Supplementary information:
Analyzing the concentration-dependent Soret coefficient minimum in salt solutions: An overview

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Contents

S1 Thermal diffusion forced Rayleigh scattering

Thermal diffusion forced Rayleigh scattering, a transient grating technique, is used to measure the thermodiffusive properties [1, 2]. We use two infrared laser beams to create a holographic grating inside the sample, which in turn creates a temperature grating due to the inherent absorption of water at this wavelength of 980 nm. The rapidly established temperature grating with a typical time constant τ_{th} of $60\mu s$ leads to a migration of the solute molecules in the temperature gradient, resulting in a concentration grating. Both temperature and concentration gradients give rise to changes in the refractive index of the sample. The heterodyne scattering intensity $\zeta_{het}(t)$ of the read-out beam is measured and fitted with

$$\zeta_{\text{het}}(t) = 1 - \exp\left(-\frac{t}{\tau_{\text{th}}}\right) - A_{\text{c}}\left(\tau - \tau_{\text{th}}\right)^{-1} \qquad \text{(S1)}$$

$$\times \left\{ \tau\left[1 - \exp\left(-\frac{t}{\tau}\right)\right] - \tau_{\text{th}}\left[1 - \exp\left(-\frac{t}{\tau_{\text{th}}}\right)\right]\right\}.$$

With the lifetimes $\tau_{th} = (D_{\text{th}}q^2)^{(-1)}$ and $\tau = (Dq^2)^{(-1)}$ of the temperature and concentration grating, respectively, where q, D_{th} and D denote the grating wave vector, the thermal diffusivity and the collective diffusion coefficient, respectively. When the so-called contrast factors, the change in refractive index with temperature and concentration, $(\partial n/\partial T)_{w,p}$ and $(\partial n/\partial w)_{T,p}$, are known, the Soret coefficient can be calculated from the amplitude A_{c} as follows,

$$A_{\text{c}} = \left(\frac{\partial n}{\partial w}\right)_{p,T}\left(\frac{\partial n}{\partial T}\right)_{p,w}^{-1} S_{\text{T}}w\left(1 - w\right), \qquad \text{(S2)}$$

where w is the weight fraction. At very low concentrations, a small $(\partial n/\partial w)_{T,p}$ and S_{T} value leads to a small amplitude A_{c}, which complicates the analysis.

S2 Relation between the factor Γ and the Soret coefficient S_{T}

Following de Groot and Mazur [3] we can write the Soret coefficient S_{T} in terms of the phenomenological coefficient L_{1q}', L_{11} and the factor Γ as follows

$$S_T = \frac{L_{1q}'}{L_{11}Tw_1} \cdot \left(\frac{\partial \mu_{s,1}}{\partial w_1}\right)_{p,T}^{-1} = \frac{1}{k_BT^2}\frac{L_{1q}'}{L_{11}} \cdot \frac{M_1}{\Gamma} \tag{S3}$$

$$\Gamma = \frac{m_1}{k_BT}\left(1 + \frac{m_1 M_1}{\Omega M_2}\right)\left(\frac{\partial \mu_1}{\partial m_1}\right)_{p,T}, \tag{S4}$$

with the specific chemical potential $\mu_{s,i} = \mu_1/M_1$, the weight fraction w_1 and the molality m_1 of component 1, the Boltzmann constant k_B and the temperature T in Kelvin. In this work, $\Omega = m_{\mathrm{H_2O}} = 1000/18$ determines the molality of the water, M_1 and M_2 the molar mass of the salt and water respectively.

The chemical potential is given by

$$\mu_{\mathrm{salt}} = \mu_{\mathrm{salt}}^0 + RT\ln\left(\gamma_\pm(m_{\mathrm{salt}})m_{\mathrm{salt}}\right) \tag{S5}$$

The derivative of the chemical potential of the salt is given by

$$\left(\frac{\partial \mu}{\partial m_{salt}}\right)_{p,T} = \frac{RT}{m_{salt} \cdot \gamma_\pm(m_{salt})}\left(m_{salt}\left(\frac{\partial \gamma_\pm(m_{salt})}{\partial m_{salt}}\right)_{p,T} + \gamma_\pm(m_{salt})\right) \tag{S6}$$

