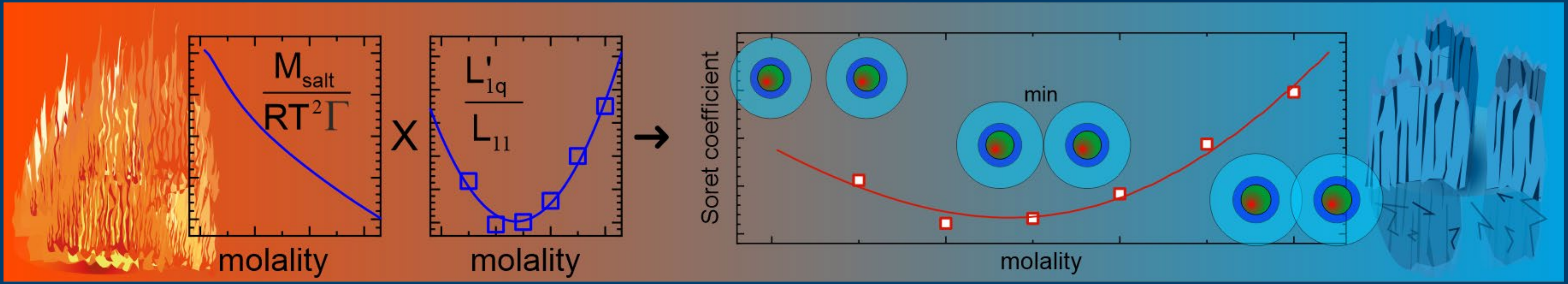
WHAT IS THE NATURE OF THE SORET EFFECT IN SALT SOLUTIONS?

Thermo(dynamic/static) or kinetic

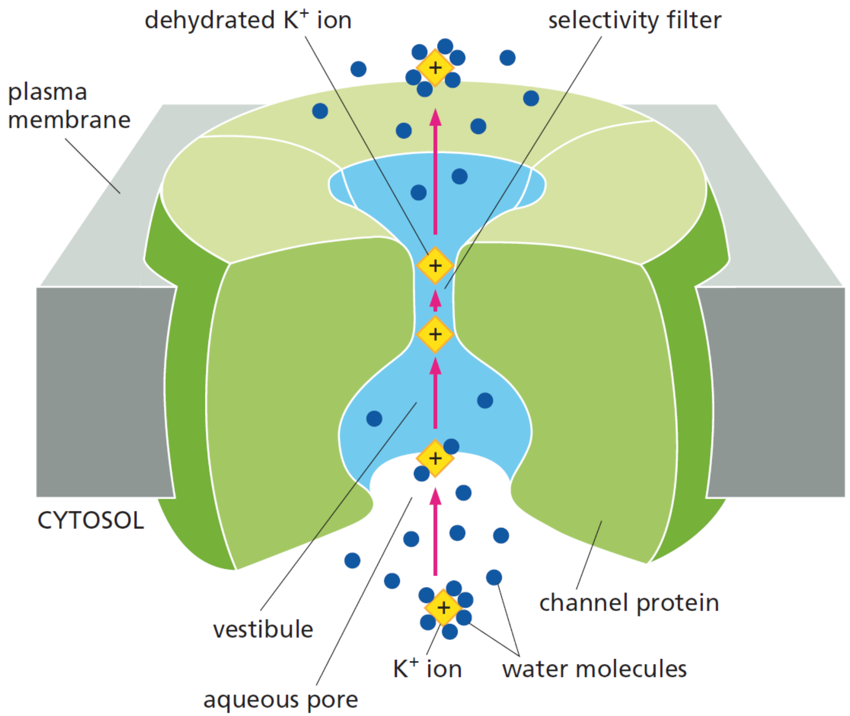
29.04.2025 I BINNY RUDANI



JÜLICH Forschungszentrum

THERMOPHORESIS

Ions in biological systems : Ion channels…



Bruce et al. (2014): Essential cell biology. 4th edition. New York, NY, Abingdon: Garland Science.

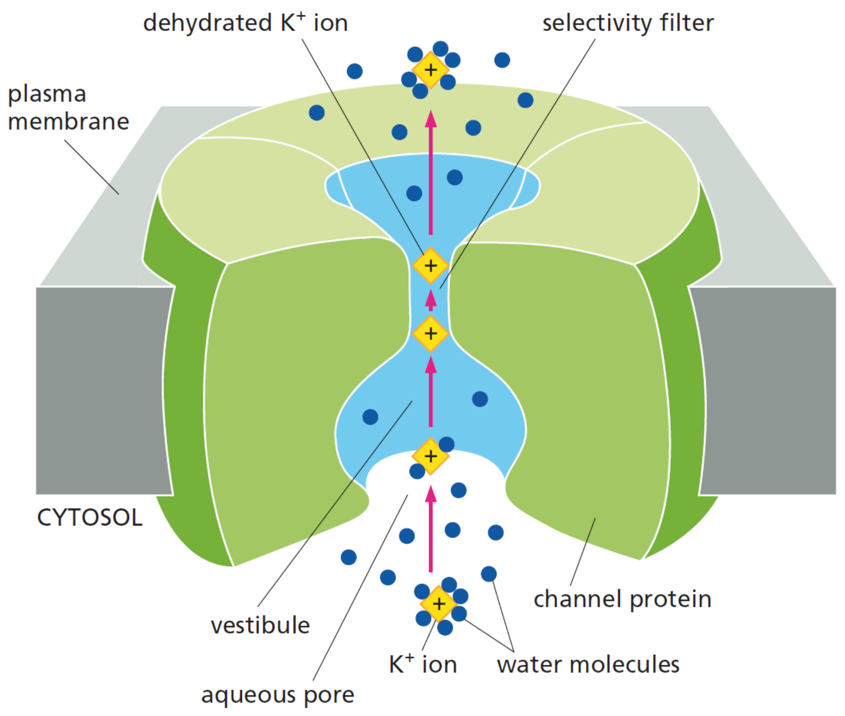
- Ion channels : hydrophilic channels (channel proteins) through which ions can pass
- Channels are ion selective and gated

Doyle et al, *Science.*, ***280*** (1998), 69
Zhao et al., *Int. J. Mol. Sci*., **18** (2017), 1838

JÜLICH Forschungszentrum

THERMOPHORESIS

Ions in biological systems : Ion channels…

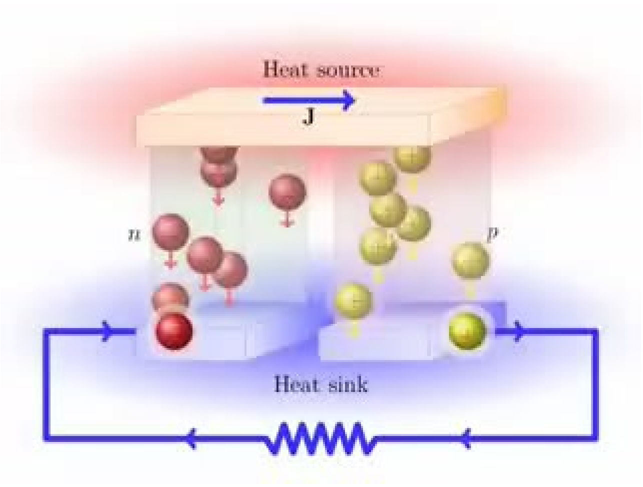


- Ion channels react different to temperatures : A theoretical model predicts a temperature gradient within the ion channel
- Thermophoresis---->sensitive to interactions----->compare different salts

