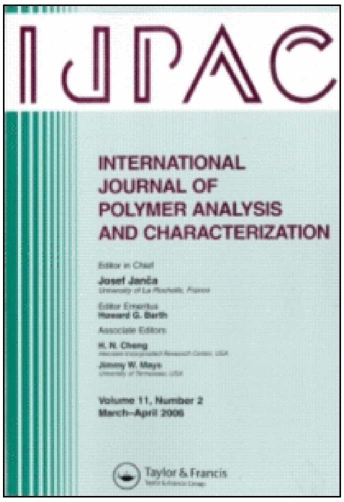

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EFFECT OF PARTICLE-PARTICLE ATTRACTIVE AND REPULSIVE INTERACTIONS ON THE RETENTION IN FIELD-FLOW FRACTIONATION

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The experimental data obtained by using various field-flow fractionation techniques and by other experimental methods are compared with the published results. All available and relevant data are analyzed with regard to the particle-particle interactions occurring in polarization and focusing mechanisms governing the field-flow fractionation of the macromolecular and colloidal species. It is concluded that these interactions strongly depend on the experimental conditions. The appearance of the organized structures, such as colloidal crystals, formed under the usual field-flow fractionation conditions is revealed. All these interactions must be taken into account for a rigorous interpretation of the experiments, especially with regard to the effect of the experimental conditions on the retention.

Keywords: Attractive and repulsive interactions; Colloidal crystals; Colloidal particles; Field-flow fractionation; Particle-particle interactions

INTRODUCTION

The main mechanisms governing the separation of polymers and particles in field-flow fractionation (FFF) are: polarization, focusing, and steric exclusion.[1] In real experiments, only the first two mechanisms are actually effective. Since these mechanisms were described in detail in Janča,[2] and several times in preceding original articles cited therein, the explanation of FFF separation mechanisms is not given again in this article.

Whatever is the mechanism of separation, the interaction of the retained species with an external physical field generates an effective force F_{EF} that produces the transport of the interacting particles across the carrier liquid flow and thus their separation in flow velocity profile. However, secondary effects can influence the resulting driving force.[1,2] These effects can also be characterized by the particular forces.

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The forces related to the secondary effects that should be taken into account are[1]:

1. Gravitational force and the resulting buoyancy force, F_G
2. Frictional drag of the retained species at the accumulation wall, F_{FD}
3. Adsorption of the retained species on the accumulation wall, F_{AD}
4. Polymer-polymer or particle-particle attractive interactions force, F_{AI}
5. Polymer-polymer or particle-particle repulsive interactions force, F_{RI}
6. Lift forces, F_{LF}

The secondary effects can play a positive role in the separation, but, on the other hand, they can deteriorate it. Colloidal particles are susceptible to undergo all of the mentioned secondary effects. The resulting driving force is defined separately for polarization mechanism and for focusing mechanism.

If the polarization mechanism governs the separation, the driving force is given by[1]:

$$\pm F(x) = \mp F_{EF} - F_G \mp F_{FD} \mp F_{AD} \mp F_{AI} \pm F_{RI} \pm F_{LF} \tag{1}$$

where F_{EF} is the force generated by an external physical field.

Whenever focusing mechanism is dominant, Equation (1) is reduced to:

$$\pm F(x) = \mp F_{EF} - F_G \pm F_{LF} \tag{2}$$

Since the focused species do not enter in contact with the walls, it holds that:

$$F_{FD} = F_{AD} = 0 \tag{3}$$

The forces of interactions F_{AI} and F_{RI} can contribute to the change of the width of the focused zone in the direction of the focusing force but they do not influence substantially the retention. The F_{AI} should lead to the sharpening of the zone and the F_{RI} should broaden the zone. Nevertheless, the occurrence of particle aggregation, in the case of effective F_{AI}, can influence the retention by an increase of F_G.[1]

It is worth noting that retention ratio R is defined, for example, as the ratio of the retention time t_0 of the unretained molecules (marker) to the retention time t_R of the retained species (particles or macromolecules):

$$R = t_0/t_R \tag{4}$$

Following this definition, if the retention time t_R, or, briefly the retention, increases for more retained species, retention ratio R decreases.

