Thermophoresis of ionic solutes: Preliminary step to protein-ligand interactions

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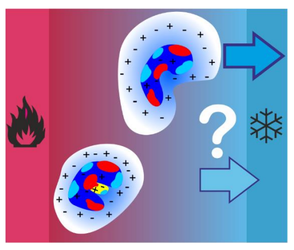
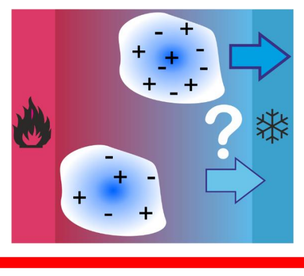
Motivation [1], [4]

Long term goal: protein-ligand binding

hydrophilic groups
hydrophobic groups
buffer (contains salt)

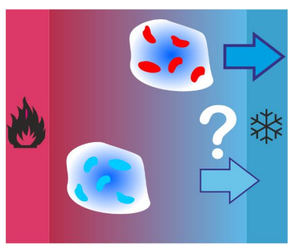


ionic solutes **Reduce Complexity** non-ionic solutes

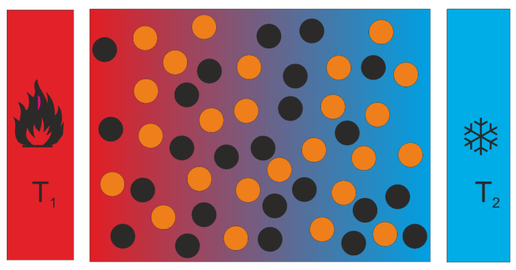


Comparison

Ion specific effects?



Thermophoresis [2]

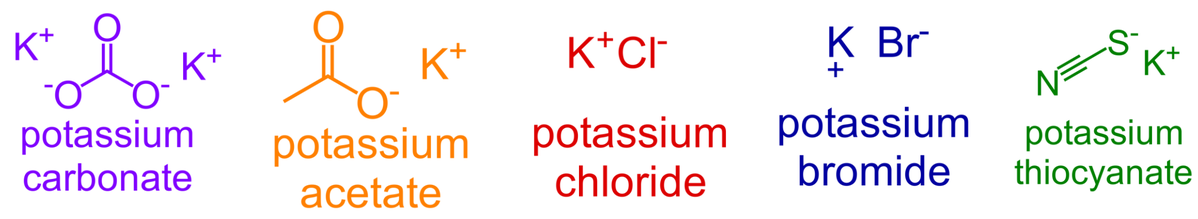


$$\vec{j} = -\rho D \vec{\nabla} c - \rho c(1-c) D_T \vec{\nabla} T$$

Steady state: $\vec{j} = 0$

$$S_T = \frac{\text{Thermodiffusion}}{\text{Diffusion}} = \frac{D_T}{D} = -\frac{1}{c(1-c)}\frac{\Delta c}{\Delta T}$$

Systems [3]

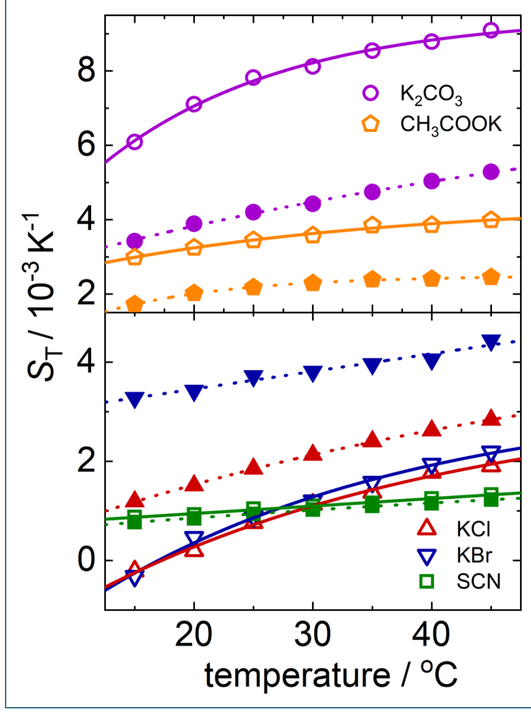


CO_3^{2-} SO_4^{2-} $S_2O_3^{2-}$ F^- CH_3COO^- Cl^- Br^- NO_3^- I^- ClO_4^- SCN^-

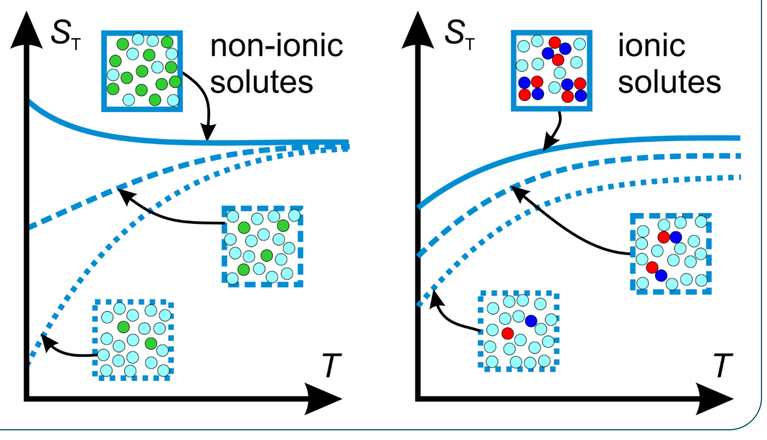
more hydrophilic **HOFMEISTER SERIES** more hydrophobic

