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On the retention mechanisms and secondary effects in microthermal field-flow fractionation of particles

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ABSTRACT

The behavior of nanometer or micrometer-sized particles, dispersed in liquid phase and exposed to temperature gradient, is a complex and not yet well understood phenomenon. Thermal field-flow fractionation (TFFF), using conventional-size channels, played an important role in the studies of this phenomenon. In addition to thermal diffusion (thermophoresis) and molecular diffusion or Brownian movement, several secondary effects such as particle–particle and/or particle–wall interactions, chemical equilibria with the components of the carrier liquid, buoyant and lift forces, etc., may contribute to the retention and complicate the understanding of the relations between the thermal diffusion and the characteristics of the retained particles. Microthermal FFF is a new high-performance technique allowing much easier manipulation and control of the operational parameters within an extended range of experimental conditions in comparison with conventional TFFF. Consequently, in combination with various other methods, it is well suited for a detailed investigation of the mentioned effects. In this work, some contradictory published results concerning the thermal diffusion of the colloidal particles, studied by TFFF but also by other methods, are analyzed and compared with our experimental findings.

1. Introduction

1.1. Primary separation mechanisms in microthermal field-flow fractionation

Microthermal field-flow fractionation (micro-TFFF) is a new high-performance technique invented recently [1] and applied to the separations of polymers and various particles (see Refs. [2,3] for review). One of three basic retention mechanisms, *polarization* [4], *steric exclusion* [5], or *focusing* [6] usually governs the separation in field-flow fractionation (FFF). A clear distinction of these mechanisms requires an *a priori* rigorous definition of the terminology in order to avoid or rectify some confusion which can be found in the literature.

The term *polarization* was proposed in relation with the FFF principle [7–9] to denote the conditions under which an asymmetrical concentration distribution of uniform retained macromolecules or particles is formed across the separation channel due to the balance between their migration, generated by the action of a polarizing field force, and either Brownian movement or Fickian diffusion, and due to the existence of a polarizing barrier (accumulation wall) impermeable to the retained species but not to the polarizing force. The definition of this *polarization* mechanism as "Brownian mode FFF" (used sometimes in the literature) is not very suitable because Brownian movement, in its original meaning [10,11], is omnipresent in FFF, independently of a particular retention mechanism, even if in some cases it can be directionally restricted. On the other hand, the Brownian movement can strongly be reduced due to the appearance of the organized structures, colloidal crystals [12], formed as a consequence of the powerful electrostatic interactions between the retained species concentrated in a narrow zone at the accumulation wall, whereas the retention mechanism conform with the definition of *polarization*, can still be effective in such a case.

The term *steric exclusion* is used to characterize the situation in which the retained macromolecules or particles are all in contact with the accumulation wall due to the excessive field force and, consequently, their free Brownian movement is restricted in the direction of the field force action. As a result, the retained particles are sterically excluded from the streamlines of low velocities of the carrier liquid at the wall and elute in decreasing size order. However, it has been proved that the action of this mechanism is rather exceptional [2,13].

The term *focusing* is used to describe the situation in which the driving force, whose amplitude varies in the direction across the channel, changes the sign and vanishes at the focusing position, generates the converging transport (focusing) across the channel of the macromolecules or particles to the focusing position. The focusing can also be produced by the effect of two or more

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counteracting forces provided that the resulting force leads to the converging transport. This principle was originally proposed by [6] and developed further (see Refs. [14–18] for review) by using the term *focusing* which is conform with the commonly used designation of static separation methods based on similar focusing transports such as isopycnic focusing or isoelectric focusing. The term *hyperlayer*, proposed later [19], is less descriptive with regard to the basic transport mechanism.

It has to be stressed that the term "focusing" is used in some papers dealing with FFF to describe the process of the longitudinal sharpening of the injected sample zone before starting the separation. In chromatography, such a procedure is usually called *peak (band, zone) compression*. This latter term should be preferred for the procedure in question in order to make the papers on FFF comprehensible to the non-specialists, without any confusion.

The action of a particular retention mechanism is determined by the imposed experimental conditions such as the nature and amplitude of the applied field, the existence of the gradient of the driving forces, and the velocity of the carrier liquid, but also by the molecular or particulate characteristics of the retained species, such as the molar mass or size, the density of the dissolved macromolecular coils or suspended particles, their chemical nature and surface properties, etc. The polarization is typical mechanism whenever the separation of macromolecules is concerned, at least up to the molar mass of roughly 1 000 000 g/mol for which the effective hydrodynamic size of the dissolved macromolecular coils is smaller than roughly few tens of nanometers and their density in solution is very close to the density of the carrier liquid. Nevertheless, the focusing mechanism might, in principle, be also effective. Above the mentioned molar-mass limit, the steric exclusion but much more frequently the focusing mechanism is effective. As concerns the FFF of the particles, the polarization mechanism is supposed to dominate the separation in nanometer-size range whereas focusing mechanism is supposed to govern the separations in micrometer-size range. This fact is also related to the size and density of the particulate species which are generally larger and denser in comparison with the dissolved macromolecules.