In addition to the above-mentioned forces and effects, the formation of organized structures such as colloidal crystals is expected. These structures can appear because of the concentrating action of the driving force, which produces the accumulation of the separated species at the proximity of one wall of the separation channel in polarization mechanism or in a focused zone in focusing mechanism.

This article deals with the analysis of the effect of particle-particle attractive and repulsive interactions. The analysis is based on the findings obtained by using different experimental techniques. However, the results thus obtained are applicable to FFF or, at least, are susceptible to explain some phenomena occurring under the usual FFF experimental conditions.

ANALYSIS

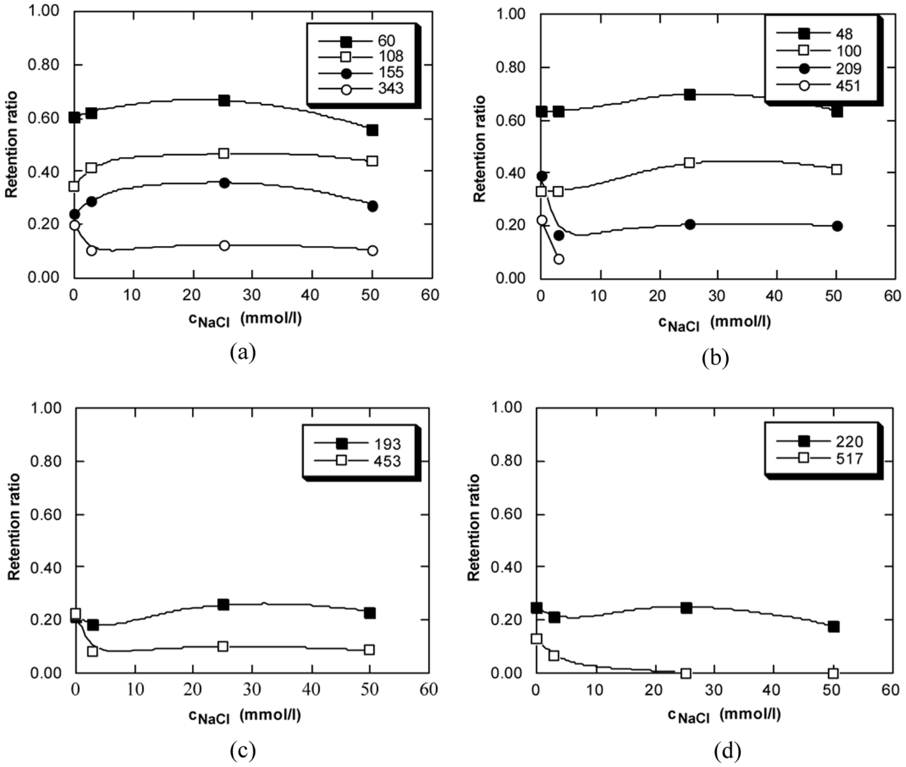
Attractive Interactions between Retained Particles

The force of the attractive interactions, F_{AI}, is multidirectional, and its action leads to an increase of the retention in the case of effective polarization mechanism. This is due to the fact that the attractive interactions usually produce the formation of bigger aggregated structures, which, in general, are more closely concentrated at the accumulation wall of the channel by an external field force F_{EF} and, consequently, are eluted in slower streamlines of the carrier liquid flow, and it means that they are more retained than the non-aggregated species. In the case of focusing mechanism, the effect on the retention is the opposite. The retention usually decreases (retention ratio increases) because larger aggregated species are pushed by lift forces to higher streamline velocities in the flow velocity profile formed inside the FFF channel.

