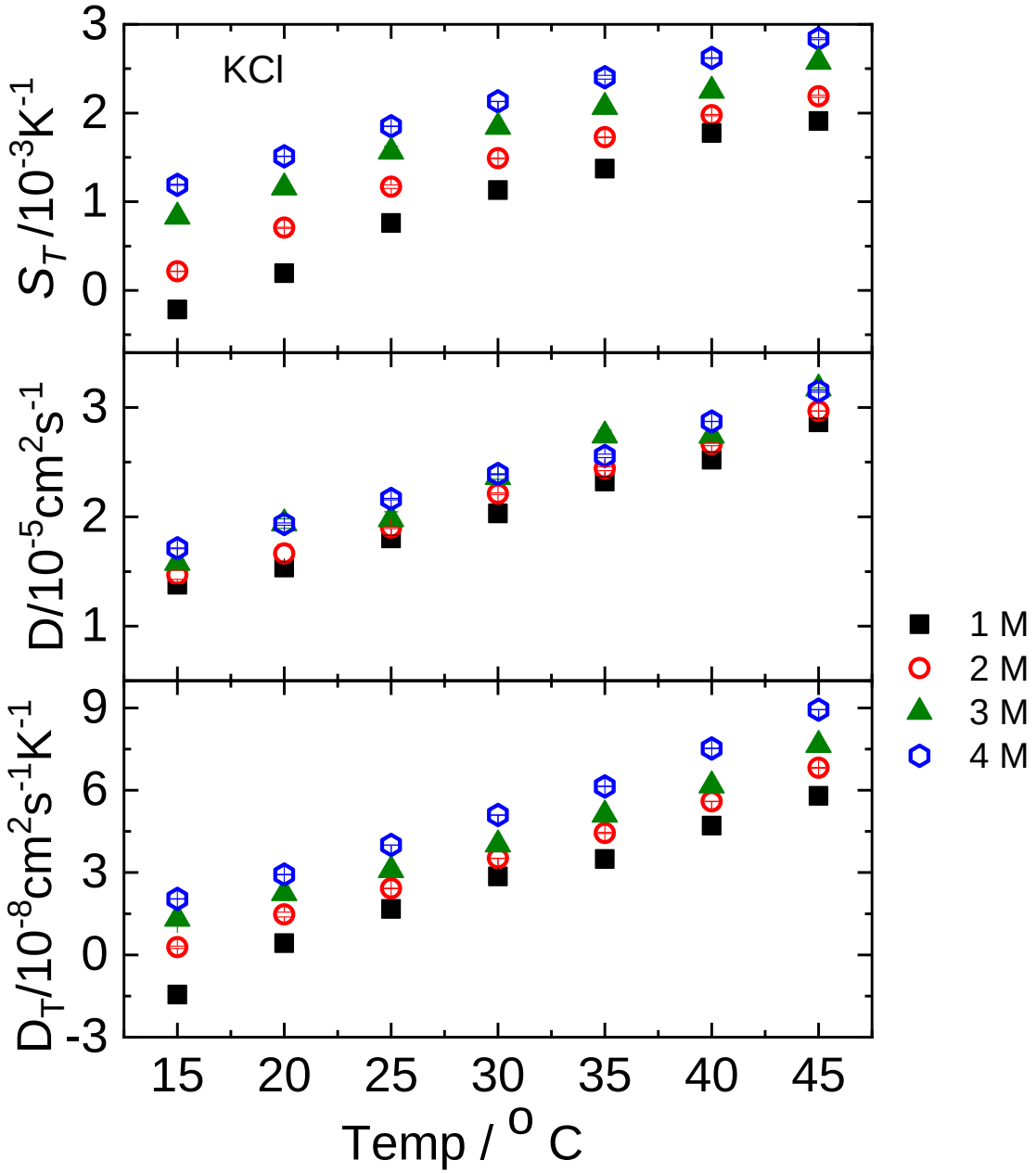
$$S_T = \frac{\delta Q}{c_1 T \left(\partial \mu_1 / \partial c_1\right)_{p,T}}$$