In addition to the above mentioned primary retention mechanisms, the secondary mechanisms and interactions may come into play and complicate the retention behavior of the fractionated species. Even if the secondary mechanisms may have a positive impact on the performance of the separation, sometimes they obscure the relations between the primary driving forces and molecular parameters of the retained species.

1.2. Experimental studies of thermal diffusion of the particles suspended in a liquid

Thermal FFF performed with the use of standard size channels played an important role in the experimental studies of thermal diffusion [20–32]. The migration of the particles exposed to temperature gradient is driven by complex mechanism including the chemical equilibria and interactions with the components of the carrier liquid. A detailed analysis of the above referenced papers was already published in our monograph [2]. In the following paragraphs this analysis is summarized.

Thermal diffusion coefficient D_T was found to be dependent on particle diameter d_p according to $D_T \approx d_\mathrm{p}^{0.5}$ [21]. Whereas the retention increased with increase in solvent polarity (ethanol, methanol, acetonitrile, water) for polymer latexes, no obvious trend was observed for silica [22]. A strong dependence of the retention of various colloidal particles on the chemical nature of the particle surface and composition of the carrier liquid was found [23,24]. The addition of an electrolyte leads to an increase in retention [25] provided that the pH is not modified [26].

Mes et al. [27] studied the influence of the particle chemical composition on thermal diffusion coefficient, size dependence of thermal diffusion coefficient, and the effect of the pH on the retention. No significant size dependence for polystyrene (PS) particles was found. On the other hand, the pH had a strong effect on the retention and this dependence was attributed to the swelling and thus to a decrease in diffusion coefficients of the particles. Various surfactants influenced differently the retention [28].

Shiundu et al. [29] proposed the hypothesis that the ability of the electrolyte ions to adsorb on the particle surface determines the osmotic pressure gradient around the particle and, consequently, the amplitude of the thermophoresis. The authors [30] observed a decrease in retention ratio R with decreasing flow rate. This effect is not surprising because the loss of the resolution, a decrease in the retention caused by the relaxation phenomena, as well as the occurrence of the lift forces at higher linear velocities of the carrier liquid are potential explanations of the observed effect.

Shiundu et al. [31] analyzed the experimental data obtained in carrier liquids containing different concentrations of ionic strength modifiers (salts) and by employing the semi-empirical interaction parameter δ_w, introduced by Williams et al. [32], they concluded that the negative value of the δ_w parameter is indicative of an attractive particle–wall electrostatic interaction. In our opinion, the negative value of δ_w indicates a decreasing distance of the centre of gravity of the cloud of the retained particles from the accumulation wall with increasing ionic strength but it is not related to the particle–wall interactions. Sedimentation experiments [33] with the suspension of charged silica particles proved clearly that the addition of NaCl produced the formation of a steeper equilibrium concentration distribution of silica particles. Since these experiments were carried out in a sedimentation cell of much larger size compared with the thickness of a TFFF channel, the interactions particle-bottom wall of the cell cannot explain the observed behavior. The screening of particle charges which reduces electrostatic particle–particle interactions allows for the formation of a steeper concentration distribution of the particles.

The theory predicts a linear increase in retention with increasing temperature drop applied across the channel. Consequently, a deviation from this linearity observed in the experiments carried out at different ionic strengths [31] might be explained by the effect of interactive forces but also by the insufficient primary relaxation of the retained particles immediately after their injection into the separation channel. Whenever the retention of the particles is low (because of lower temperature drop or of their smaller size), they are more susceptible to exhibit lower than appropriate retention which is due to the insufficient primary relaxation [34]. Shiundu et al. [31] observed the adsorption of latex particles on a freshly cleaned channel surface. Our investigation [35] of the retention of the PS particles in freshly cleaned channel and after several injections of the same sample did not confirm such an observation but, on the other hand, some aging of the stock suspension of PS particles was found. The old stock suspensions were retained more in comparison with freshly prepared diluted suspension and this behavior correlated with a gradual decrease in zeta-potential of the particles.

It has been found [31] that the thermal diffusion coefficient decreases with increasing size of the retained particles and with decreasing ionic strength because the screening effect causes a measurable reduction of the apparent size of the charged particles. Nonetheless, the effect of the electrical double-layer on the hydrodynamic size of the particles is not minor but substantial, as already proved by our former viscometry measurements [36]. Moreover, the variation of the particle–particle electrostatic interactions with the changes in ionic strength can completely obscure the variation of the true thermal diffusion coefficient. The observation by Shiundu et al. [31] that the retention of the charged silica particles increases with increasing ionic strength until reaching