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Supplementary Information: Non-monotonic Soret coefficients of aqueous LiCl solutions with varying concentration

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coefficient $S_{\rm T}$

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S1 Thermal diffusion and diffusion coefficient for aqueous lithium chloride solutions



Figure S1: Concentration dependence of D for for aqueous lithium chloride solutions.

The dependence of diffusion coefficients on concentration is shown in Fig.S1 at various temperatures for aqueous LiCl solutions. Diffusion of LiCl gets faster with increasing temperature and increases slightly with concentration. The increase in D with temperature is due to a decrease in viscosity. The dependence of the thermodiffusion coefficient on concentration is shown in Fig.S2. It is striking that the thermal diffusion coefficients show a minimum with concentration as also observed for the Soret coefficient.



Figure S2: Concentration dependence of $D_{\rm T}$ for aqueous lithium chloride solutions. The lines have been calculated according to the model considering the overlap of hydration shells.

S2 Refractive index increments

Refractive index contrast factors are required to calculate $S_{\rm T}$. The refractive index as a function of concentration was measured with an Abbe refractometer (Anton Paar Abbemat MW) at a wavelength of 632.8 nm. Refractive indices at five concentrations around the desired contraction were measured for all salts. The slope of the linear interpolation of the refractive indices as a function of concentration gives $(\partial n/\partial c)_{p,T}$. Figure S3 shows the refractive index increment with concentration $(\partial n/\partial c)_{p,T}$ for aqueous LiCl solutions.



Figure S3: Concentration dependence of $(\partial n/\partial c)_{p,T}$ for aqueous lithium chloride solutions at various temperatures.

The refractive index increments with temperature $(\partial n/\partial T)_{p,c}$ was measured interferometrically [1]. Measurements were performed over a temperature range of 25-45°C, with a heating rate of 1.6 mK/sec. The refractive index varied linearly with concentration and temperature in the investigated range. Figure S4 shows the refractive index increment $(\partial n/\partial T)_{p,c}$ for aqueous LiCl solutions.



Figure S4: Concentration dependence of $(\partial n/\partial T)_{p,c}$ for aqueous lithium chloride solutions at various temperatures.

S3 Additional information

S3.1 Comparison with literature values



Figure S5: Individual fit parameter A, $S_{\rm T}^i$ and T_0 according to Eq.(2) in the main manuscript for the various concentrations.

We performed individual simultaneous fits using Eq.(2) in the main manuscript to describe the temperature dependence of $S_{\rm T}$ for all concentrations in the range between 0.5 and 2 mol/kg. Figure S5 shows the adjusted fit parameters, which exponential functions can describe. Implementing the fitted curves in the following equation, we can extrapolate $S_{\rm T}$ -values at selected concentrations and temperatures.

$$S_{\rm T}(m,T) = y_{y0} + y_{A1} \cdot exp(-m/y_{t1})$$

$$+ [A_{A1} \cdot exp(-m/A_{t1}) + A_{y0}] \cdot exp\left(\frac{-T}{t_{A1} \cdot exp(-m/t_{t1}) + t_{y0}}\right)$$
(S1)

As mentioned in the main manuscript, Colombani *et al.* [2] also measured $S_{\rm T}$ of aqueous LiCl solutions. In Table S1, we list the calculated $S_{\rm T}$ -values using Eq. ?? with our fitting parameter. Colombani *et al.* found their minimal Soret coefficient of $-7.57 \times 10^{-3} \, {\rm K}^{-1}$ at a molality of $m = 0.56 \, {\rm mol/kg}$. At this concentration, we find the largest deviation of the order of 50%, while at $m = 0.93 \, {\rm mol/kg}$ and $m = 1.85 \, {\rm mol/kg}$ the agreement is between 1-10% and 20-30%, respectively. Note that for $m = 1.85 \, {\rm mol/kg}$, the measurements

have been performed at -3°C and -7°C, which is roughly 10°C below our last measurement point, so that the extrapolation has large uncertainties.

Table S1: Comparison of selected $S_{\rm T}$ -values published by Colombani *et al.* [2] with extrapolated values of our work. Further details are given in the text.

m /	T/	$S_{\rm T}$ [2] /	$S_{\rm T}$ [calc. Eq.??] /	deviation /
mol/kg	°C	$10^{-3} \mathrm{K}^{-1}$	$10^{-3} \mathrm{K}^{-1}$	%
0.56	-0.5	-7.57	-4.4	53
0.93	-0.9	-4.54	-4.6	-1
0.93	1.4	-4.57	-4.3	6
1.85	-7.1	-3.76	-5.2	-32
1.85	-3	-3.64	-4.5	-23

S3.2 Depth and position of the minimum concentration

The upper part of Fig. S6 shows the depth of the minimum, which has been calculated as the difference between the Soret coefficient at a molality of 2 mol/kg and $S_{\rm T}$ at the minimum concentration as a function of temperature. Using the overlap model, the depth of the minimum decreases with concentration. At the same time, the minimum concentration increases as a function of temperature, as shown in the lower part of Fig. S6.



Figure S6: Depth of the minimum and the minimum concentration as a function of temperature.