μ chemical potential

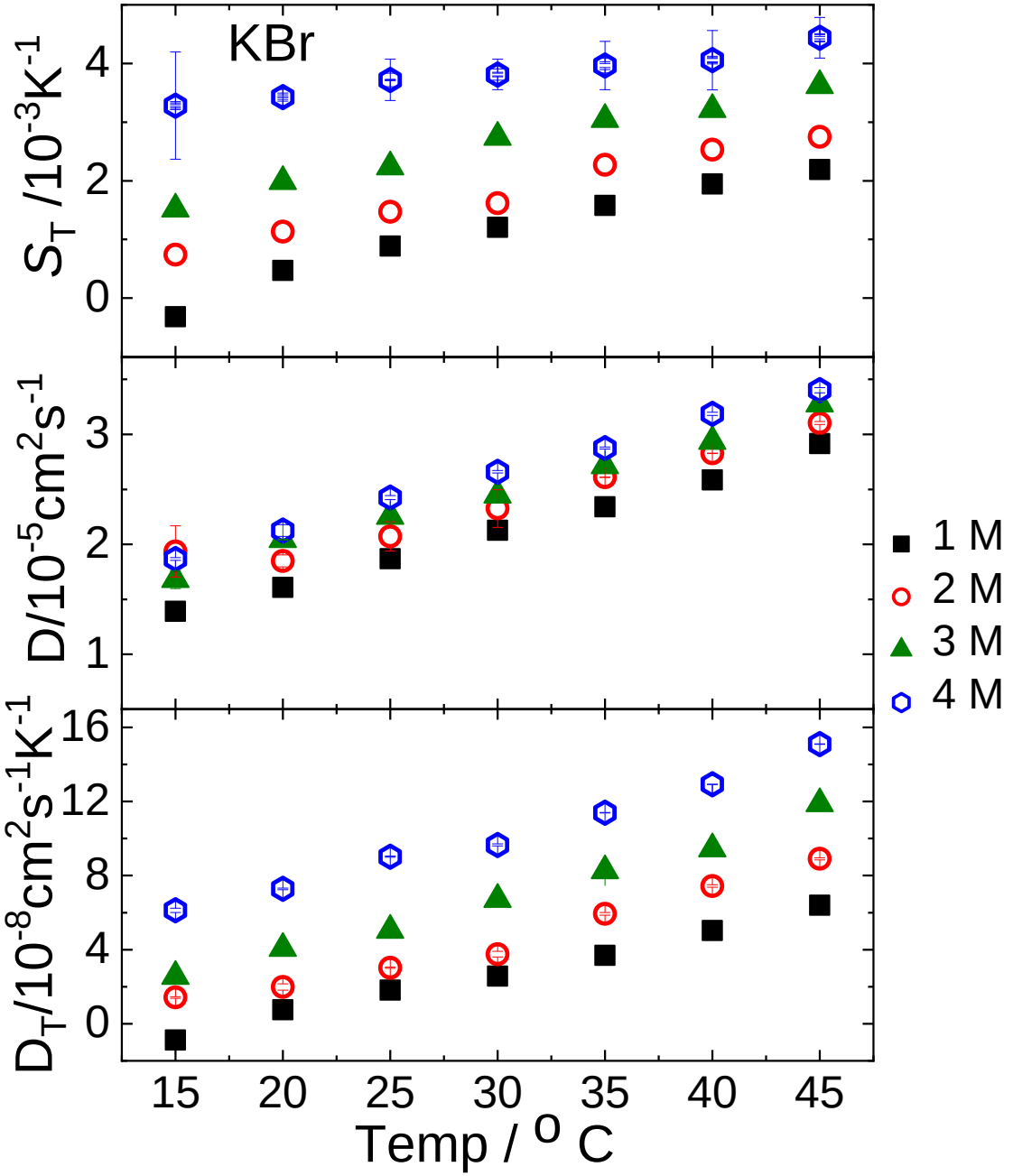
assuming $(\partial \mu_1 / \partial c_1)_{p,T} > 0$
$\rightarrow S_T > 0$