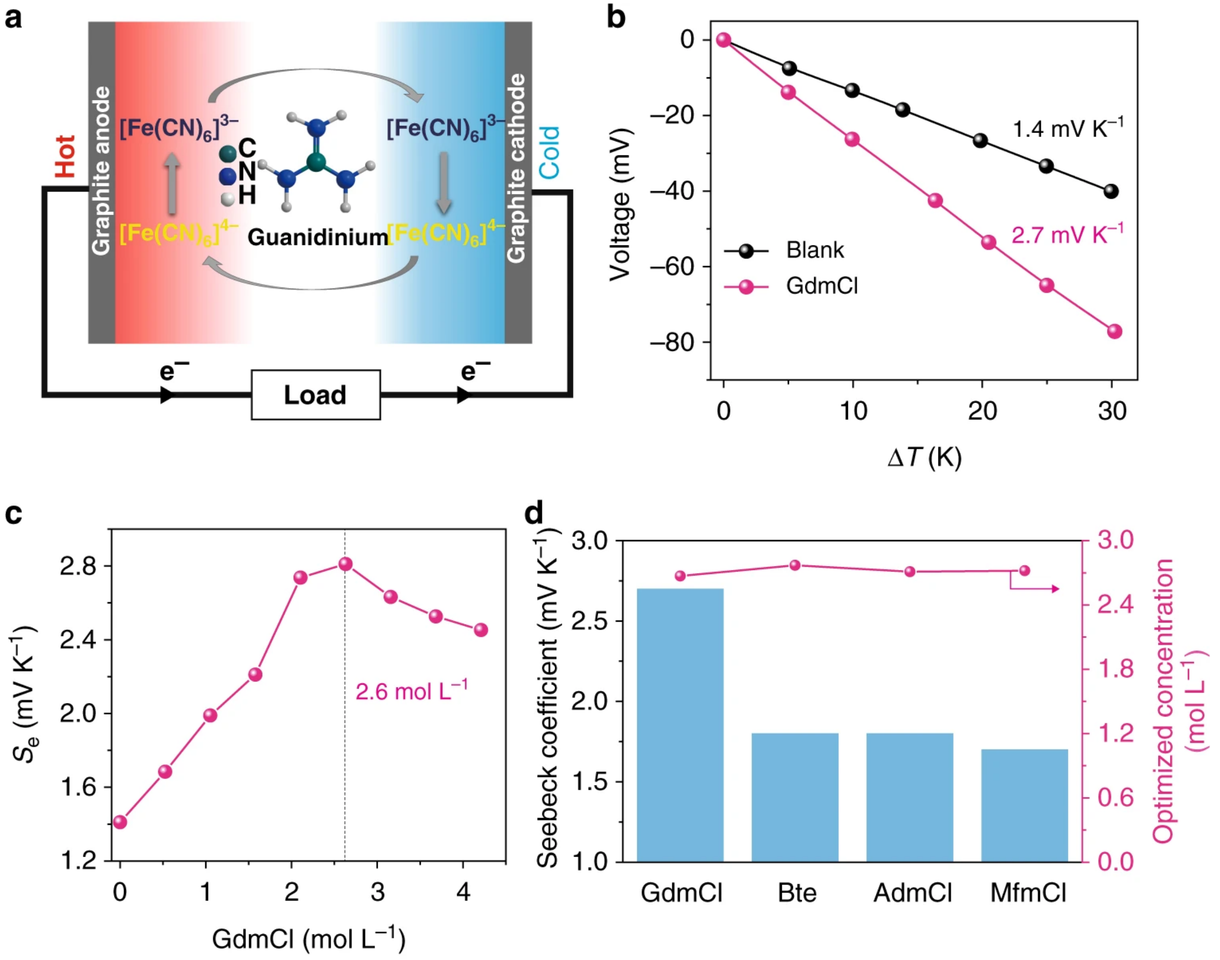
Chen et al, *Biophys. J.*, ***69*** (1995), 2304

SORET AND SEEBECK EFFECT IN IONIC SYSTEMS

Applications: liquid-based systems to convert low-grade waste heat into electricity



https://youtu.be/21EC0lZ0imw?feature=shared



J. Duan *Nat. comm.* **20** (2018), 5146.

MAXIMIZE:

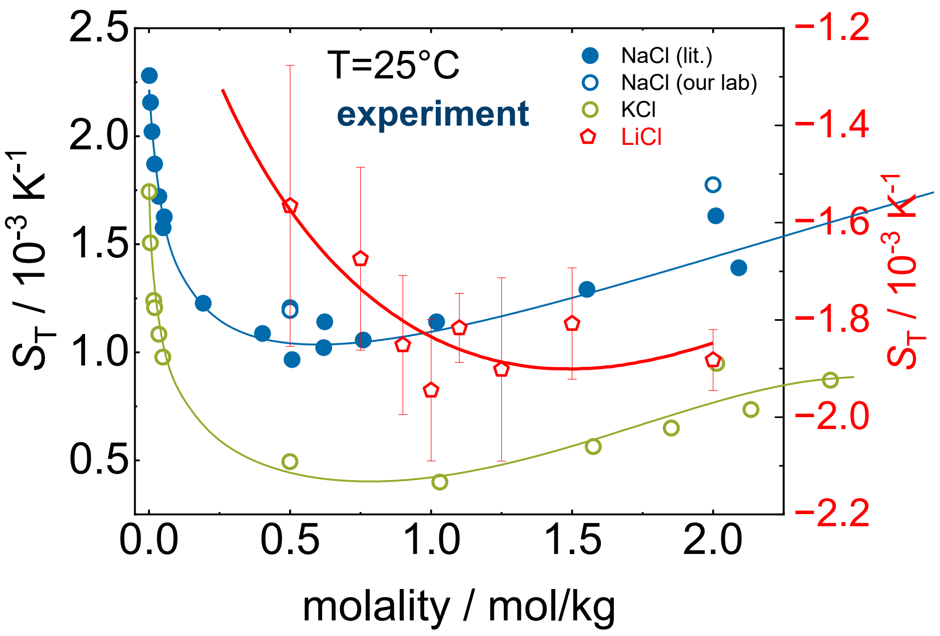
$$ZT = \frac{S^2\sigma}{k}T$$

S .. Seebeck constant
σ .. Electrical conductivity
k .. Thermal conductivity
T .. Absolute temperature