The Soret coefficient of one mole can be expressed as follows

$$S_T = \frac{1}{RT^2}\frac{L_{1q}'}{L_{11}} \cdot \frac{M_{\mathrm{salt}}}{\Gamma} \tag{S7}$$

$$\Gamma = \left(1 + \left(\frac{m_{\mathrm{salt}}M_{\mathrm{salt}}}{\Omega M_{\mathrm{H_2O}}}\right)\right) \cdot \frac{m_{\mathrm{salt}}}{RT} \cdot \left(\frac{\partial \mu_{\mathrm{salt}}}{\partial m_{\mathrm{salt}}}\right)_{p,T} \tag{S8}$$

Using the experimentally determined Soret coefficients and the thermodynamic data for aqueous salt solutions [4], we can calculate the ratio of the phenomenological Onsager coefficients.

$$RT^2\frac{\Gamma}{M_{\mathrm{salt}}}S_{\mathrm{T}}^{\mathrm{exp}} = \frac{L_{1q}'}{L_{11}} \tag{S9}$$

S3 Relation between the rational activity coefficient of water and molal activity coefficient of the salt

In the molal system the molality of water is a constant $m_w = \Omega = 1000/M_w$ [5]. Therefore, we write the chemical potential of water μ_w in terms of the mole fraction. This implies that the activity coefficient $\gamma_w^{(x)}$ is also the mole fraction system.

$$\mu_w = \mu_w^{0,(x)} + RT \ln\left(\gamma_w^{(x)} x_w\right) \tag{S10}$$

$$\mu_s = \mu_s^{0,(m)} + \nu RT \ln\left(\gamma_\pm^{(m)} m_s\right) \tag{S11}$$

There are different ways to define the mole fraction. If we assume that the salt is not dissociated $x_s^{(0)}$ or $x_s^{(2)}$, if we assume full dissociation [6].

$$x_s^{(\mathrm{IP})} = \frac{m_s}{m_s + \Omega} \quad \text{and} \quad x_w^{(\mathrm{IP})} = \frac{\Omega}{m_s + \Omega} \tag{S12}$$

$$x_s^{(\mathrm{DI})} = \frac{\nu m_s}{\nu m_s + \Omega} \quad \text{and} \quad x_w^{(\mathrm{DI})} = \frac{\Omega}{\nu m_s + \Omega} \tag{S13}$$

The first expression neglects the dissociation of the ions completely, while the second expression assumes full dissociation. As strong electrolytes are dominantly dissociated we use Eq.S13 to calculate the water activity coefficient [7].

Gibbs Duhem with molality of salt using Ω results in

$$\Omega \frac{d\mu_w}{dm_s} = -m_s \frac{d\mu_s}{dm_s} \tag{S14}$$

This leads to

$$\frac{\partial \ln \gamma_w^{(x)}}{\partial m_s} + \frac{\partial \ln (1 - x_s)}{\partial m_s} = -\nu \frac{m_s}{\Omega}\left[\frac{\partial \ln \gamma_\pm^{(m)}}{\partial m_s} + \frac{\partial \ln m_s}{\partial m_s}\right] \tag{S15}$$

S3.1 Assuming ion pairs (IP)

Using $x_s = x_s^{(\mathrm{IP})}$ as defined in Eq.S12 we find

$$\frac{\partial \ln \gamma_w^{(x)}}{\partial m_s} - \frac{1}{m_s + \Omega} = -\nu \frac{m_s}{\Omega}\left[\frac{\partial \ln \gamma_\pm^{(m)}}{\partial m_s} + \frac{1}{m_s}\right] \tag{S16}$$

$$\frac{\partial \ln \gamma_w^{(x)}}{\partial m_s} = \left[\frac{1}{m_s + \Omega} - \frac{\nu}{\Omega}\right] - \frac{\nu}{\Omega}\left[\frac{m_s \partial \ln \gamma_\pm^{(m)}}{\partial m_s}\right] \tag{S17}$$

