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Separation of different-sized silica nanoparticles using asymmetric flow field-flow fractionation by control of the Debye length of the particles with the addition of electrolyte molecules

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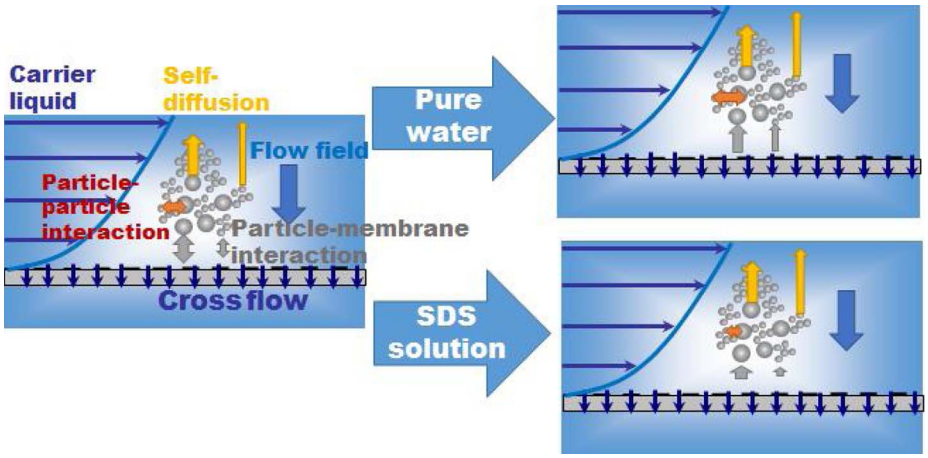
GRAPHICAL ABSTRACT



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ABSTRACT

Asymmetric flow field-flow fractionation (AF4) is widely used in nanotechnology to fractionate objective size from samples with wide size distributions. Essentially, the size separation of nanoparticles by AF4 is based on the diffusivity/size of the objects; however; we found unexpected results when using AF4 for the separation of different-sized silica nanoparticles. Using pure water as the carrier liquid in the AF4 assessment, silica nanoparticles of 50 and 100 nm were eluted out at almost the same retention time because of the cooperative diffusion derived by larger amounts of particles. After reducing the total concentration of silica particles, since the interaction between silica particles decreased with decreasing number of particles, better separation of the two different-sized silica nanoparticles was obtained. Furthermore, in order to reduce the electrostatic interaction between silica particles, electrolyte molecules (sodium dodecyl sulfate: SDS) were added to the carrier liquid, resulted that the excellent separation of 50 and 100 nm sized silica particles was achieved using 0.005 mg/mL of SDS aqueous solution as the carrier liquid. However, it was surprisingly observed that the zeta-potential of particles and membrane were not changed at all after addition of SDS into aqueous carrier. A theoretical estimation using the zeta-potential assessment and DLVO (Derjaguin-Landau-Verwey-Overbeek) theory indicated the Debye length of silica particles is the most important factor to induce appropriate separation of silica particles using AF4. Namely, the cooperative diffusion of different sizes of silica nanoparticles were suppressed by

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the change of the effective distance of the electrostatic interaction between particles (Debye length of particles). Although there are many studies focused on membrane-particle interactions or loading sample concentration effect in AF4 separation supported by the obvious change of zeta potential of particles by adding electrolyte, this study clearly demonstrates that not only diffusivity/size and zeta potentials of particle/membrane, but also Debye length of particles as well as that of the membrane significantly contribute to determining the appropriate separation conditions for AF4 assessment of nanomaterials.

1. Introduction

Because of the specific/enhanced characteristics of nanoparticles based on their size and functional properties [1–10], reliable and appropriate sizing of particles focused on not only the mean size but also the size distribution is significant in nano- and bio- technological fields. There are various approaches to characterizing the size of nanoparticles, e.g. electron microscopy (EM), dynamic light scattering (DLS), Brunauer-Emmett-Teller method, particle tracking analysis etc.; however; people still encounter difficulty selecting the appropriate sizing method based on their materials. In fact, there are inherent problematic characteristics that exist for each method; for example, the determined mean size and size distribution of nanoparticles over a wide size distribution as determined by the DLS method strongly depends on the particular analytical algorithm [11,12]. Since the definition of nanomaterials by the European Commission is “a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm–100 nm” [13], a reliable method for accurately determining the size distribution of the particles is strongly desired.