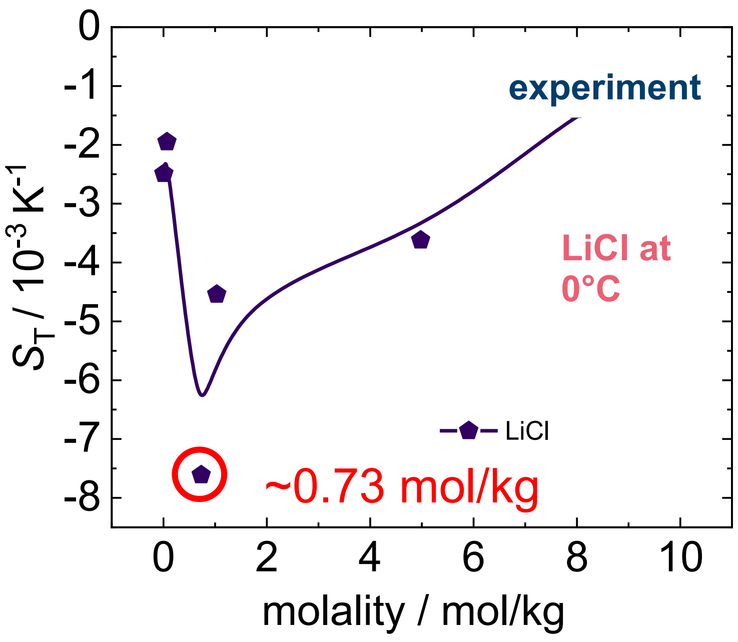
JÜLICH Forschungszentrum

MINIMUM OF S_T WITH CONCENTRATION

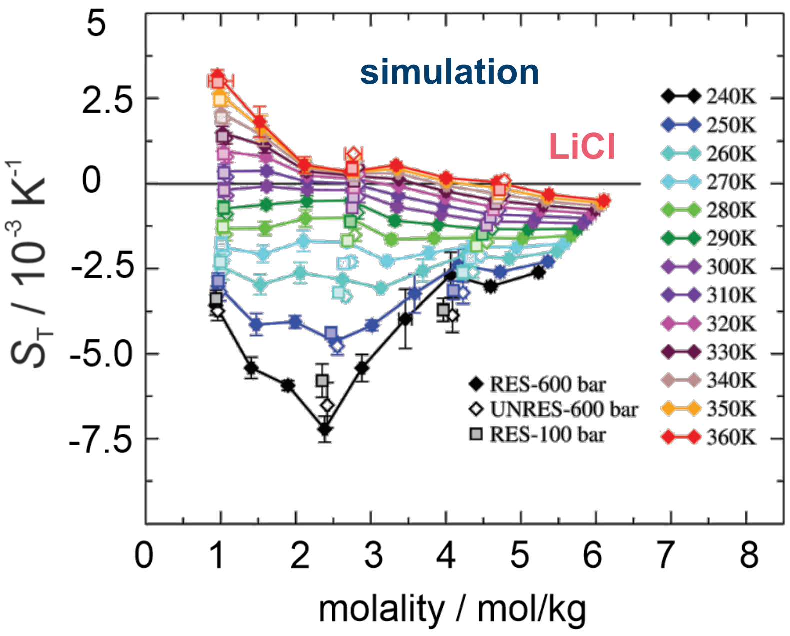
Aqueous salt solutions



M. Jokinen et al., J. Membr. Sci. **499** (2016) 234.
N. Lee, PCCP, **26** (2024) 7830.



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



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

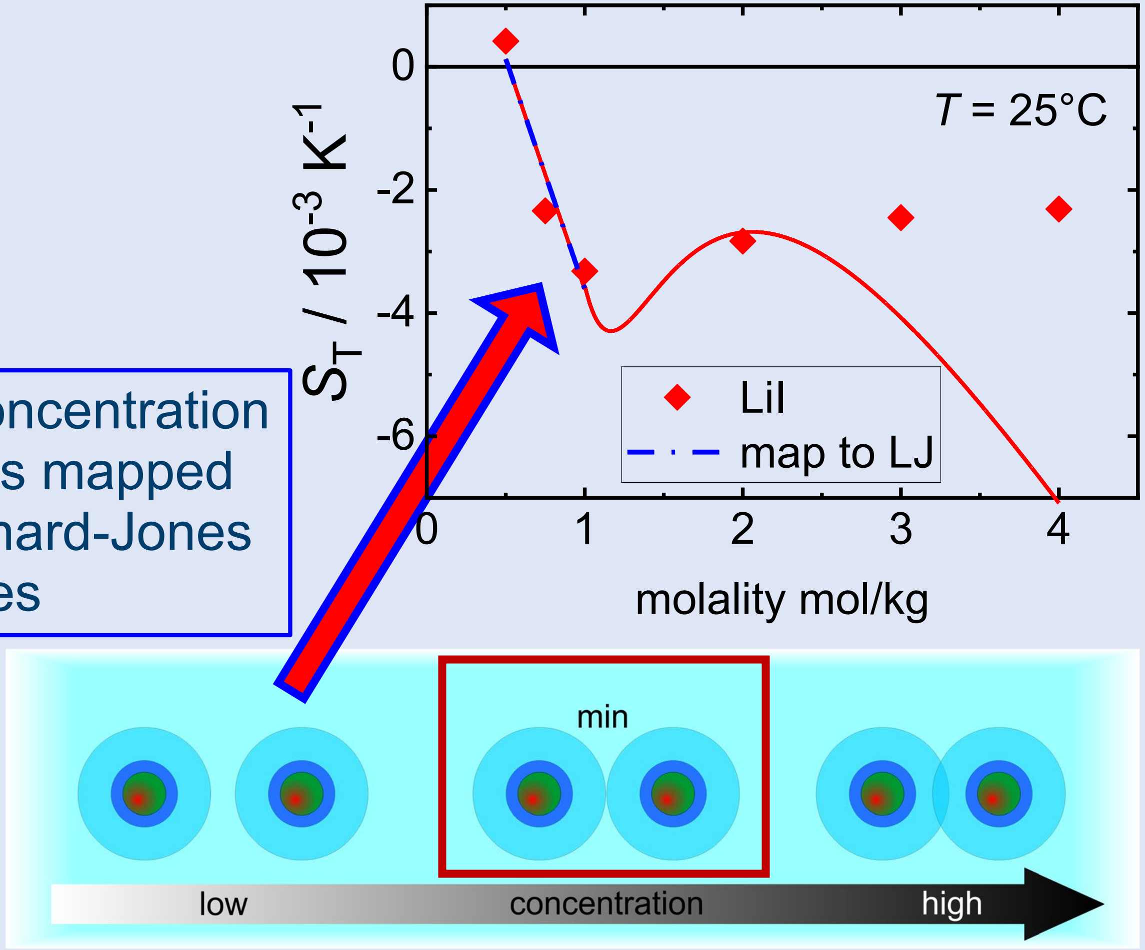
Why S_T of many salts shows a minimum with concentration?

JÜLICH Forschungszentrum

HYDRATION LAYER HYPOTHESIS

Aqueous salt solutions

Low concentration range is mapped to Lennard-Jones Particles



Shilpa Mohanakumar

Wim Briels

Prerequisite:

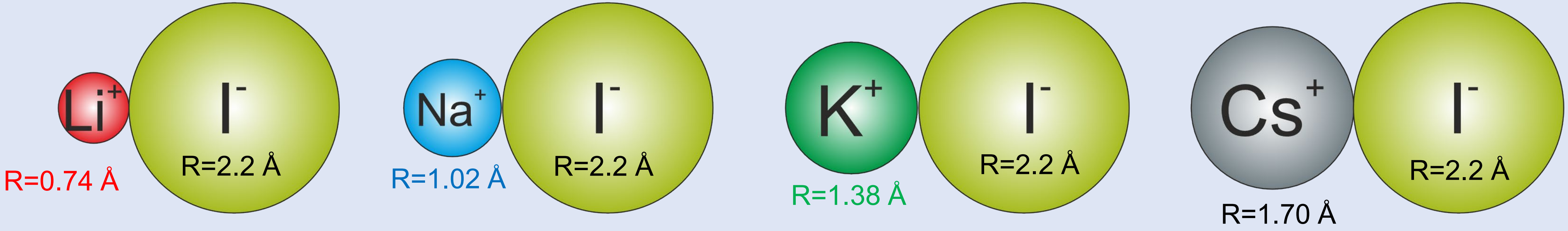
- tight hydration shell
- treatment as ion pairs

Procedure:

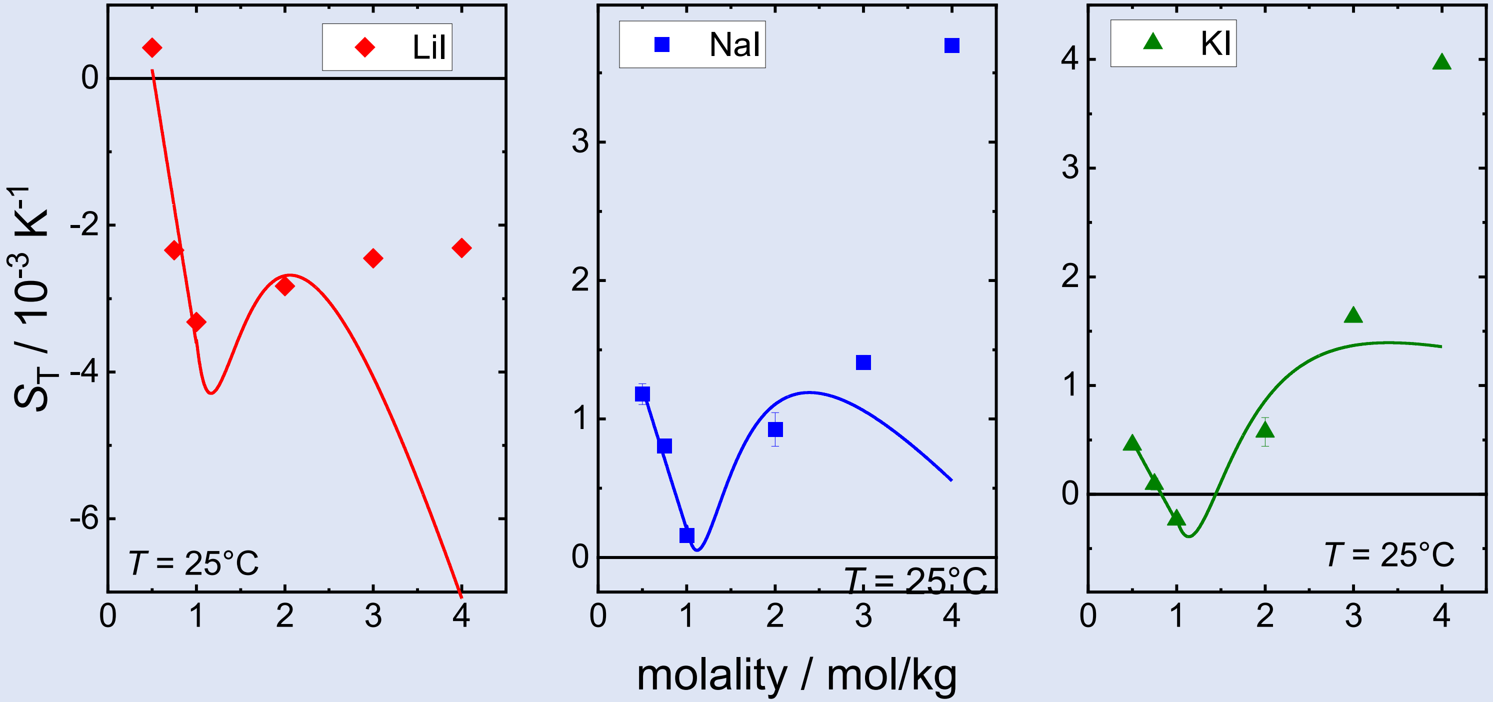
- minimum position is selected
- two step process

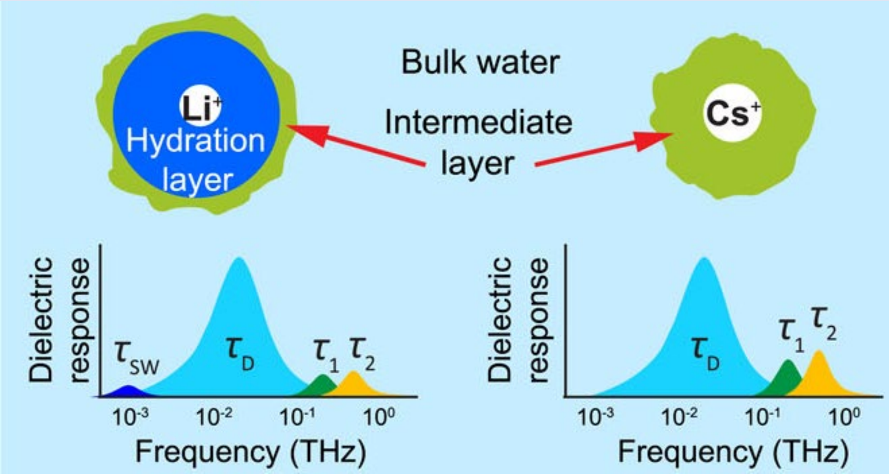
S. Mohanakumar et al., PCCP **24** (2022), 27380.

IODIDE SALTS



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





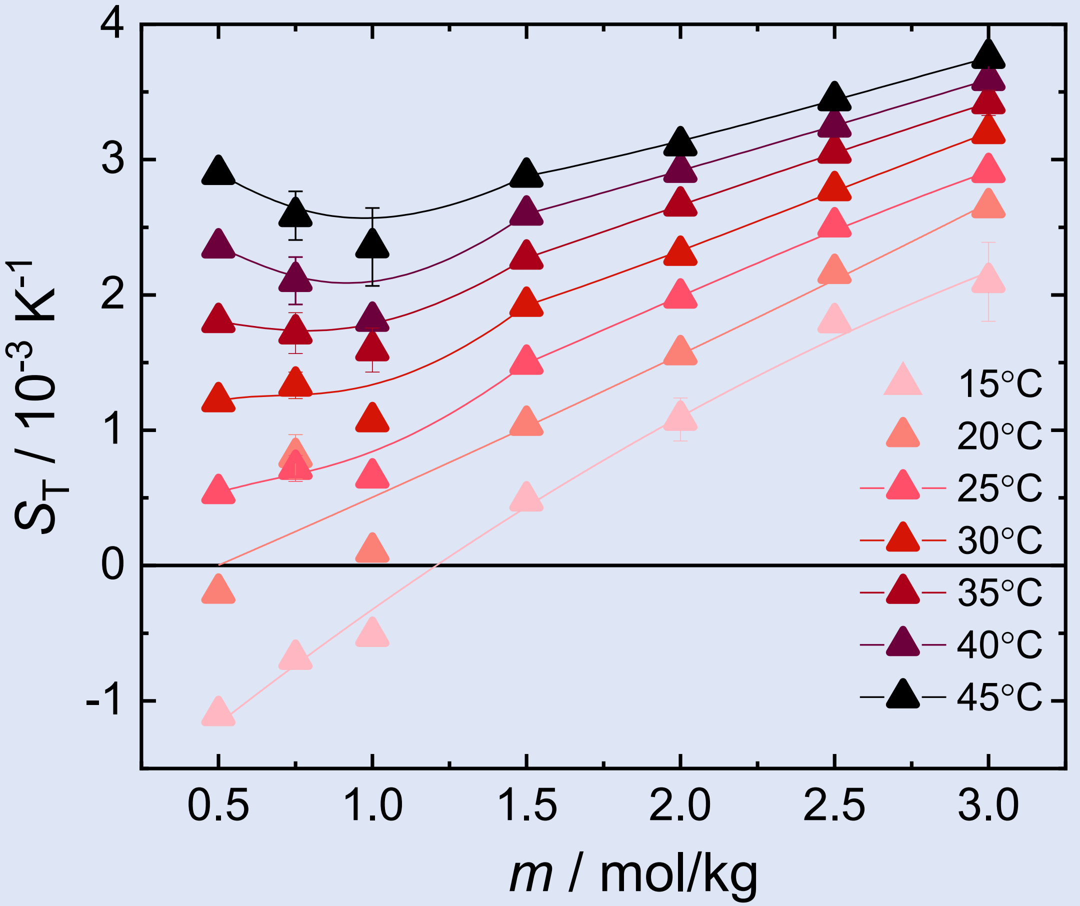
No tight hydration shell for large cations