Integration of the equation leads to

$$\ln \gamma_w^{(x)} = \left[\ln \frac{m_s + \Omega}{\Omega} - \frac{\nu}{\Omega} m_s \right] - \frac{\nu}{\Omega} \int_0^{m_s} \tilde{m}_s \frac{\partial \ln \gamma_\pm^{(m)}}{\partial \tilde{m}_s} d\tilde{m}_s \qquad (S18)$$

Using partial integration we can solve the integral as follows

$$\int_0^{m_s} \tilde{m}_s \frac{\partial \ln \gamma_\pm^{(m)}}{\partial \tilde{m}_s} d\tilde{m}_s = m_s \ln \gamma_\pm^{(m)} - \int_0^{m_s} \ln \gamma_\pm^{(m)} d\tilde{m}_s \qquad (S19)$$

Now we can rewrite Eq.S18 this results in

$$\ln \gamma_w^{(x)} = \left[\ln \frac{m_s + \Omega}{\Omega} - \frac{\nu}{\Omega} m_s \left(1 + \ln \gamma_\pm^{(m)} \right) \right] + \frac{\nu}{\Omega} \int_0^{m_s} \ln \gamma_\pm^{(m)} d\tilde{m}_s \qquad (S20)$$

$$\gamma_w^{(x)} = exp \left(\left[\ln \frac{m_s + \Omega}{\Omega} - \frac{\nu}{\Omega} m_s \left(1 + \ln \gamma_\pm^{(m)} \right) \right] + \frac{\nu}{\Omega} \int_0^{m_s} \ln \gamma_\pm^{(m)} d\tilde{m}_s \right) \tag{S21}$$

S3.2 Assuming full dissociation of the ions (DI)

Using $x_s = x_s^{(\text{DI})}$ as defined in Eq.S13 we find

$$\frac{\partial \ln \gamma_w^{(x)}}{\partial m_s} - \frac{\nu}{\nu m_s + \Omega} = -\nu \frac{m_s}{\Omega} \left[\frac{\partial \ln \gamma_\pm^{(m)}}{\partial m_s} + \frac{1}{m_s} \right] \qquad (S22)$$

$$\frac{\partial \ln \gamma_w^{(x)}}{\partial m_s} = \left[\frac{\nu}{\nu m_s + \Omega} - \frac{\nu}{\Omega} \right] - \frac{\nu}{\Omega} \left[\frac{m_s \partial \ln \gamma_\pm^{(m)}}{\partial m_s} \right] \qquad (S23)$$

Integration of the equation leads to

$$\ln \gamma_w^{(x)} = \left[\ln \frac{\nu m_s + \Omega}{\Omega} - \frac{\nu}{\Omega} m_s \right] - \frac{\nu}{\Omega} \int_0^{m_s} \tilde{m}_s \frac{\partial \ln \gamma_\pm^{(m)}}{\partial \tilde{m}_s} d\tilde{m}_s \qquad (S24)$$

Using partial integration we can solve the integral as follows

$$\int_0^{m_s} \tilde{m}_s \frac{\partial \ln \gamma_\pm^{(m)}}{\partial \tilde{m}_s} d\tilde{m}_s = m_s \ln \gamma_\pm^{(m)} - \int_0^{m_s} \ln \gamma_\pm^{(m)} d\tilde{m}_s \qquad (S25)$$

Now we can rewrite Eq.S24 this results in

$$\ln \gamma_w^{(x)} = \left[\ln \frac{\nu m_s + \Omega}{\Omega} - \frac{\nu}{\Omega} m_s \left(1 + \ln \gamma_\pm^{(m)} \right) \right] + \frac{\nu}{\Omega} \int_0^{m_s} \ln \gamma_\pm^{(m)} d\tilde{m}_s \qquad (S26)$$

$$\gamma_w^{(x)} = exp \left(\left[\ln \frac{\nu m_s + \Omega}{\Omega} - \frac{\nu}{\Omega} m_s \left(1 + \ln \gamma_\pm^{(m)} \right) \right] + \frac{\nu}{\Omega} \int_0^{m_s} \ln \gamma_\pm^{(m)} d\tilde{m}_s \right) \tag{S27}$$

Note that for both choices of the mole fraction it holds that

$$\ln(\gamma_w^{(x)} x_w) = \left[-\frac{\nu}{\Omega} m_s \left(1 + \ln \gamma_\pm^{(m)} \right) \right] + \frac{\nu}{\Omega} \int_0^{m_s} \ln \gamma_\pm^{(m)} d\tilde{m}_s \qquad (S28)$$

S4 Properties of aqueous salt solutions

In the following, we summarize for all aqueous salt solutions mean ionic activity coefficients $\gamma_\pm$ and calculated rational activity coefficients of water γ_w. For a few systems we also display the factor Γ defined in Eq.S4, the diffusion coefficients D and the degrees of dissociation α as a function of molality.

