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# Explicit role of ionic strength in retention behavior of polystyrene latex particles in sedimentation field-flow fractionation: Slip boundary model

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## ABSTRACT

We investigate an explicit role of the ionic strength in the retention behaviors of polystyrene (PS) latex particles in sedimentation field-flow fractionation (SdFFF) by hinging upon the retention theory recently developed [1] as  $R = (R_o + v_b^*) / (1 + v_b^*)$ . Here  $R$  is an experimental retention ratio, and  $R_o$  is the analytical expression of the standard retention theory based on the parabolic flow velocity. The reduced boundary velocity  $v_b^*$  is expressed in terms of the ionic strength  $I$  of the carrier liquid as  $v_b^* = v_{b,o}^* / (1 + \sqrt{\varepsilon I})$ , where  $v_{b,o}^* = 0.070$  and  $\varepsilon = 60 \text{ mM}^{-1}$  for all the PS latex systems under investigation. We then apply this to study the explicit ionic strength effect on the retention behaviors of PS beads of 200, 300, 400, and 500 nm, respectively. As a primary result, the strong dependence of the retention ratio on the ionic strength can be quantitatively accounted for in an excellent accuracy: The slip effect at the channel surface is significant, particularly when  $I \lesssim 0.5 \text{ mM}$ , without showing any distinguishable dependence on the specific additives to control  $I$ , such as FL-70, SDS,  $\text{NaNO}_3$ , and  $\text{NaN}_3$ . Based on the present study, we put forward an experimental means to estimate the ionic strength of an aqueous solution using an FFF technique.

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## 1. Introduction

Field-flow fractionation (FFF) is a family of elution-based separation techniques, where the sample components are retained by an external field acting perpendicularly to the laminar flow in a thin channel [2,3]. FFF is applicable to separation and characterization of macromolecules and micron or sub-micron sized particles [3] of various types [1,4–13]. As one of the members of FFF family, sedimentation field-flow fractionation (SdFFF) is particularly useful for separation of colloidal particles at a high level resolution. From the measured retention time, physical properties such as hydrodynamic diameter and density for various types of colloidal particles can be determined [14–20].

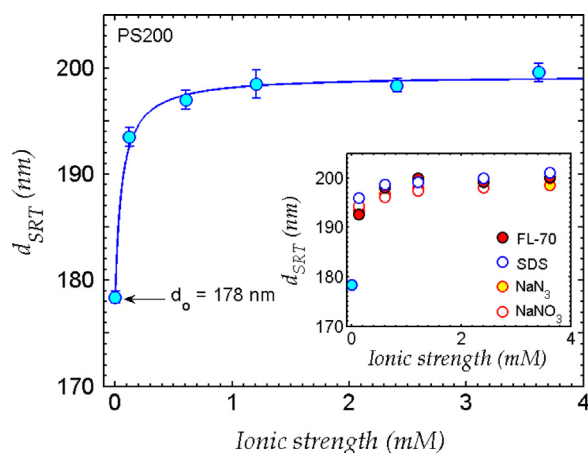
As an essential component, a first order retention theory has been developed [21] on a set of ideal conditions including a parabolic channel flow profile in order to make the theory tractable as much as possible. The “standard” retention ratio expression

derived thereby (see Eq. (6)) describes the retention behavior of an ideal system consisting of “point” particles of no interaction with the channel surface. Despite the set of ideal conditions upon which the standard retention theory (SRT) was built, its resulting retention ratio expression has been applied to explain the retention behaviors of many colloidal systems [17–20] with great success. This indicates that the primary features of the assumed ideal retention behaviors can be translated successfully into laboratory practice, in one way or another, so as to make the SRT applicable as widely as possible. Most of those prescriptions are focused to effectively minimizing the perturbing effects that would potentially lead to non-ideal retention behaviors unless appropriately controlled.

Nevertheless, there have been many cases in which departures from the ideal retention behaviors as described by the SRT are evident. Many theoretical and experimental efforts have been made to bridge the gap between the SRT and experiment. For example, some corrections have been considered for the non-ideal perturbations induced from, e.g., finite particle size effects due to steric exclusion at the walls [22,23], nonequilibrium effects due to flow [24], the presence of extraneous forces arising because of adsorption [25,26], hydrodynamic lifting forces, especially for large particles [27,28],

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**Fig. 1.** Apparent diameters estimated from the standard retention theory (SRT)  $d_{SRT}$  for PS200 with respect to ionic strength  $I$  (mM). The  $d_o = 178$  nm is estimated in pure water of  $I = 1.6 \times 10^{-4}$  mM. The nominal value is  $d_n = 200 \pm 6$  nm. This solid curve is fitted into a Langmuir adsorption isotherm expression to guide an eye. In the inset, various symbols are for  $d_{SRT}$  estimated for specific additives to control  $I$ .

and the existence of the interactions between particles as well as between the particles and the channel surface [7,29,30].

The no-slip boundary condition (BC) represented by the parabolic flow profile is perhaps paramount among the ideal behaviors that the SRT assumes. In reality, however, the no-slip BC often exposes some limitations in accurately describing the characteristic flow properties, particularly for systems with large surface to volume ratio as in microfluidics [31,32] or with channel walls having very weak interactions with the fluid and particles owing to ultra-smooth channel surface [33,34] or highly water-repellent walls [35], let alone for low density gas flows in micro-channels [36]. Such deviations from the predictions based on the no-slip BC have spurred a number of studies on the limitations thereof, for instance, via apparent slip of particles at the wall [37,38] or models based on “drainage” experiments [33–35,39–47].

