Effect of Electrolyte Species and Concentration on the Soret Coefficient of Aqueous Dispersions observed by Thermal Field-Flow Fractionation

K. A. Eslahian¹, M. Maskos¹*

¹ BAM Federal Insitute for Materials Research and Testing, 12205 Berlin, Unter den Eichen 87, Germany  
* e-mail: michael.maskos@bam.de

Understanding of interactions at the particle-solvent interface is of great interest for colloid science. To get experimental access to these interactions, thermal diffusion of charged colloids in aqueous dispersions is an important phenomenon, as it strongly depends on ionic shielding and hydration properties.¹ While the effect of ionic shielding is quite well understood, there is still lack of knowledge concerning the dependence on electrolyte hydration properties, described by Hofmeister series.² In this study, Thermal Field-flow fractionation (ThFFF) was used in order to separate negatively charged polystyrene according to their Soret coefficient (Sₜ)³ and to analyze the dependence of Sₜ on species and concentration of added electrolytes in the carrier liquid.

In previous studies, thermal diffusion of negatively charged particles was independently described to enlarge with increasing electrolyte concentration in the millimolar range ⁴ and to minimize with decreasing Debye length if κ⁻¹ < 20 nm.⁵ We expand the concentration range studied and our observations for chaotropic electrolytes are consistent with these reports: The Soret coefficient increases with electrolyte concentration up to a maximum ionic strength of I ≈ 10⁻³ M; further addition of chaotropic salt causes a decrease of retention. The intensity of this effect is consistent to Hofmeister series: Kosmotropic ions generate a weaker effect on thermal diffusion than chaotropic ones and retention shows opposed concentration dependencies for kosmotropic and chaotropic electrolytes. In addition, we observed a much stronger effect of hydration properties in case of anions as compared to cations. Our results can not be explained completely by surface charge variation of the nanoparticles. Hydration properties must be taken into account to describe the origin of the effect. Due to strong dependence of the Soret coefficient on viscosity, influence of the primary electroviscous effect is discussed.

We conclude that there is a strong dependence of the Soret effect on hydration properties of added electrolytes. A correlation with Hofmeister series is found. To compare our results with latest theoretical studies according to Soret effect, surface potential will to be taken into account in further studies.

---

⁴ S. J. Jeon, M. E. Schimpf, Anal. Chem., 69 (1997); 3442-3450  
⁵ Duhr, S., Braun, D., PNAS, 103 (2006), 52, 19678