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# Hofmeister effect in thermal field-flow fractionation of colloidal aqueous dispersions

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#### 1. Introduction

Field-flow fractionation (FFF) is a versatile and well known family of methods for analytical separation of colloidal particles [1,2]. Interaction with an externally induced field drives particles towards one channel wall, whilst the particle cloud is decompressed by particle Brownian motion. Consequently, a size dependent concentration profile is established, resulting in shorter retention times of small particles as compared to larger ones due to the parabolic flow profile.

In thermal field-flow fractionation (ThFFF) as FFF-subtechnique, a thermal gradient is placed between upper and lower channel boundaries [3]. The phoretic motion of particles as response to a thermal field is called thermophoresis, thermal diffusion or Ludwig–Soret effect [4,5] and depends on particle hydrodynamic size and surface composition. In ThFFF, particles are fractionated according to their Soret coefficient ( $S_T$ ) [6]. This dependence of retention on hydrodynamic size and bulk composition gives rise to the scientific interest of ThFFF besides the well developed, hydrodynamic size dependent asymmetrical flow field-flow fractionation (AF-FFF).

In ThFFF, the fractionation channel is of simple architecture without any organic membranes. Because of the resulting

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#### ABSTRACT

In this study, the retention of colloidal polystyrene beads in aqueous dispersion in thermal field-flow fractionation (ThFFF) is investigated as function of various types and concentrations of electrolytes in the carrier liquid. A specific ion effect is observed and can be interpreted in terms of Hofmeister series. Addition of salt composed of chaotropic anions to the carrier liquid increases particle retention with increasing ionic strength up to several mM. This effect is less pronounced the more kosmotropic the anions are, up to a decrease of retention by increasing concentration of sulphate and citrate. It is demonstrated that the effect of varying cations is minor as compared to the one of anions with this model system.

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compatibility with nearly all common solvents, ThFFF was developed as analytical separation method of polymers in organic media. In this application, it was demonstrated that resolution power in ThFFF is advantageous as compared to Size Exclusion Chromatography (SEC) [7]. Potential of ThFFF as sensitive tool to investigate particle-solvent interactions and changes in the particle surface composition of colloids in aqueous media was illustrated more than a decade ago [8,9]. Unfortunately, lack of understanding of the physical origin of thermophoresis inhibited a more detailed investigation. The origin of thermophoresis is brought into light by development of a variety of methods alternative to ThFFF to determine  $S_T$ , such as beam deflection [10,11], halographic scattering [12,13], electrical heating [14], thermal lensing [15] and fluorescence microfluidic imaging [16,17]. Nowadays, some theoretical models explaining thermophoresis are established [18,19], enabling an interpretation of ThFFF data.

The dependence of retention in ThFFF on slight changes in the water/solvent interface was illustrated in previous studies. Retention is shown to be dependent on particle size [20,21], particle surface composition [8,9,21], strength of the induced thermal field [22], cold wall temperature [23], carrier acidity [9] and ionic strength of the carrier liquid [8,9,22]. In this study, we display a specific ion effect on retention of charged polystyrene beads in aqueous carriers.

#### 2. Materials and methods

The ThFFF apparatus used in this study is based on a T100 Polymer Fractionator from FFFractionation Inc. (Salt Lake City, UT, USA)

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