Amongst the perturbing forces that may lead to non-ideal conditions, the most crucial one is perhaps due to the wall effect. Successful application of the SRT or its derivatives, therefore, requires effective means to make the overall wall effect as little as possible so that the latex particles obey the presumed ideal retention behaviors. An introduction of appropriate additives into a latex system is one of the most frequently practiced prescriptions to control the retention/elution behaviors of the latex particles in ordinary SdFFF operations: Surfactants, pH controllers, salts, stabilizers, and so on are added to adjust mostly the surface charges or ionic strength, consequently affecting the retention behaviors via orchestrating the interactions between the latex beads and the channel wall. For instance, as demonstrated in Fig. 1, an SRT estimate of the apparent hydrodynamic diameter for polystyrene (PS) latex particles of 200 nm is 178 nm in pure water of ionic strength of  $\sim 10^{-4}$  mM, while it becomes 197 nm at 0.60 mM and 200 nm at 3.60 mM, respectively.

Such additive effects on the SdFFF retention behaviors are quantitatively far from comprehensive as yet, and are open to further investigations, both experimentally and theoretically. At this point, we notice that the SRT approach as it stands would be inadequate to account for any significant wall effects, unless the intrinsic limitations borne by the no-slip BC embedded in the parabolic flow profile are effectively alleviated without costing the primary key features and creating undue complexity.

As an effort to shed light on this outstanding problem, we have recently developed [1] a retention theory by exploiting the slip BC, thereby removing the limitations set by the parabolic velocity pro-

file bound to the SRT. As a primary result, a generalized retention ratio expression  $R$  has been obtained as  $R = (R_o + v_b^*) / (1 + v_b^*)$ , where  $R_o$  is the sterically-corrected standard retention ratio expression and  $v_b^*$  is the reduced (dimensionless) boundary velocity. We have then applied [1,36] this to calculate the hydrodynamic diameters of the PS latex beads as a function of the surfactant (FL-70) concentration,  $S_o$ . As a result, the boundary slip effect was found profoundly significant in the case of  $S_o \lesssim 0.05\%$  in weight, particularly for large latex beads. This approach allows an insight of importance into the mechanism of the possible transition from the slip BC to the no-slip BC and vice versa depending on the additive (surfactant) concentration or ionic strength.

Without loss of generality, the additive effect can be interpreted in terms of the effective particle-wall interaction forces, where the overall competition between the attractive (dynamic adsorption) and repulsive (dynamic desorption) forces may depend on not only the nature of additives used (e.g., FL-70, SDS,  $\text{NaN}_3$ ,  $\text{NaNO}_3$ , and so on), but also their concentrations or the ionic strength in general. Along with the concentration effect on the retention behaviors, an investigation of any dependence on the nature of additives such as surfactants or salts should be worthwhile to pursue. In other words, it should be interesting to study if the ionic strength could constitute the general and representative term or measures to describe the additive effects on the retention behaviors in SdFFF in any quantitative manner regardless of the nature of specific additives employed. To serve the purpose, we will investigate in this work the retention behaviors of PS latex particles of about 200, 300, 400, and 500 nm in diameter with respect to the ionic strength of the carrier liquids (pure water) controlled by adding FL-70, SDS,  $\text{NaN}_3$ , and  $\text{NaNO}_3$ , respectively.

## 2. Theory

### 2.1. Retention ratio in SdFFF

We have recently developed [1] a retention theory in SdFFF by exploiting the slip BC that allows an alleviation of the no-slip BC constraint bound to the SRT. Here we will briefly review how we have arrived at the retention ratio expression by taking into consideration the potential slip at the channel surface.

The retention ratio  $R$  in SdFFF is given by the ratio of the sample band velocity to the average fluid velocity in the channel, as generally expressed [21] as:

$$R = \frac{\langle c(x)v(x) \rangle}{\langle c(x) \rangle \langle v(x) \rangle} = \frac{w \int_a^{w-a} c(x)v(x)dx}{\int_a^{w-a} c(x)dx \int_0^w v(x)dx} \quad (1)$$

where  $c(x)$  and  $v(x)$  are the sample concentration and velocity profiles, respectively, as a function of the channel thickness coordinate  $x$ ,  $a$  is particle radius, and  $w$  is the channel thickness. As a measure of the excluded distance for latex particles from the wall, we will take the particle radius  $a$ , for which the hard-sphere-like behavior has been assumed for the particle-wall interaction, namely,  $c(x) = 0$  for  $x > w - a$  as well as  $x < a$ . The angular brackets in Eq. (1) denote cross sectional averages. Note that the retention ratio above is equivalent to the ratio of channel void volume  $V_o$  to retention volume  $V_r$  and it is this quantity  $R = V_o/V_r$  that is measured in practice in most SdFFF experiments.

The concentration profile  $c(x)$  in Eq. (1) is postulated [7,29,30] to take the Boltzmann distribution,

$$c(x) = c_o \exp[-\beta V(x)], \quad (2)$$

where  $c_o$  is the concentration at a reference point and  $\beta \equiv 1/k_B T$  is the Boltzmann factor with  $k_B$  and  $T$  denoting the Boltzmann constant and absolute temperature, respectively. And  $V(x)$  is the potential energy exerted on a particle of which center of mass is

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