How do the LiI data compare with Colombani measurements



Could you please update the figures and include all concentrations



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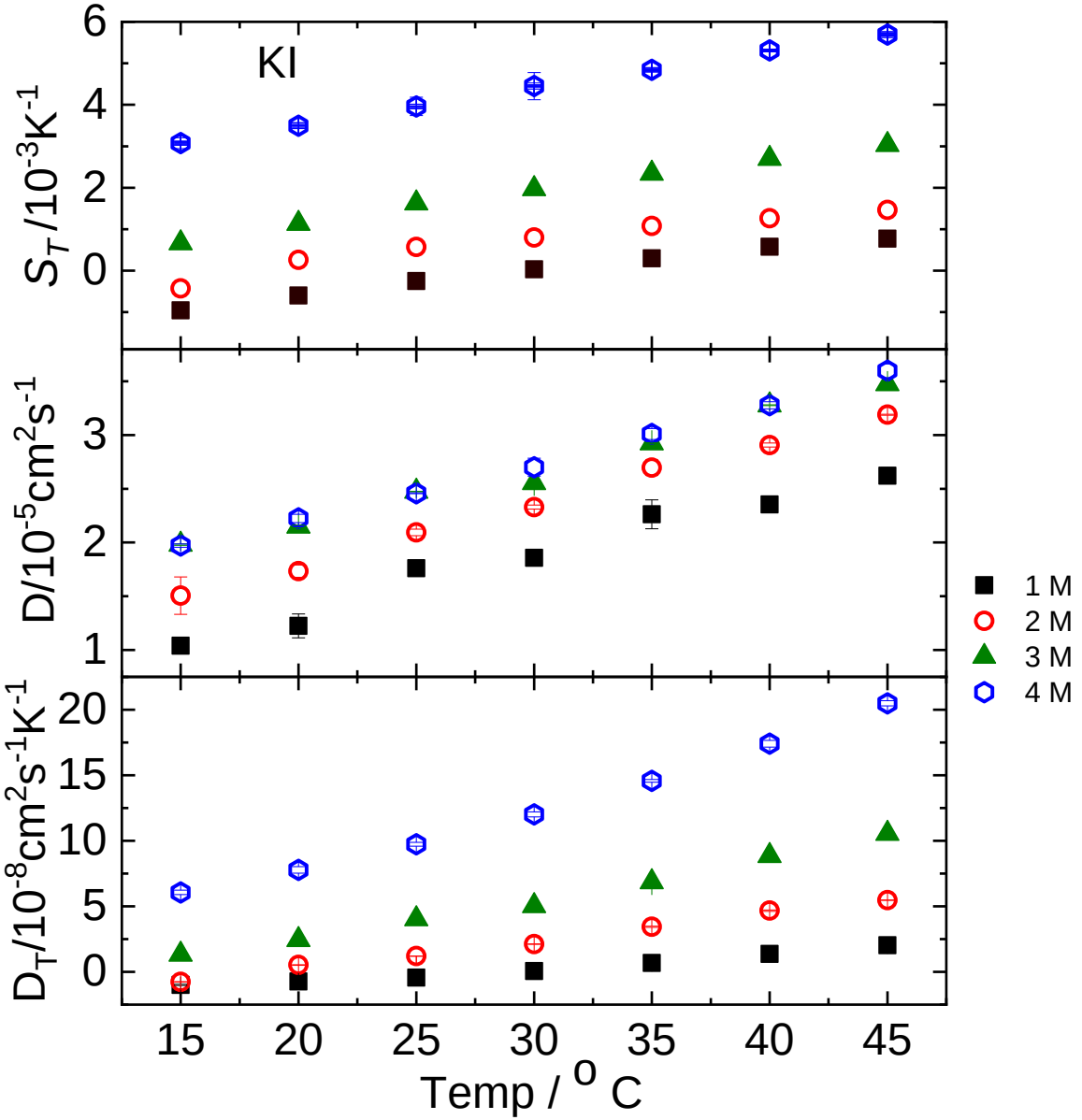
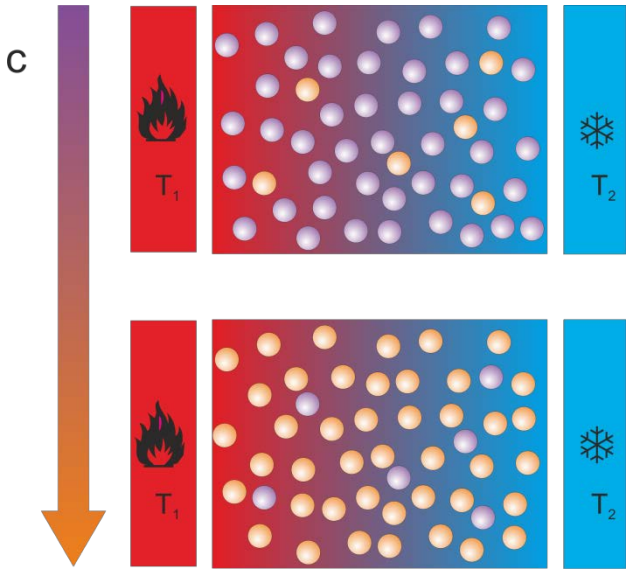


Could you please update the figures and include all concentrations

EXPLANATION FOR THE SIGN CHANGE

If the cross interactions are stronger than the pure interaction ...