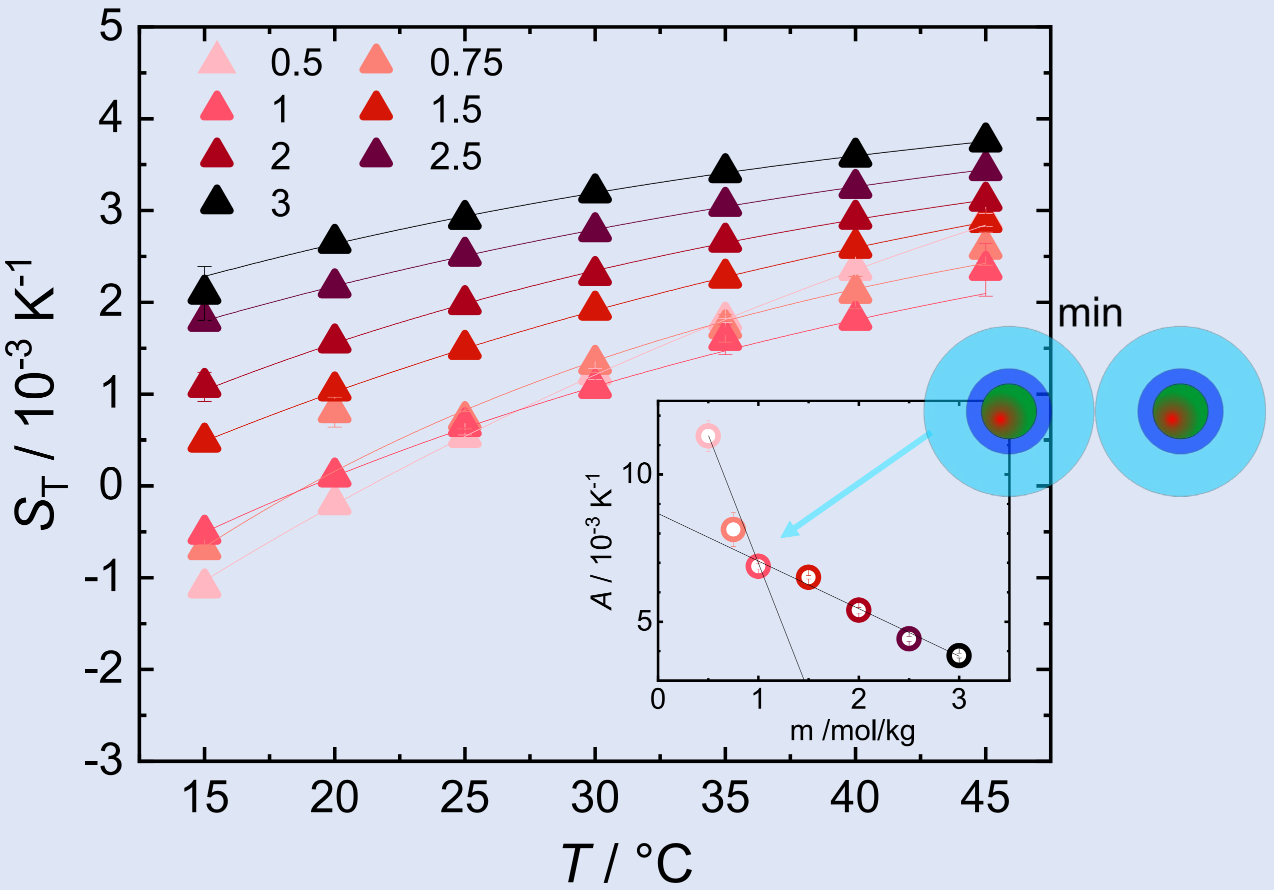
S. Mohanakumar et al., PCCP **24** (2022), 27380.

A. K. Singh, L. C. Doan, D. Lou, C. Wen, and N. Q. Vinh, J Chem Phys 157, 54501 (2022).

CAESIUM IODIDE

No minimum at low temperature, but behaviour changes at 1 mol/kg





- $S_T\ (T) = S_T^{\infty} + Aexp(-\frac{T}{T_0})$

S. Iacopini, R. Rusconi, and R. Piazza, *Eur. Phys. J. E,* **19**, 59–67 (2006)

B.A. Rudani et al., PCCP **27** (2025) 4746.

B.A. Rudani et al., PCCP (2025), accepted.

MINIMUM OF S_T WITH CONCENTRATION

Lennard-Jones mixture

S.R. de Groot, S. R. de. Thermodynamics of irreversible processes (1966):

Kinetic contributions?

Eq.(1)

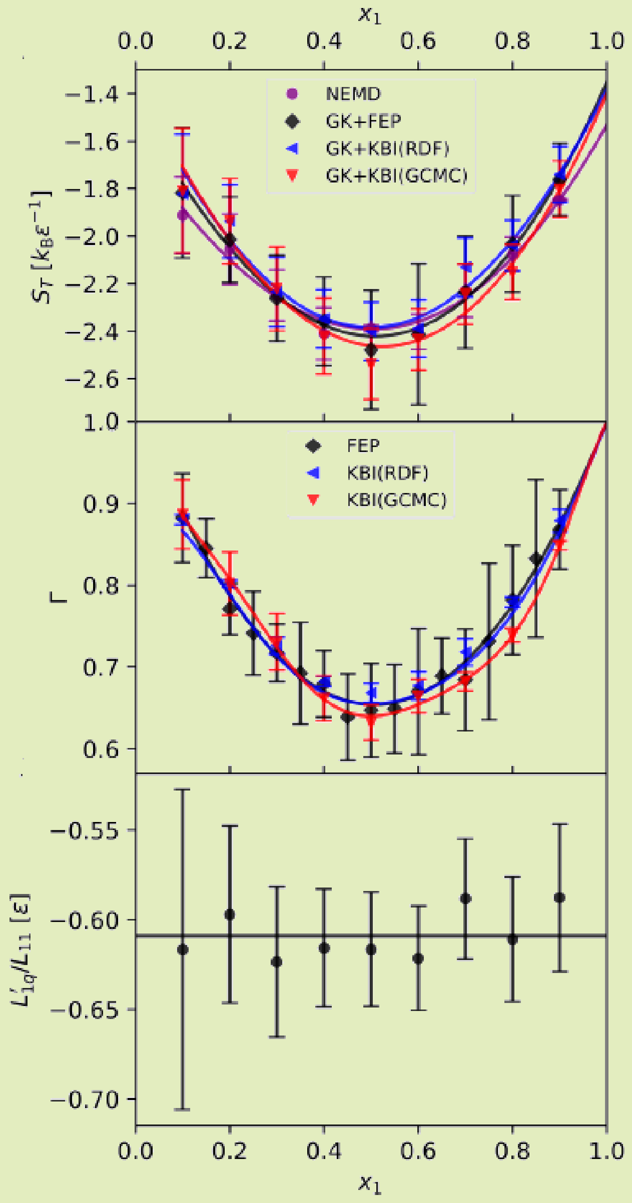
$$S_{\mathrm{T}} = \underbrace{\frac{1}{RT^2}\frac{M_1}{\Gamma}}_{thermodynamic\ factor} \cdot \underbrace{\frac{L_{1q}'}{L_{11}}}_{Onsager ratio}$$

O.R. Gittus & F. Bresme PCCP **25** (2023), 1606.