S4 Determination of $S_{\rm T}^i$

Wittko and Köhler suggested the following empirical Ansatz describing the *temperature* and *concentration* dependence of $S_{\rm T}$ [3],

$$S_{\rm T}(m,T) = \alpha(m)\beta(T) + S_{\rm T}^i \tag{S2}$$

with polynomial serial expansions for $\alpha(m)$ and $\beta(T)$

$$\alpha(m) = a_0 + a_1 m + a_2 m^2 + a_3 m^3 + \dots,$$

$$\beta(T) = 1 + b_1 (T - T_0) + b_2 (T - T_0)^2 + \dots$$
(S3)

m is the molality, T_0 is an arbitrary reference temperature, set to $T_0 = 25^{\circ}$ C and S_T^i is a temperature and concentration independent constant. Although the approach was suggested for non-polar systems, it has been successfully used to describe the temperature and concentration dependence of non-ionic and ionic aqueous solutions [4, 5]. For both system classes, it turns out that S_T^i correlates with the hydrophilicity of the solute, which can be characterized by $\log P$, whereas the partition coefficient P is a measure for the relative difference of solubility for a solute in two different solvents. Most commonly, the octanol/water partition coefficient is used. A negative $\log P$ signifies stronger hydrophilicity. Further, $\log P$ of a given solute molecule is proportional to its activity coefficient in water $\log \gamma_{water}$ and is used as a measure of solute-solvent interactions in aqueous solutions [6].

Using Eqs. S2 and S3, we fit the Soret coefficients using a third-order fit in concentration and a second-order fit in temperature (c.f. Fig. S7). The $S_{\rm T}^i$ values are plotted against log P in Fig. S8, alongside values for other salts. An evident linear correlation between $S_{\rm T}^i$ and the hydrophilicity parameter, log P, becomes apparent. As the salt's log P value increases, indicative of higher hydrophilicity, there is a concurrent reduction in $S_{\rm T}^i$. Notably, the decline in $S_{\rm T}^i$ with log P is considerably milder for salts compared to the recently investigated non-ionic compounds [7]. This tendency could potentially be attributed to the more pronounced temperature sensitivity of hydrogen bonds in contrast to electrostatic interactions.



Figure S7: Soret coefficient $S_{\rm T}$ as a function of molality m for five different temperatures. Temperature increases from left to right. The error bars show the measurement uncertainty of the mean. The solid lines correspond to an empirical fit according to Eq.S2 considering all concentrations simultaneously. Further details are given in the text.



Figure S8: $S_{\rm T}^i$ an adjustable parameter in Eq.S2 as function of log P. The red line is a linear fit.

S5 Relation between the thermodynamic factor Γ and the Soret coefficient $S_{\rm T}$

Gittus and Bresme [8] wrote the Soret coefficient $S_{\rm T}$ in terms of the phenomenological coefficient L_{1q}' , L_{11} and the thermodynamic factor Γ as follows

$$S_T = \frac{L_{1q}'}{L_{11}Tw_1} \cdot \left(\frac{\partial\mu_{s,1}}{\partial w_1}\right)_{p,T}^{-1} = \frac{1}{k_B T^2} \frac{L_{1q}'}{L_{11}} \cdot \frac{M_1}{\Gamma}$$
(S4)

$$\Gamma = \frac{x_1}{k_B T} \left(\frac{\partial \mu_1}{\partial x_1} \right)_{p,T},\tag{S5}$$

with the chemical potential μ_1 , the weight fraction w_1 and the mole fraction x_1 of component 1, the Boltzmann constant k_B and the temperature T in Kelvin. The specific chemical potential is defined as $\mu_{s,1} = \mu_1/M_1$. Note that Eq. S5 holds only if both components have the same mass otherwise Γ as a function of mole fraction is given by

$$\Gamma = \frac{x_1 + (1 - x_1) \cdot \frac{M_2}{M_1}}{(M_2/M_1)} \cdot \frac{x_1}{k_B T} \cdot \left(\frac{\partial \mu_1}{\partial x_1}\right)_{p,T}$$
(S6)

or in terms of molality

$$\Gamma = \left(1 + m_1 \frac{18}{1000} \left(\frac{M_1}{M_2}\right)\right) \frac{m_1}{k_B T} \left(\frac{\partial \mu_1}{\partial m_1}\right)_{p,T},\tag{S7}$$

This work identifies M_1 and M_2 with the molar mass of lithium chloride and water, respectively. With Eq. S7, the Soret coefficient of one mole can be expressed as follows

$$S_T = \frac{1}{RT^2} \frac{L_{1q}'}{L_{11}} \cdot \frac{M_{\text{LiCl}}}{\Gamma}$$
(S8)

$$\Gamma = \left(1 + \left(\frac{m_{\rm LiCl}M_{\rm LiCl}}{m_{\rm H_2O}M_{\rm H_2O}}\right)\right) \cdot \frac{m_{\rm LiCl}}{RT} \cdot \left(\frac{\partial\mu_{\rm LiCl}}{\partial m_{\rm LiCl}}\right)_{p,T}$$
(S9)

Using the experimentally determined Soret coefficients and the thermodynamic data for aqueous LiCl solutions [9], we can calculate the ratio of the phenomenological Onsager coefficients.

$$RT^2 \frac{\Gamma}{M_{\rm LiCl}} S_{\rm T}^{\rm exp} = \frac{L_{1q}'}{L_{11}} \tag{S10}$$

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