TDFRS: results [4], [5]

1. Temperature dependence of S_T

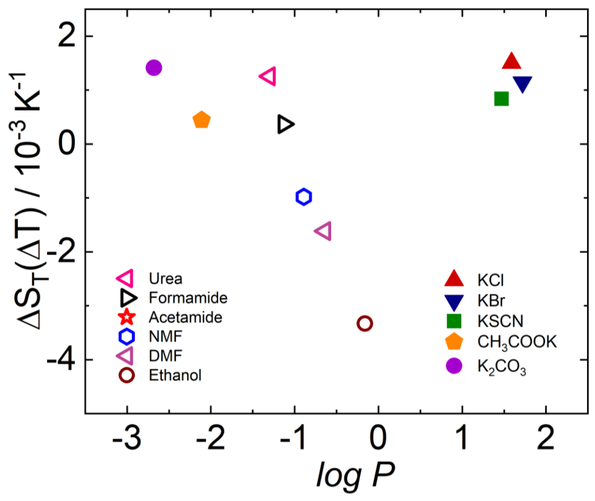


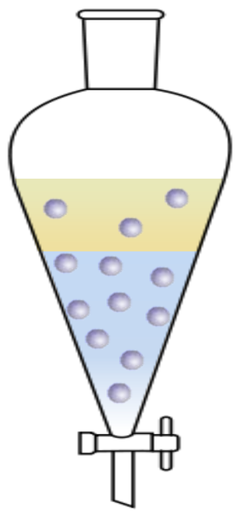
- Temperature dependence of salts: similar to dilute solutions of hydrophilic non-ionic solutes



TDFRS: results [6], [7]

2. $\Delta S_T(\Delta T)$ vs log P





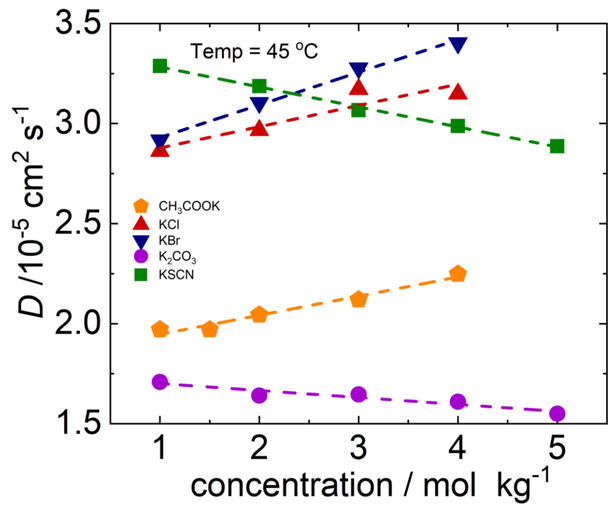
organic phase → c_{org}

water → c_{aq}

$$P = \frac{c_{org}}{c_{aq}}$$

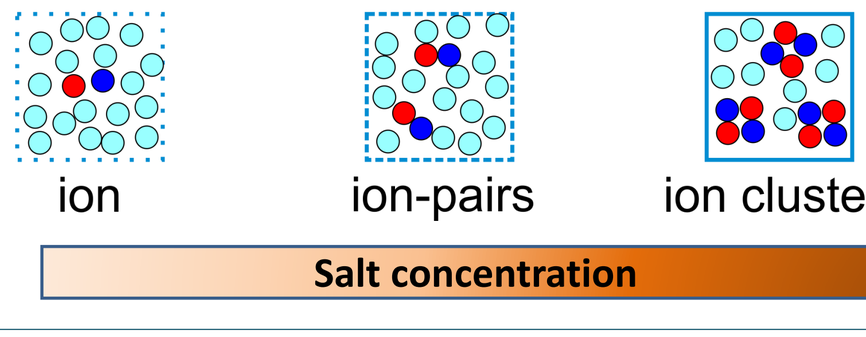
- Hydrophilic salts follow trend of non-ionic solutes

3. Diffusion coefficient



- KCl,KBr,CH_3COOK: follows predicted behavior[7,6]
- KSCN, K_2CO_3: decrease in D with concentration

What is the diffusing entity?



Conclusion [8]

- Salt specific effects can be observed
- Thermophoresis scale differs from Hofmeister series

CO_3^{2-} CH_3COO^- SCN^- Cl^- Br^-

more hydrophilic **THERMODIFFUSION** more hydrophobic

- Different entities as a function of concentration respond to temperature gradients

References

[1] D. Niether et al., *Polymers*, **12** (2020), 376 **[2]** S. Di Lecce et al., *Phys. Chem. Chem. Phys.*, **19** (2017), 9575 **[3]** A. Salis et al, *Chem. Soc. Rev.*, 43(2014), 7358 **[4]** D. Niether et al., *J. Chem. Phys.*, **149** (2018), 44506 **[5]** R. Piazza et al., *Eur. Phys. J. E*, **19** (2006), 59
[6] G. H. Gao et al., *Fluid Phase Equilibr.*, **256** (2007), 105 **[7]** G. E. Zaikov at al., In *Advances in kinetics and mechanism of chemical reactions*, ., Apple Academic Press, 2013; pp 21–33.
[8] S Mohanakumar et al., *J. Chem. Phys.*, **154** (2021), 084506