Conclusion for Lennard Jones particles:

Minimum of S_T related to the minimum of thermodynamic factor Γ.

Is this approach valid for electrolyte solutions?



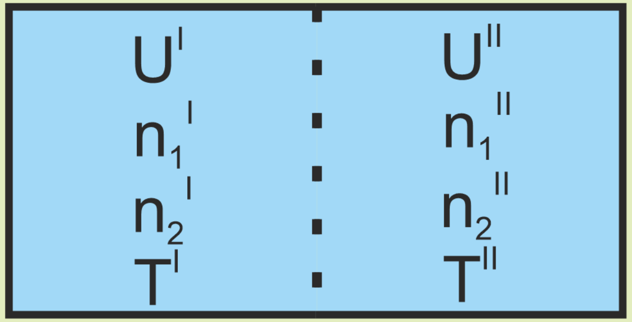
O.R. Gittus & F. Bresme PCCP **25** (2023), 1606.

$$\underbrace{\frac{L_{1q}'}{L_{11}}}_{\text{Onsager ratio}}$$ constant

JÜLICH Forschungszentrum

SIDE NOTE: ONSAGER COEFFICIENTS

Nature of the Onsager ratio: thermo(dynamic/static) or kinetic



Change of Entropy:

$$dS = \Delta\left(\frac{1}{T}\right) dU - \Delta\left(\frac{\mu_1}{T}\right) dn_1 - \Delta\left(\frac{\mu_2}{T}\right) dn_2$$

with $\Delta(A) = (A^{I}) - (A^{II})$

with $dn_1 = -dn_2$

$$dS = \underbrace{\Delta\left(\frac{1}{T}\right)}_{=0\ \text{in equilibrium}} dU - \underbrace{\Delta\left(\frac{\mu_1 - \mu_2}{T}\right)}_{=0\ \text{in equilbrium}} dn_1$$

driving force for energy and mass flow

In non-equilibrium:

$\Delta \rightarrow$ grad
introducing Onsager coefficients
factor *T* is conventional
we know thermodiffusion happens

$$\vec{j}_m = L_{1q} T \cdot \mathrm{grad}\, T - L_{11} T\ \mathrm{grad} \frac{\mu_1^{\cdot} - \mu_2^{\cdot}}{T}$$

 B.A. Rudani et al., PCCP (2025), accepted.

SIDE NOTE

Nature of the Onsager ratio: thermo(dynamic/static) or kinetic

1. $$\vec{j}_m = L_{1q} T \cdot \mathrm{grad}\, T - L_{11} T\, \mathrm{grad} \frac{\mu_1^{\bullet} - \mu_2^{\bullet}}{T}$$

2. $$\vec{j}_m = -\underbrace{\left(L_{1q} - L_{11}\left[h_1^{\bullet} - h_2^{\bullet}\right]\right)}_{L'_{1q}} \frac{1}{T} \mathrm{grad}\, T - L_{11} \frac{\partial}{\partial c}[\mu_1^{\bullet} - \mu_2^{\bullet}]\, \mathrm{grad}\, c$$

3. Steady state: $$S_T = \underbrace{\frac{1}{RT^2} \frac{M_1}{\Gamma}}_{\text{thermodynamic factor}} \cdot \underbrace{\frac{L'_{1q}}{L_{11}}}_{\text{Onsager ratio}}$$

With a common dynamic factor *L*-ratio can be thermodynamic

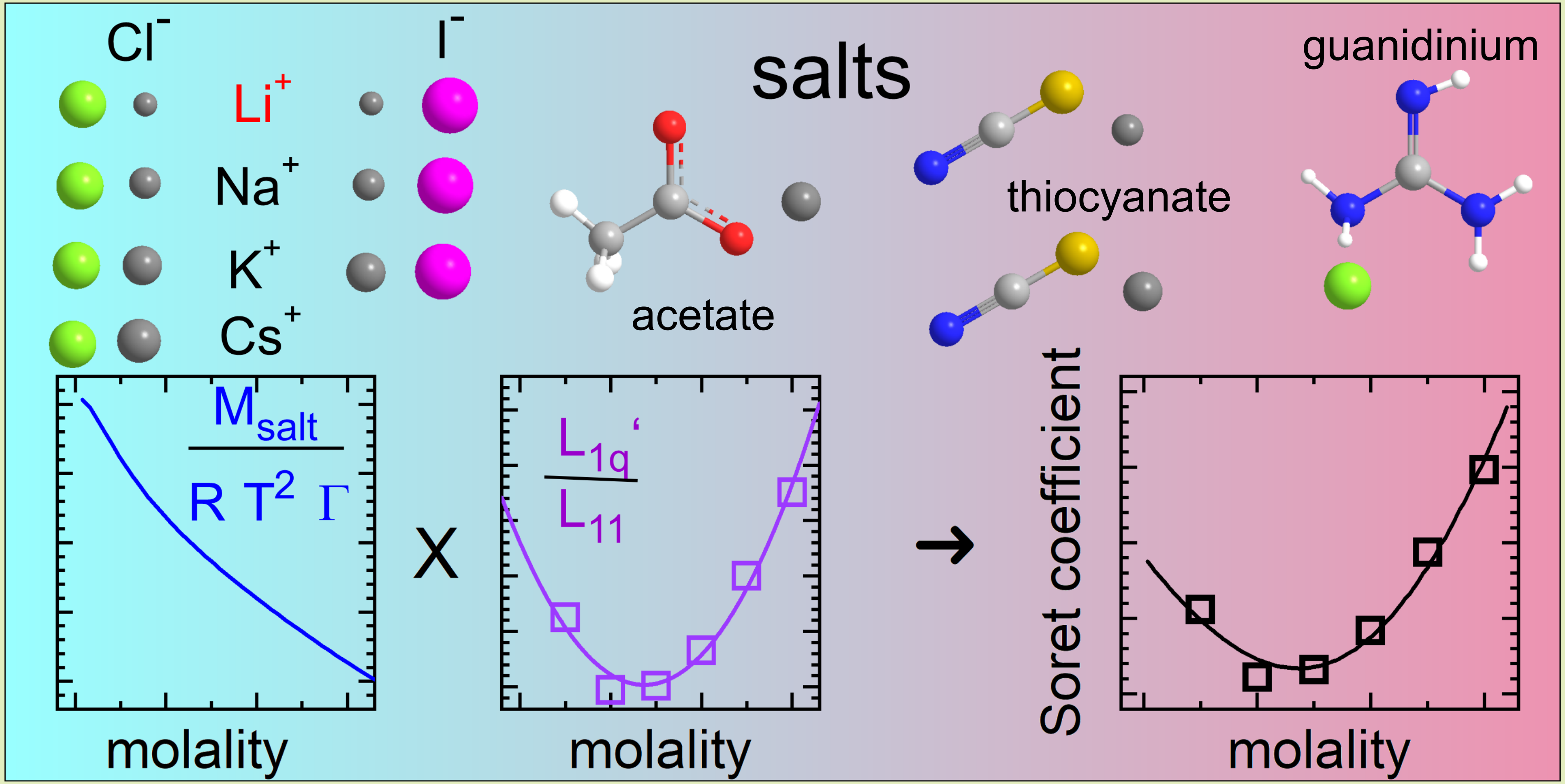
Another side note

$$\frac{L'_{1q}}{L_{11}} = \frac{L_{1q}}{L_{11}} - \left[h_1^{\bullet} - h_2^{\bullet}\right] = \underbrace{Q^*}_{\text{heat of transfer}} - \left[h_1^{\bullet} - h_2^{\bullet}\right]$$

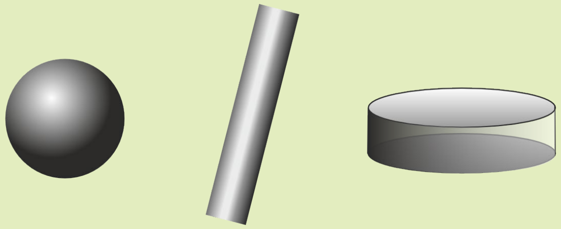
B.A. Rudani et al., PCCP (2025), accepted.