S4.0.1 Lithium, sodium and potassium chloride

We performed an empirical unweighted fit of S_T/K as a function of molality for NaCl and KCl in Fig. 2(a) of the main manuscript. For NaCl, we used the following equation

$$S_\mathrm{T} = a + b \cdot m + c \cdot \sqrt{m} \cdot \ln{(m)} + d/\sqrt{m} + e \cdot exp(-m) \qquad \text{(S29)}$$

with the numerical values of the parameters $a = 2.04 \cdot 10^{-3}$, $b = -1.26 \cdot 10^{-3}$, $c = 1.87 \cdot 10^{-3}$, $d = -1.06 \cdot 10^{-5}$, and $e = 9.85 \cdot 10^{-4}$. In the case of KCl, we used the following empirical equation

$$S_\mathrm{T} = a + b \cdot m + c^2 + d \cdot \exp{(m)} + e \cdot \sqrt{m} \cdot \ln{(m)} \qquad \text{(S30)}$$

with the numeric values of the parameters $a = 2.20 \cdot 10^{-3}$, $b = -1.85 \cdot 10^{-3}$, $c = 5.72 \cdot 10^{-4}$, $d = -1.85 \cdot 10^{-4}$, and $e = 1.38 \cdot 10^{-3}$.
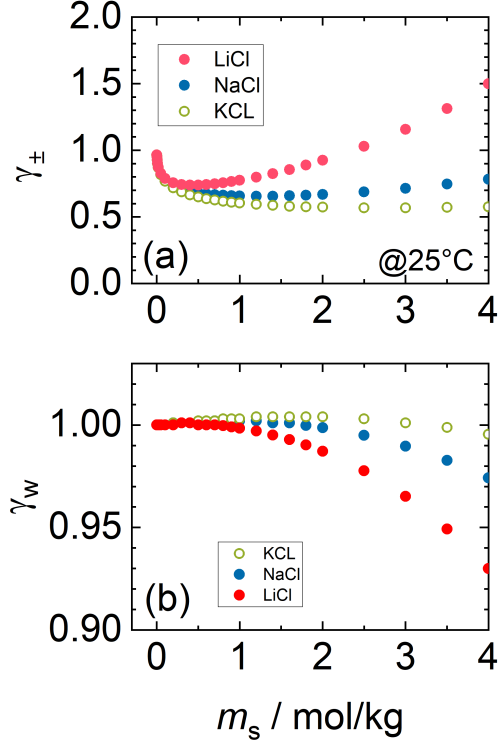
Figure S1: (a) The mean ionic $\gamma_\pm$ and (b) the rational activity coefficient of water γ_w in aqueous solutions of alkali metal chlorides at T = 298 K calculated from experimental data [4].

Figure S1 shows the mean ionic activity coefficient and the rational activity coefficient of aqueous chloride solutions as a function of molality. All chloride salts show a minimum as a function of concentration, where the position of the minimum is as follows $m_{min}^{LiCl} = 0.5$, $m_{min}^{NaCl} = 1.2$, $m_{min}^{KI} = 2.7$. There is a clear trend with increasing radius towards higher concentration and the concentration dependence of $\gamma_\pm$ is flatter for the larger cation. The rational water activity coefficient γ_w of all salts slopes downwards and shows the largest deviations from 1 for the LiCl. Note that we have assumed fully dissociated ions in the calculation of γ_w, which is justified since even for KCl the degree of dissociation in the concentration range is well above 75

