

How Does the Hydration Layer Influence the Thermodiffusion of Aqueous Systems?

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Thermodiffusion, also called the Ludwig-Soret effect, has gained popularity in recent years as an analytical approach (Microscale Thermophoresis (MST)) to monitor binding reactions in biological molecules that are relevant in pharmaceutical applications. The success of this technique relies on the superb sensitivity of thermodiffusion to changes in the hydration layer around a solute. While for non-polar systems, the “heat of transfer” concept has been successfully applied, the mechanism in aqueous systems is more complicated due to charge effects and strong specific cross interactions. On the other hand, a detailed understanding of aqueous systems would be valuable due to important applications in biotechnology. To get a better comprehension of the underlying processes, we systematically investigated various small molecules and charged colloids by a holographic grating method called infrared Thermal Diffusion Forced Rayleigh Scattering (IR-TDFRS). We elucidate the often-found typical temperature dependence of the Soret coefficient of solute molecules in water. From a literature survey and measurements of hydrogen bond formers like amides in water, we claim that this simple empirical approach to describe the temperature dependence breaks down at higher solute concentrations, when interactions between different solute molecules start to play a role. Additionally, the concept also requires a hydrogen bond network without micro-heterogeneities or cage structures. Performing temperature and concentration dependent measurements, we observe a clear correlation of the temperature and concentration dependence of the Soret coefficient with the hydrophilicity, which can be quantitatively described by the logarithm of the 1-octanol/water partition coefficient P , which is a measure for the hydrophilicity/hydrophobicity balance of a solute. This coefficient is often used to model the transport of a compound in the environment or to screen for potential pharmaceutical compounds. The clear correlation between $\log P$ and the temperature sensitivity of the Soret coefficient opens a route for a more sophisticated hydrophilicity scale.