$$\varepsilon_{12} > \varepsilon_{11}$$

$$\varepsilon_{12} > \varepsilon_{22}$$

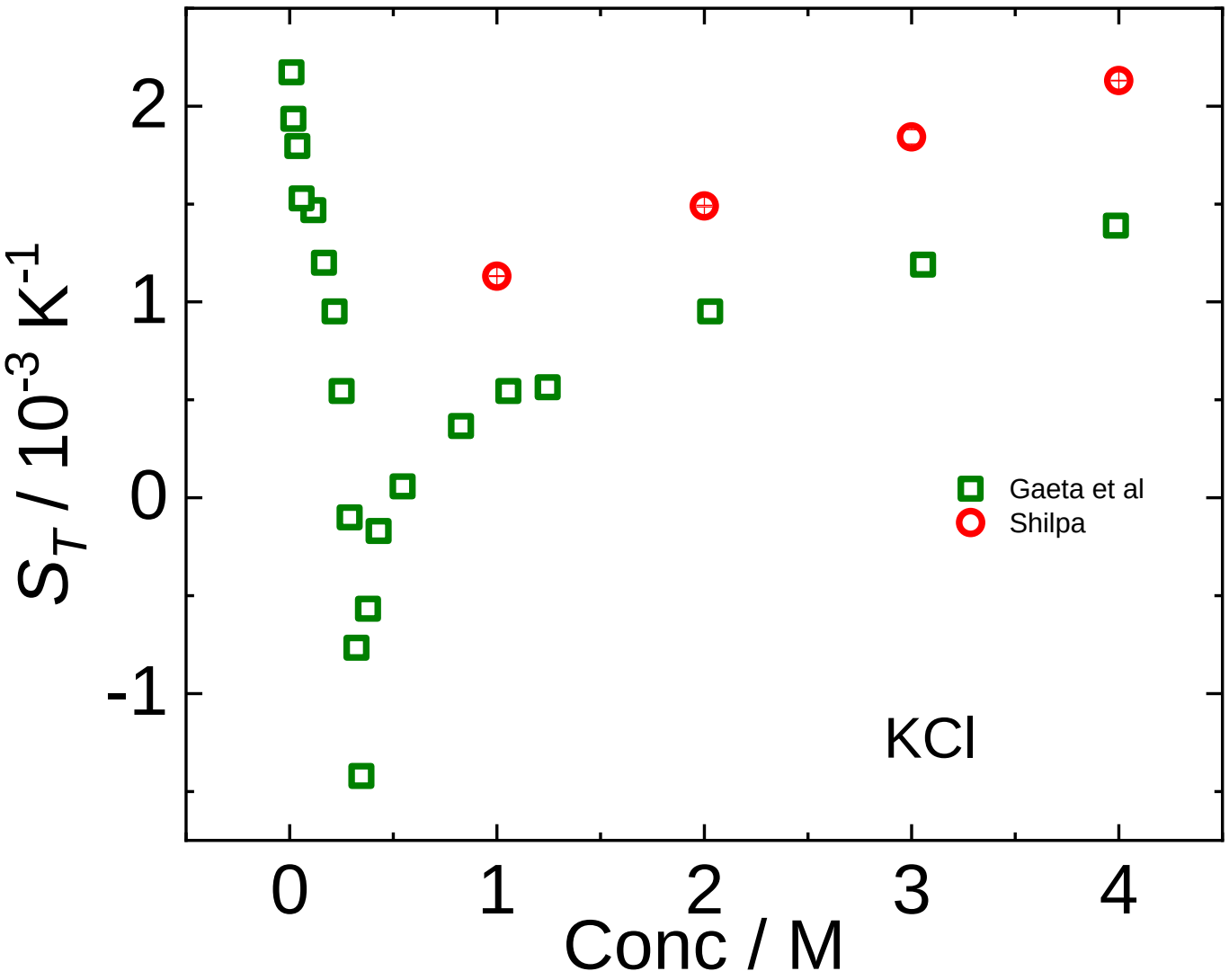
$$T_1 > T_2$$

$$\Rightarrow \underbrace{e^{-\varepsilon_{12}/kT_1}}_{\propto E(T_1)} > \underbrace{e^{-\varepsilon_{12}/kT_2}}_{\propto E(T_2)}$$

For energetic reasons most mixed interaction take place on the cold side

... Minority component goes to the cold side

I. Prigogine et al., *Physica,* **16** (1950), 851


S_T / 10^{-3} K^{-1}
2
1
0
-1
0
1
2
3
4
Conc / M
Gaeta et al
Shilpa
KCl

1. According to Chanu-Gaeta model when an ion gets solvated in water entropy decreases due to more structure formation, high number of hydrogen bonds, ion-dipole interaction etc. This leads to a liberation of heat and ion migrate towards the cold side . i.e, S_T is positive

How this is explained?