Figure S2 shows Γ defined in Eq.S4 for LiCl, NaCL and KCl solutions as function of molality at $T = 298$K.
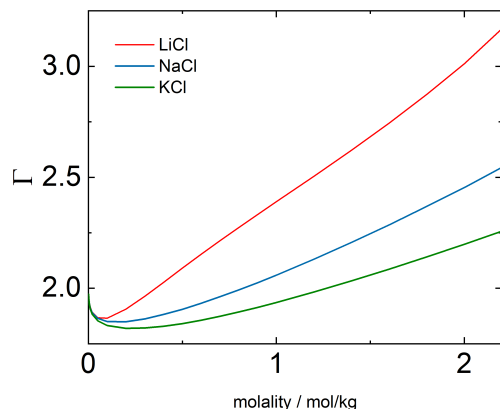
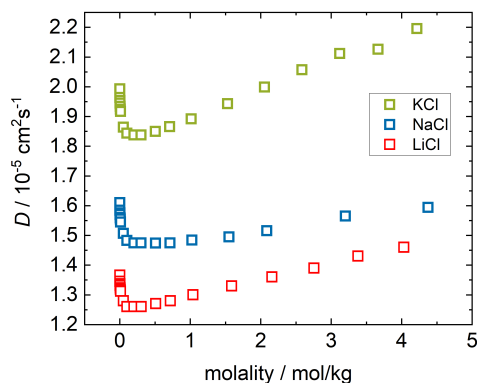Figure S2: Γ defined in Eq.S4 aqueous solutions of alkali metal chlorides at $T = 298$K calculated using Eq.S7.

Figure S3: Diffusion coefficient of lithium, sodium and potassium chloride in water as a function of molality at $T = 298$K [6].

Figure S3 shows the diffusion coefficient of lithium, sodium and potassium chloride in water as a function of molality at $T = 298$K [6]. Although lithium is the smallest cation, the diffusion coefficient of LiCl is the lowest, which is probably due to the fact that the hydration shell moves with the small cation. The diffusion coefficients of all chloride salts exhibit a minimum as a function of concentration, with the position of the minimum being as follows: $m_{\min}^{\mathrm{LiCl}} = 0.2, m_{\min}^{\mathrm{NaCl}} = 0.5, m_{\min}^{\mathrm{KI}} = 0.3$. There is no clear trend of the minimum concentration with increasing radius and the minimum concentration differs from those observed for the mean ionic activity coefficient $\gamma_{\pm}$.
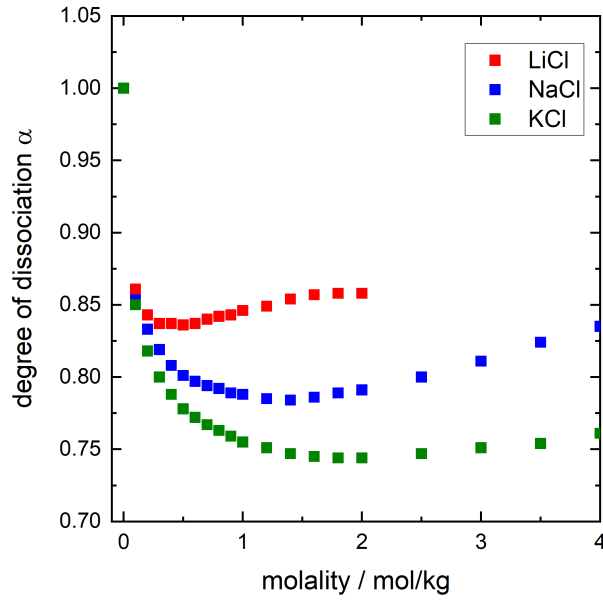
S8

Figure S4: Degrees of dissociation α alkali metal chlorides in water at $T = 298K$ [8].

Figure S4 shows the degree of dissociation α of alkali metal chlorides in water [8]. As the radius of the cation increases, α decreases. The chloride salts show a minimum as a function of concentration, with the position of the minimum shifting to higher concentrations with increasing radius as follows $m_{\min}^{\mathrm{LiCl}} \leq 0.4$, $m_{\min}^{\mathrm{NaCl}} = 1.3$ and $m_{\min}^{\mathrm{KCl}} = 2.0$.