IS THE APPROACH APPLICABLE FOR SALT SYSTEMS?

Salt sytems show a general trend - exception lithium salts



cation shapes



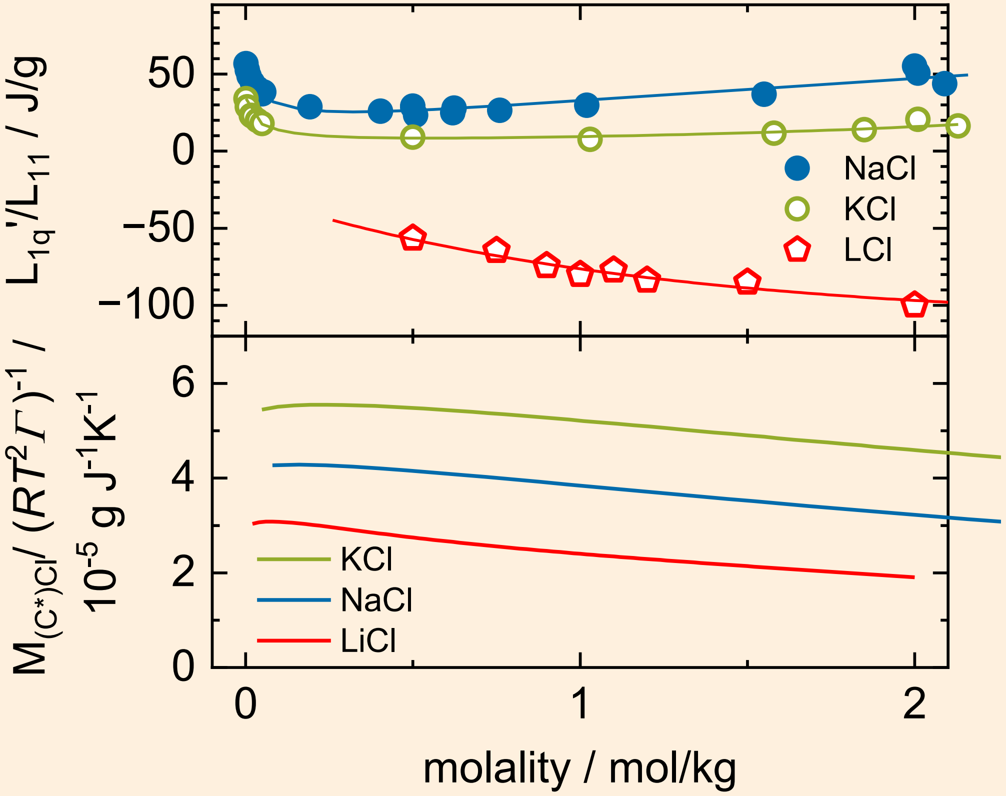
$$S_T = \frac{1}{RT^2} \frac{M_1}{\Gamma} \cdot \frac{L_{1q}'}{L_{11}}$$

B.A. Rudani et al., PCCP **27** (2025) 4746.

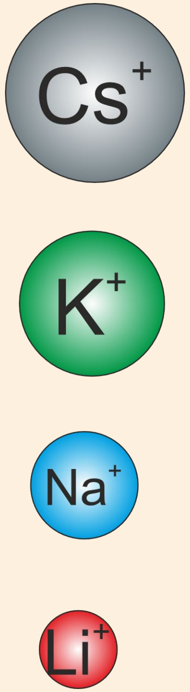
THERMODYNAMIC FACTOR FOLLOWS PAULI RADIUS