When free ions move through water there are 3 factors that contribute towards the heat of transport

a) Local energy fluctuations associated with the interactions
b) Electrostatic interaction between ionic charges and water molecules Polarization effect are certainly important?
c) Structure making or structure breaking ability of ion These structure breaking and making concepts are very va

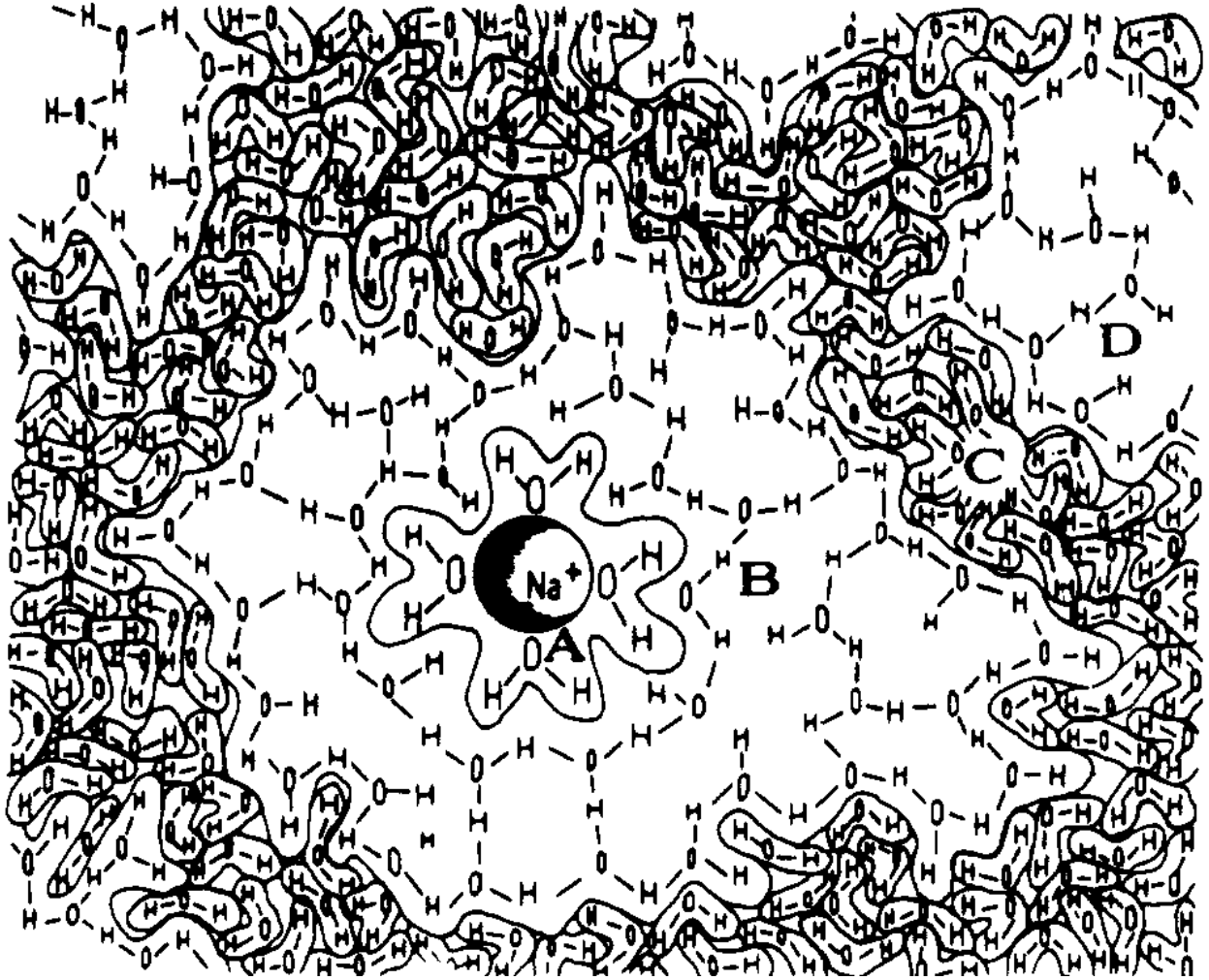
High positive heat …….low entropy

Concentration can be divide into 2

1)Till C* Since concentration is less water is not bound to ions and is increasingly disordered due to long range interactions

2)After C* Q increases with concentration. At this point there is an ordered configuration with a polarized solvent which leads to this increase in Q