S4.0.2 Iodide salts

In the main manuscript we presented the Soret coefficients of aqueous CsI solutions. The temperature dependence of S_T was fitted using Equation 4 in the main manuscript. The obtained fitting parameters and their uncertainties are listed in S1.

Table S1: The table contains the fitting parameters determined for aqueous CsI solutions using equation 4 in the main manuscript to describe the temperature dependence of S_T for all concentrations studied.

m / mol/kg	S_T^∞ / 10^{-3} K^{-1}	$-A$ / 10^{-3}	$-T^0$ / °C
0.5	7.2 ± 0.7	11.3 ± 0.5	47 ± 5
0.75	3.6 ± 1.0	8.1 ± 0.6	23 ± 12
1	3.9 ± 0.2	6.9 ± 0.1	33 ± 2
1.5	4.9 ± 0.1	6.5 ± 0.1	38 ± 1
2	4.2 ± 0.2	5.4 ± 0.1	29 ± 3
2.5	4.7 ± 0.1	4.4 ± 0.1	36 ± 2
3	4.6 ± 0.2	3.9 ± 0.1	31 ± 5

Figure S5 shows the mean ionic activity coefficient and the rational activity coefficient of aqueous iodide solutions as a function of molality at $T = 298$K [4]. With the exception of CsI $\gamma_\pm$, the iodide salts show a minimum as a function of concentration, where the position of the minimum is as follows $m_\mathrm{min}^\mathrm{LiI} = 0.2, m_\mathrm{min}^\mathrm{NaI} = 0.6, m_\mathrm{min}^\mathrm{KI} = 0.4$. There is no clear trend with increasing radius. The rational water activity coefficient γ_w of cesium iodide differs greatly from the other salts. Note that we have assumed fully dissociated ions in the calculation of γ_w, which is least true in the case of CsI as only about 70% of the ions are dissociated.
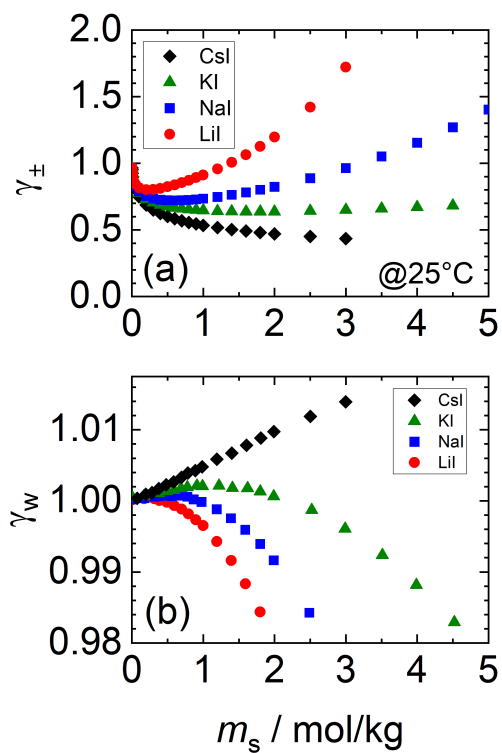
Figure S5: (a) The mean ionic $\gamma_{\pm}$ and (b) the rational activity coefficient of water γ_w in aqueous solutions of alkali metal iodides at $T = 298K$ calculated from experimental data [4].
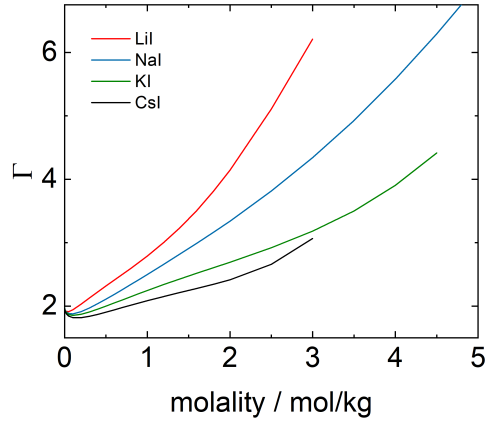
Figure S6: Γ aqueous solutions of alkali metal iodides at $T = 298K$ calculated using Eq.S7.

