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Physical origin of the non-monotonic behavior of the Soret coefficient in salt solutions

Binny Rudani[1], Wim Briels[1,2] and **Simone Wiegand[1,3*]**

[1] IBI-4:Biomacromolecular Systems and Processes, Forschungszentrum Jülich, 52428 Jülich, Germany,
[2] University of Twente, Computational Chemical Physics, Postbus 217, 7500 AE Enschede, The Netherlands
[3] Institute for Light and Matter, University Cologne, 50939 Cologne, Germany

*Corresponding Author: s.wiegand@fz-juelich.de

Temperature gradients can induce partial separation of components in liquid mixtures through thermodiffusion, a process quantified by the Soret coefficient. Recent experiments and simulations have examined the occurrence of minima in the concentration dependence of the Soret coefficient S_T for various aqueous salt solutions [1-4]. We compile and analyze data for twelve electrolytes in water, consisting of various cations (such as lithium, sodium, potassium, cesium, ammonium, and guanidinium) and anions (such as chloride, iodide, acetate, and thiocyanate). One proposed explanation for the non-monotonic behavior of the Soret coefficient relates the concentration at the minimum, m_{min} to the onset of overlap between ion hydration shells [1]. According to this hypothesis, m_{min} corresponds to the concentration at which hydrated spheres approach random close packing. Although this picture involves simplified ion-pairing and adjustable parameters, it can account for the fact that some systems exhibit a minimum only at high temperatures. For salts such as cesium iodide and ammonium chloride (Fig.1(a) and Fig-1(b)), the minimum may occur at low temperatures and concentrations that fall outside the experimentally accessible range. This interpretation is supported by observations for aqueous lithium chloride and guanidinium chloride, where m_{min} shifts to higher concentrations with increasing temperature (Fig. 1(c)). A thinner and more flexible hydration shell at elevated temperatures would naturally shift the minimum in this way. From irreversible thermodynamics, the Soret coefficient can be written as the product of a purely thermodynamic factor and the ratio of two Onsager coefficients. In contrast to trends reported for binary Lennard–Jones mixtures [2], where the minimum of the Soret coefficient coincides with the minimum of the thermodynamic factor, our analysis of 1:1 aqueous electrolytes shows that the dominant contribution to the observed non-monotonic concentration dependence arises from the Onsager-coefficient ratio. For salts sharing the same anion, thermodynamic factors increase with the Pauling radii of the cations, whereas the Onsager-coefficient ratios increase monotonically with the radii of the hydrated cations, highlighting the essential role of hydration structure in thermodiffusion. Overall, our results emphasize that ion hydration is the key determinant of thermodiffusive behavior in aqueous electrolytes.

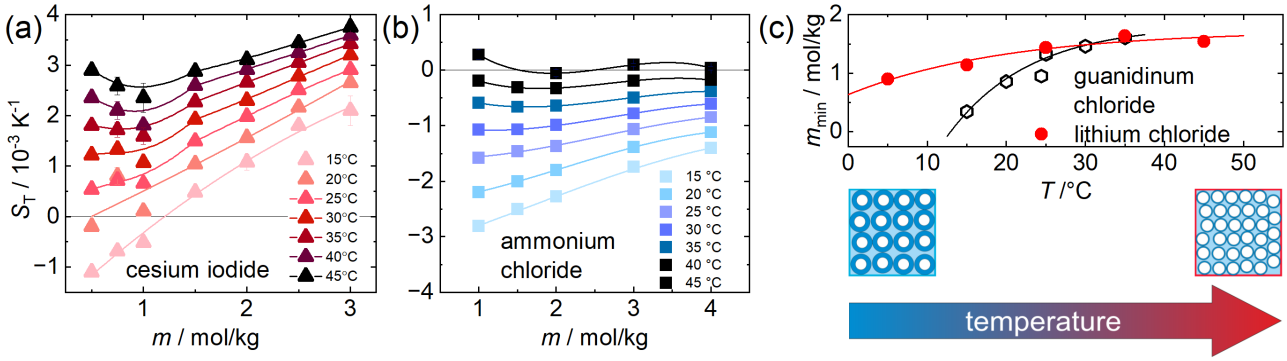

Figure 1. S_T of cesium iodide (a) and ammonium chloride (b) as function of molality for various temperatures. (c) The concentration m_{min} at which S_T has a minimum increases with temperature in aqueous lithium and guanidinium chloride solutions [3,4].

Significant references

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