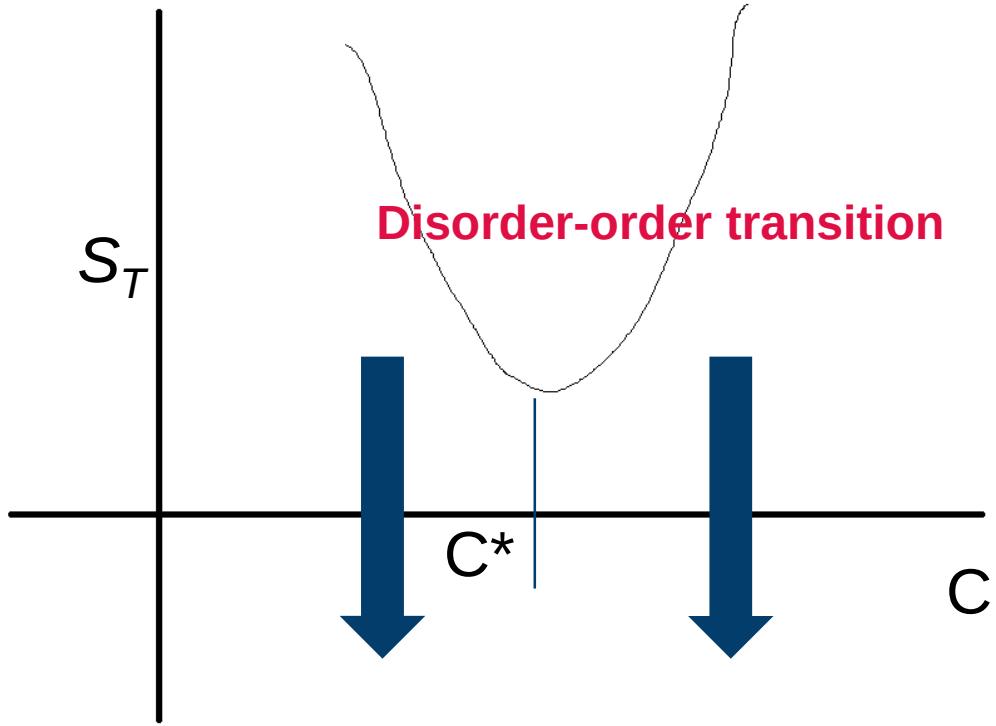
The drifting particle is ion with its hydration shell. With increasing salt concentration there is a total disappearance of free water which indicates it is then e very ordered free medium.



Region A is not affected by temperature and concentration changes, but is strongly dependent on the nature of the ion.

Region B and C are affected by these changes.

Remark: I expect that also region A should be influenced by Temperature, because the number of hydrogen bonds will decrase with temperature



Is this argumentation in the colombani paper?

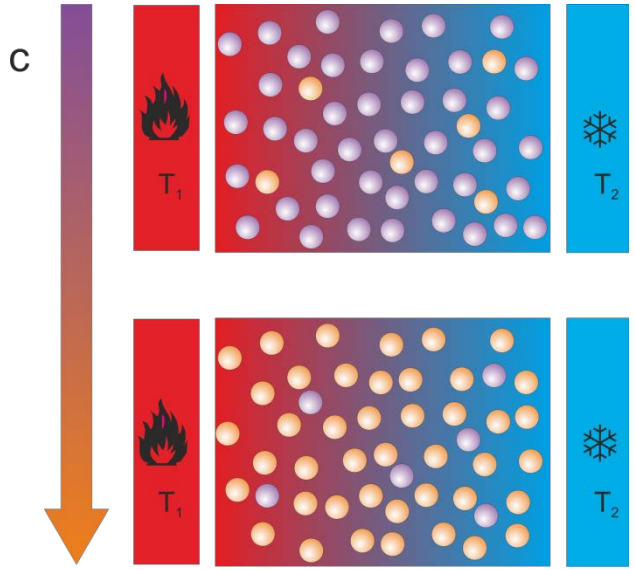
Conc is less and there are long range interactions. Water is not so bound to ions and highly disordered structure. Large entropy and less positive or negative heat. S_T becomes less positive

Conc increases. Water is bound to ions and comparatively ordered structure. Less entropy and more positive heat. S_T becomes more positive

CONCENTRATION DEPENDENCE

Cross interactions

If the cross interactions are stronger than the pure interaction ...



$$\varepsilon_{12} > \varepsilon_{11}$$

$$\varepsilon_{12} > \varepsilon_{22}$$

$$T_1 > T_2$$

$$\Rightarrow \underbrace{e^{-\varepsilon_{12}/kT_1}}_{\propto E(T_1)} > \underbrace{e^{-\varepsilon_{12}/kT_2}}_{\propto E(T_2)}$$