Within the nano-technological field, field-flow fractionation (FFF) has recently emerged as a characterization/separation technique of nanoparticles [14]. Specifically, asymmetric flow field-flow fractionation (AF4), an elution technique whereby nanoparticles are separated by flow control in an aqueous medium, has been widely utilized in various nano-technological areas [15–19]. As shown in Fig. 1, size distributed particles are injected into the AF4 channel and focused; then, the continued flow (carrier and cross flow) drives the components of the injected particles along the length of the channel and flushes them out. In order to achieve cross flow, the bottom of the AF4 channel consists of a membrane on a porous frit. Thus, there are two different flows inside the AF4 channel; the first is a laminar channel flow (directed to the right), and the second is a cross-flow (downward direction). Larger particles that are more affected by the cross-flow compared to smaller particles accumulate near the accumulation wall at the bottom in the figure. The smaller particles tend to accumulate near the center of the channel and reach the exit earlier compared to larger particles because of their relatively faster self-diffusion coefficients. In other words, a cross flow field is applied perpendicular to the carrier liquid flow direction to achieve separation based on nanomaterial diffusivity/size in the AF4 system. Therefore, according to Giddings' theory [14], the retention time (t_r) of an object in normal/Brownian mode AF4 separation can be predicted by Eq. (1):

$$t_r = \frac{\pi\eta d w^2}{2kT}\frac{V_C}{V_0} \tag{1}$$

where kT is the thermal energy, η is the viscosity of the carrier liquid, d is the nanoparticle diameter, w is the channel thickness, V_0 is the volumetric flow rate through the channel, and V_C is the cross-flow rate. Again, this equation indicates that the smaller particles will be eluted out from AF4 separation channel faster than larger particles, when one applies the same cross-flow and channel-flow rates to different-sized nanoparticles. Thus, even if the cross-flow and channel-flow rates are constant, the retention time is proportional to the size of the nanoparticles in an AF4 system.

Compared with other sizing techniques of nanomaterials, this technique along with chromatographic techniques, i.e. size exclusion chromatography, is exclusively used for fractionation/classification of nanomaterials depending on their size. Therefore, it is necessary to couple FFF with sizing/concentration-evaluation detectors to determine the size or concentration of nanomaterials of respective fractions. Because the size distribution of the materials is highly important to the reliability of the determined size, i.e. obtaining an ensemble evaluation of the size distribution for wider size distributed nanomaterials by EM method is extremely hard work, combining an FFF technique with a sizing method is a good solution for reliable characterization of nanomaterials [15].

Considering the dynamics of nanoparticles in an AF4 channel, Eq. (1) only represents the relationship between the elution flow rate and self-diffusion coefficient of nanoparticles in an AF4 system. According to this equation, after consideration of the band broadening effect that is caused by the differential displacement velocities of particles in the flow profile of an AF4 system, only the optimization of the sample focusing/cross-flow conditions significantly contributes to obtaining good separation by AF4 assessment. However, in the AF4 channel, it is easy to imagine that other interactions occur in the channel, such as the interaction between nanoparticles or that between nanoparticles and the membrane at the bottom of the channel [20,21]. According to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [22,23], the interactions between particles or between particles and the membrane are evaluated by two types of interactions: electrostatic repulsive interactions and van der Waals attractive interactions. The electrostatic repulsive energy results from the overlap between diffuse double layers of objects, and it decays exponentially with the distance between the objects. Thus, interactions between the objects continue even over long ranges. On the other hand, the van der Waals attractive energy levels decay according to a power law. Therefore, the electrostatic interactions between particles or particles and the membrane are a key factor in achieving effective separation within an AF4 system.

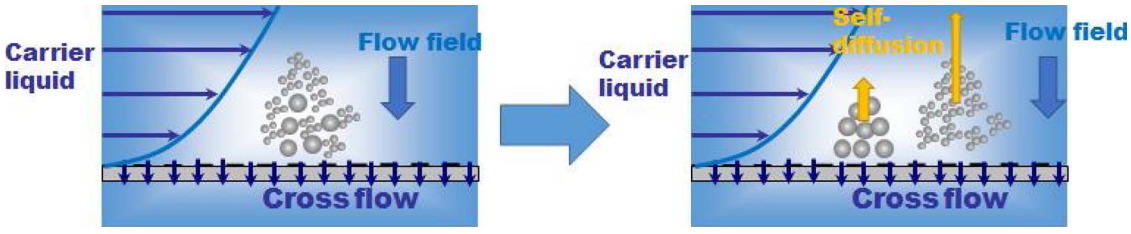

Fig. 1. Schematic of the AF4 separation. Since the self-diffusion coefficients of smaller particles are larger than those of larger particles, size separation of nanoparticles could be accomplished.