L-ratio and also S_T do not follow r_P in the case of Na^+ and K^+

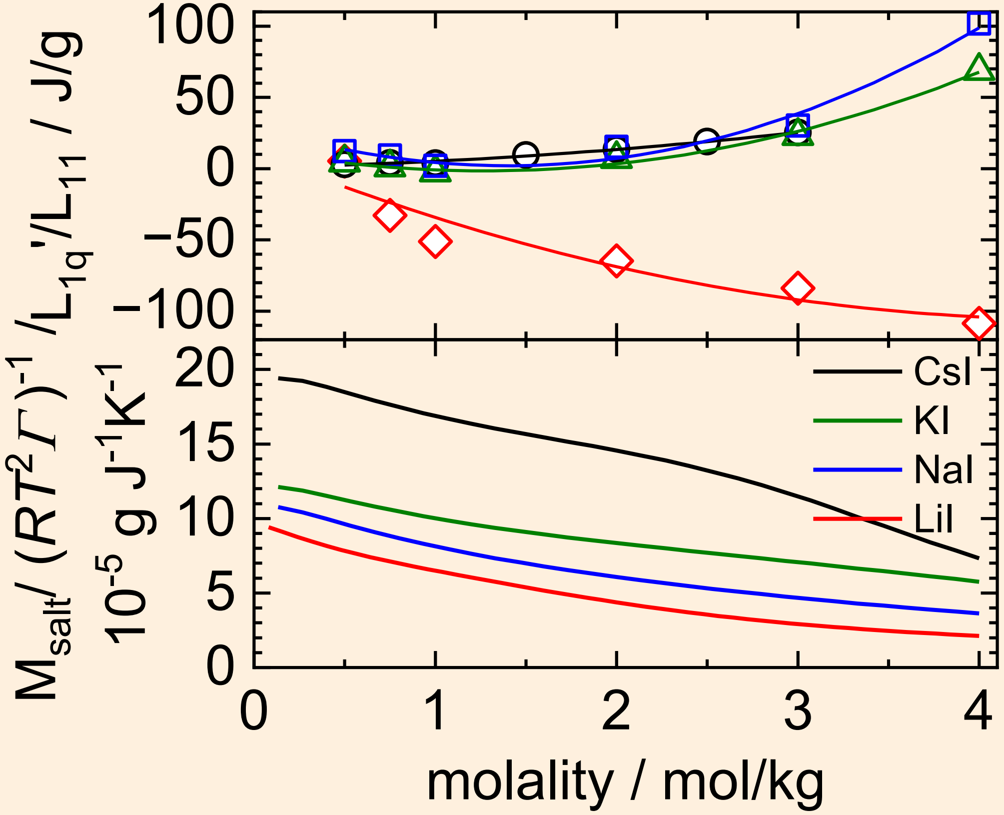
Chloride salts



Pauli radii r_P



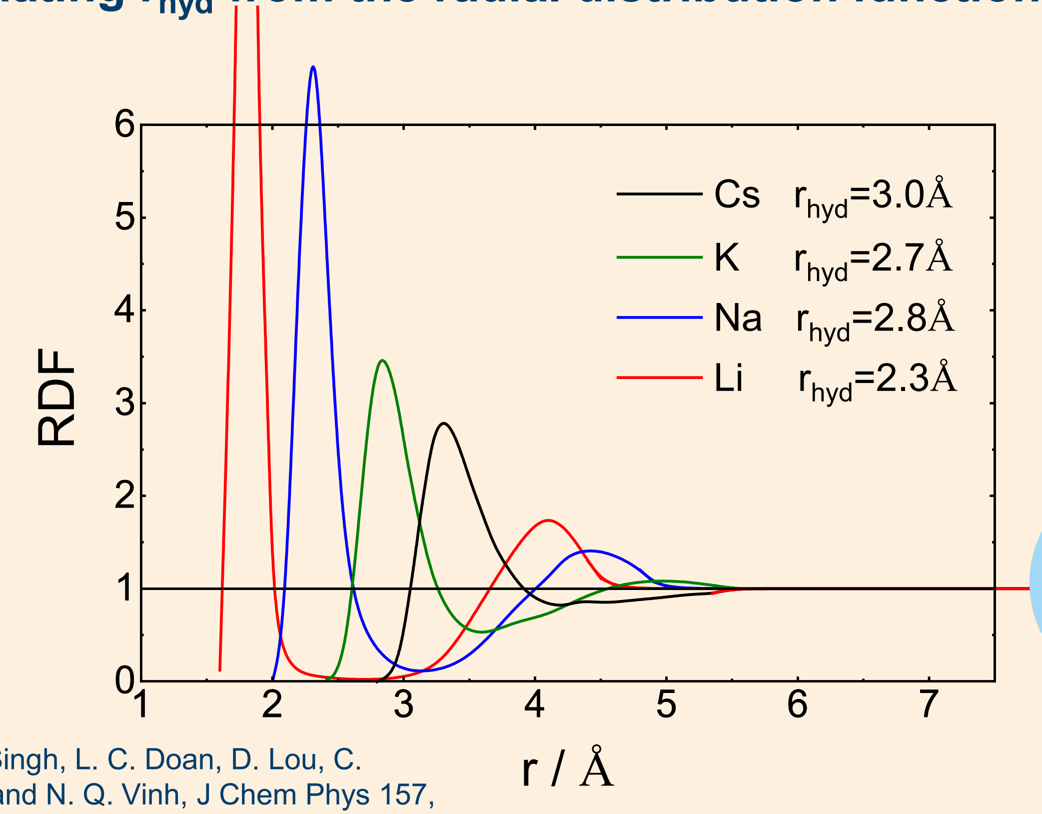
Iodide salts



B.A. Rudani et al., PCCP **27** (2025) 4746.

L-RATIO AND S_T INCREASE WITH HYDRODYNAMIC RADIUS

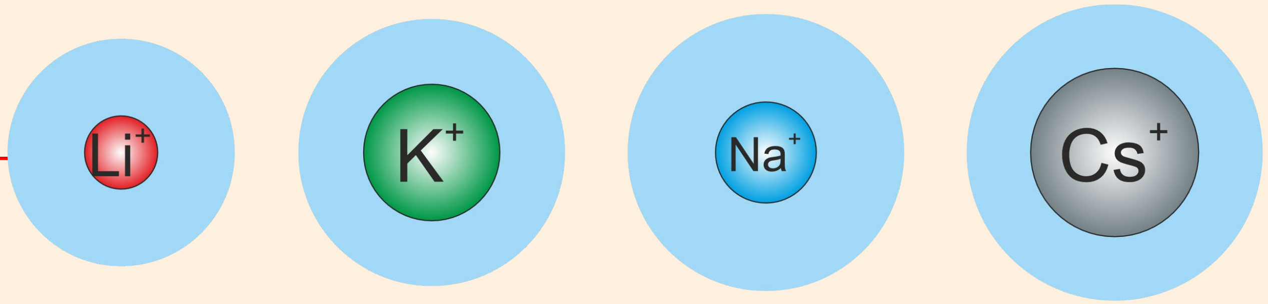
Estimating r_{hyd} from the radial distribution function (RDF)



A. K. Singh, L. C. Doan, D. Lou, C. Wen, and N. Q. Vinh, J Chem Phys 157, 54501 (2022).

$$r_{hyd} = \frac{\int r^3 [g(r) - 1] dr}{\int r^2 [g(r) - 1] dr}$$

B.A. Rudani et al., PCCP **27** (2025) 4746.



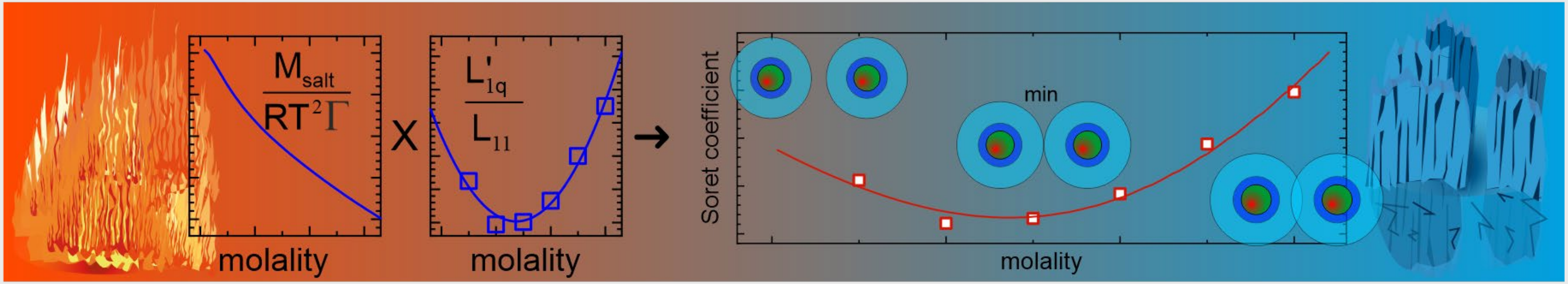
$\frac{L'_{1q}}{L_{11}}$ and S_T scale with the hydrodynamic radius

JÜLICH Forschungszentrum

TAKE HOME MESSAGE

Thermodiffusion of salts is

- **influenced by hydration layer**
- **S_T of spherical salts scales with r_{hyd} of the cation**
- **L_{1q}'/L_{11} cannot be explained by thermodynamics**



JÜLICH Forschungszentrum

FINISHED AND FUTURE PROJECTS

Done projects:

- Rudani, B. A., Jakubowski, A., Kriegs, H., Wiegand, S. **Deciphering the guanidinium cation: Insights into thermal diffusion**. The Journal of chemical physics 2024,160,214502.
- Rudani, Binny A.; Briels, W. J.; Wiegand, S. **Analyzing the concentration-dependent Soret coefficient minimum in salt solutions: an overview.** In Phys Chem Chem Phys 2025,27(9),4746–4755.

Currently ongoing:

- Rudani, B. A.; Docter, S. ; Schott-Verdugo, S.; Buitenhuis, J.; Stadler A. M.; Gohlke H.; Wiegand, S. **Thermophoresis: The case of apomyglobin**: Manuscript in progress, waiting for simulation results.
- Ammonia salts (collaboration Holger Gohlke, IBG 4): experimental part

Future work:

- Protein ligand binding (myoglobin binds with ligand)

ACKNOWLEDGEMENT

Simone Wiegand

Wim Briels

Shilpa Mohanakumar

Group of IBI-4

Thanks for your attention

BioSoft
Biophysics and Soft Matter

JÜLICH
Forschungszentrum