Figure S6 shows Γ for LiI, NaI, KI and CsI solutions as function of molality at $T = 298K$.

Figure S7 shows the degree of dissociation α of alkali metal iodides in water [8]. As the radius of the cation increases, α decreases. The iodide salts show a minimum as a function of concentration, with the position of the minimum shifting to higher concentrations with increasing radius as follows $m_{\min}^{\text{NaI}} \leq 0.1, m_{\min}^{\text{NaI}} = 0.4, m_{\min}^{\text{KI}} = 0.8$ and $m_{\min}^{\text{CsI}} = 1.4$.
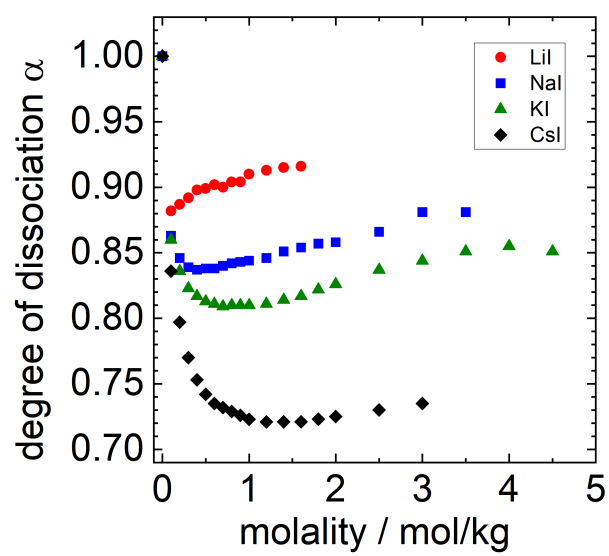
Figure S7: Degrees of dissociation α alkali metal iodides in water at $T = 298K$ [8].
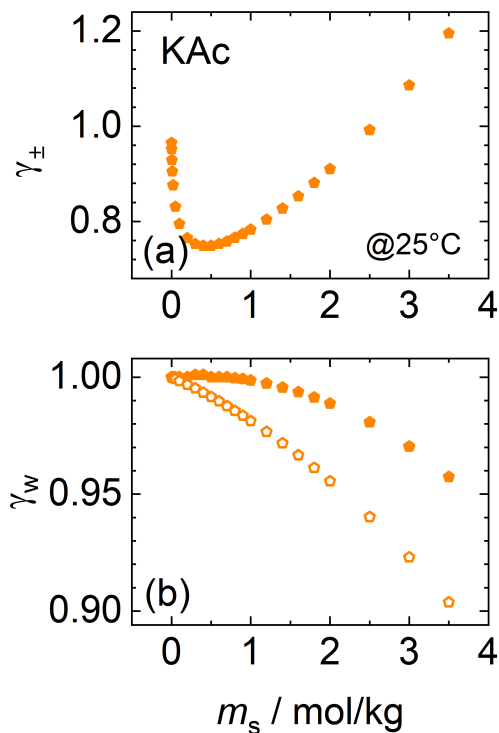
Figure S8: (a) The mean ionic $\gamma_{\pm}$ and (b) the rational activity coefficient of water γ_w assuming full dissociation (solid symbols) and full association (open symbols) in aqueous solutions of potassium acetate at $T = 298$K calculated from experimental data [4].

S4.0.3 Potassium acetate

Figure S8 shows the mean ionic activity coefficient and the rational activity coefficient of aqueous potassium acetate (KAc) solutions as a function of molality at $T = 298$K [4]. $\gamma_{\pm}$ becomes minimal at $m_{\min}^{KAc} = 0.5$. The corresponding rational water activity coefficients γ_w were calculated assuming complete dissociation and complete association, as KAc is a weaker electrolyte, so the assumption of complete dissociation may not be justified.