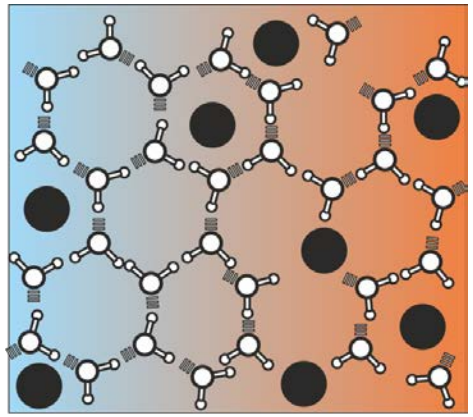
For energetic reasons most mixed interaction take place on the cold side

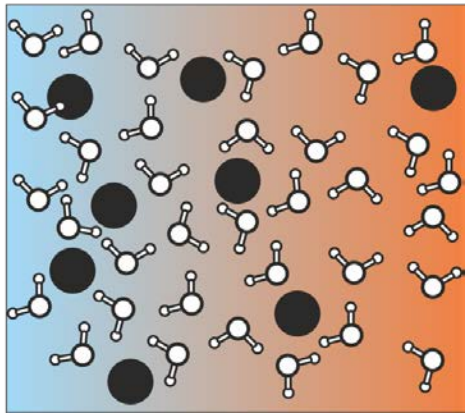
[I. Prigogine et al. Physica **16** (1950) 851]

... Minority component goes to the cold side

TEMPERATURE DEPENDENCE

Gedankenexperiment





Assuming local thermodynamic equilibrium

At low temperatures:
minimization of the free energy

$$G = H - TS$$

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

→ water goes to the **cold** side

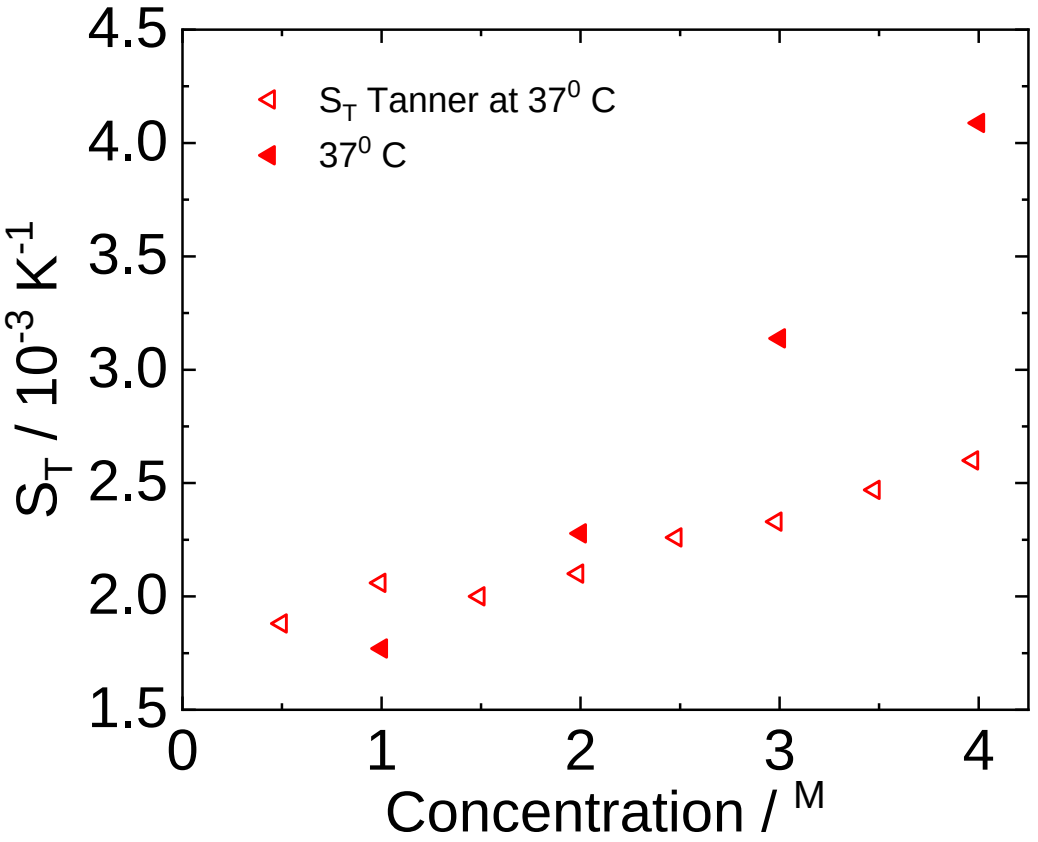
At high temperatures:
minimization of the free energy