S4.0.4   Sodium and Potassium thiocyanate

Figure S9 shows the mean ionic activity coefficient and the rational activity coefficient of aqueous NaSCN and KSCN solutions as a function of molality at $T = 298$K. $\gamma_\pm$ of NaSCN shows a minimum at $m_{min}^{NaSCN} = 0.8$, while $\gamma_\pm$ of KSCN decreases monotonically. The corresponding rational water activity coefficients γ_w were calculated assuming complete dissociation and complete association, since NaSCN and KSCN are weaker electrolytes, so the assumption of complete dissociation may not be justified.
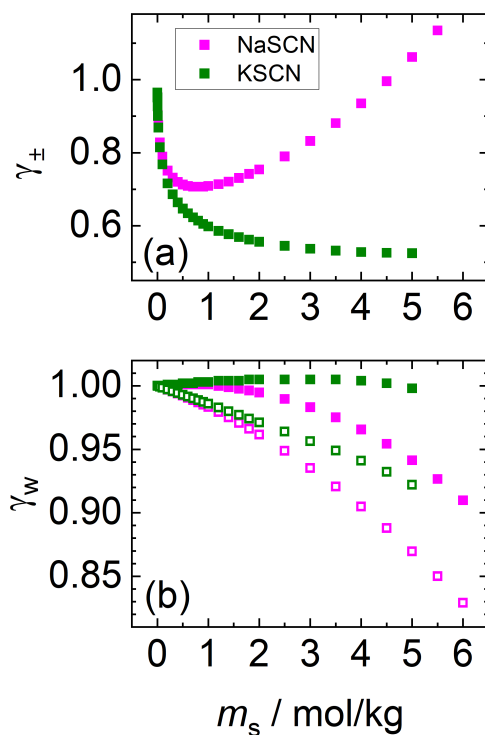

Figure S9: (a) The mean ionic $\gamma_\pm$ and (b) the rational activity coefficient of water γ_w assuming full dissociation (solid symbols) and full association (open symbols) in aqueous solutions of sodium and potassium thiocyanate at $T = 298$K calculated from experimental data [4].
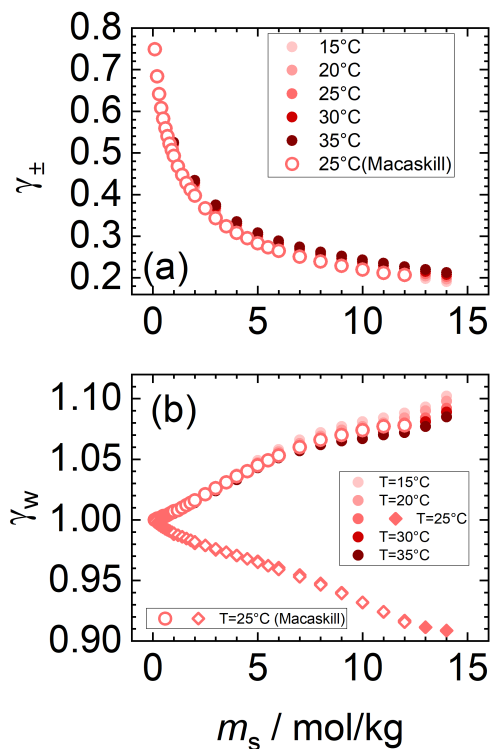
S4.0.5 Guanidinum chloride

Figure S10: (a) The mean ionic $\gamma_\pm$ and (b) the rational activity coefficient of water γ_w in aqueous solutions of guanidinium chloride at different temperatures, calculated from experimental data by Makhatdze *et al.* (solid symbols) [9] and by Macaskill *et al.* at $T = 298$K (open symbols) [10]. The bullet points and the open circle refer to the assumption of a complete dissociation, the solid and open diamonds to a complete association.

Figure S10 shows the mean ionic activity coefficient and the rational activity coefficient of aqueous GdmCl solutions as a function of molality at $T = 298$K [10] and in a temperature range between $T = 288$K and $T = 308$K. $\gamma_\pm$ decreases monotonically for all temperatures. The corresponding rational water activity coefficients γ_w were calculated for all temperatures under the assumption of complete dissociation and at $T = 298$K γ_w was also calculated under the assumption of association. For GdmCl, γ_w changes significantly when assuming complete association instead of complete dissociation. As far

as we know, the degree of dissociation for GdmCl has never been measured, but due to the large size of the cation and the weaker surface charge, we assume a lower degree of complete dissociation than for the simple alkali halide salts.

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