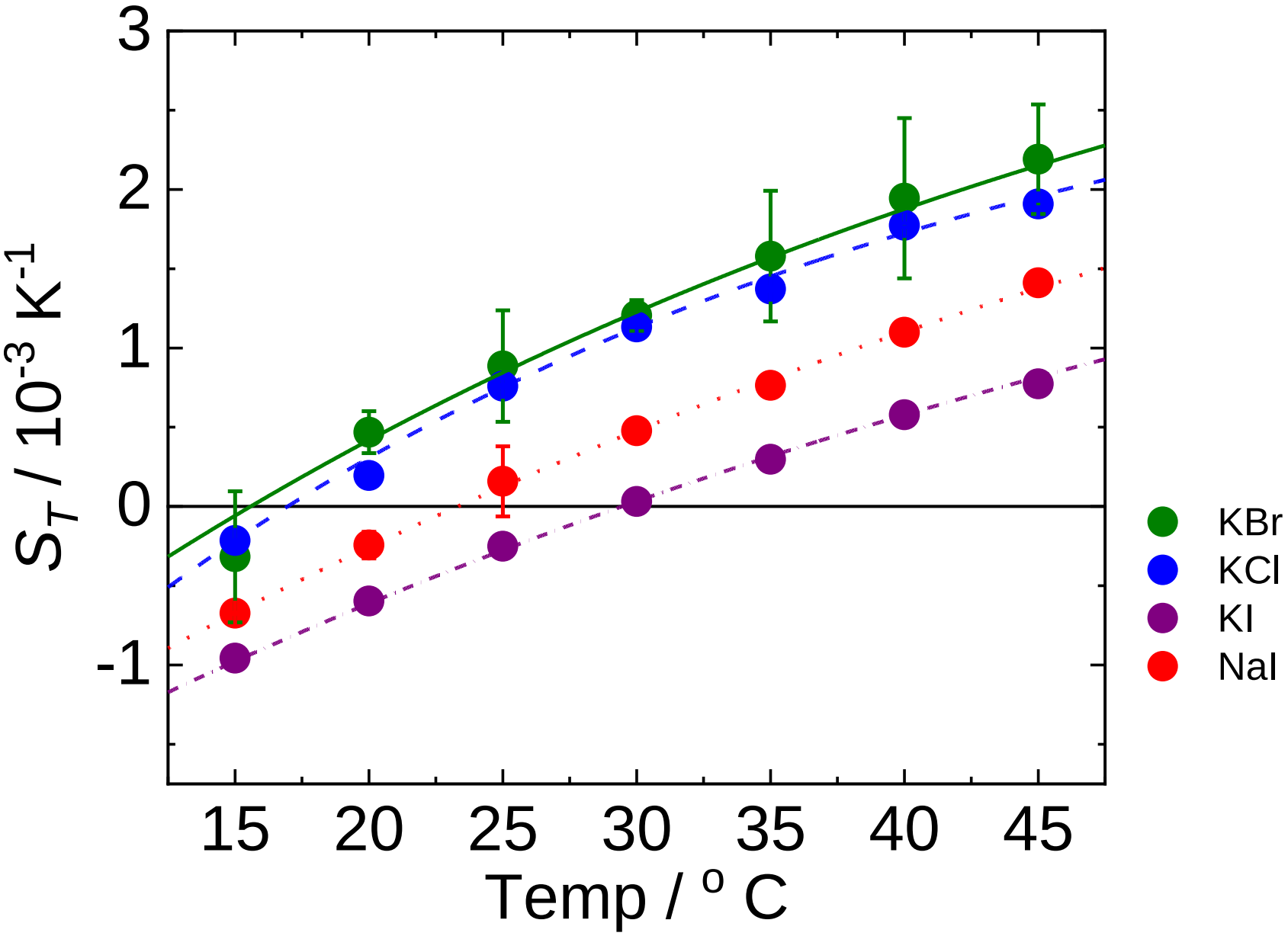
$$G = H - TS$$

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.]


4.5
4.0
3.5
3.0
2.5
2.0
1.5
0
1
2
3
4
S_T / 10^{-3} K^{-1}
Concentration / M
S_T Tanner at 37^0 C
37^0 C



less H-bonds with temperature

- S_T increases
- **ΔS_T decreases**

Which concentration?