Repulsive Interactions between Retained Particles

The force of the repulsive interactions, F_{RI}, is also multidirectional. However, as a result it opposes the concentrating effect of an external field force, F_{EF}. The most important repulsive particle-particle interactions are due to the electrostatic repulsions of the charged particles. These repulsions are strongly influenced by the concentration of the ionic species in the suspensions of the particles. The effect of the ionic strength on the particle-particle repulsive interactions is a well-known phenomenon. The experimental study[3] of this effect on the retention of various polystyrene latex particles, plain or modified by surface groups (–COOH, –OH, and $-NH_2$), revealed that the gravitation-buoyancy generated force F_G could have a non-negligible effect on the retention of the particles whose diameter is of the order of 200 nm and larger.

Figure 1 shows that the retention ratio obtained in microthermal FFF experiments[3] of all the above-mentioned particles, independently of the size and chemical nature of surface groups, slightly varies above the concentration 3 mmol/L of NaCl. Retention ratio of the particles whose diameter is more than approximately 200 nm systematically decreases in the range of concentrations between 0 and 3 mmol/L of NaCl. All particles exhibited negative zeta-potential lying between -40 and -80 mV in deionized water. If a decrease in retention ratio (an increase in retention) corresponded exclusively to a decrease of the repulsive electrostatic particle-particle interactions caused by the screening of their charges, all particles independently of their size should exhibit similar decrease in retention ratio. The explanation of the observed behavior of larger size particles is thus by a non-negligible contribution of F_G.



(a)

(b)

(c)

(d)

Figure 1. Dependence of the retention ratio in microthermal FFF of different size polystyrene latexes with different surface groups on the concentration of NaCl dissolved in water used as a carrier liquid: (a) plain PS, (b) PS-COOH, (c) PS-OH, (d) PS-NH_2. The diameters of the particles are given in nm.[3]

Jeon et al.[4] also observed in thermal FFF experiments the decrease in retention ratio with increasing ionic strength, which was independent of surface modification of the studied polystyrene latexes. The effect was attributed to the collapse in the electrical double layer allowing the particles to reach slower flow streamlines near the accumulation wall. This conclusion is supported by our microthermal FFF experiments.[3] Nevertheless, according to Jeon et al.,[4] the electrostatic particle-particle interactions should have minor effect on the retention in comparison with the particle-wall interactions producing steric exclusion from the accumulation wall.

Shiundu et al.[5] analyzed the effect of the ionic strength of the aqueous or nonaqueous carrier liquids on the particle retention in thermal FFF. They concluded that the semi-empirical interaction parameter δ_w, introduced by Williams et al.,[6] is indicative of attractive electrostatic interactions of the particles and accumulation wall of the channel. The negative value of the δ_w parameter certainly indicates a decreased distance of the center of gravity of the cloud of the retained particles from the accumulation wall with increasing ionic strength. Nevertheless, this negative value should not be due exclusively to the particle-wall interactions.

Our sedimentation experiments[7] with the suspension of charged silica particles are in major disagreement with the conclusion that the particle-wall interactions

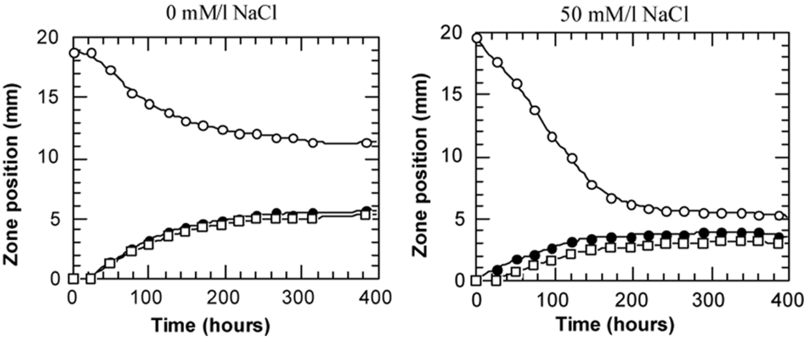


Figure 2. Comparison of sedimentation kinetics of the charged silica particles suspended in water and in a solution of NaCl. The experimental points indicate the evolution of the positions of three different density marker beads focused at the corresponding isopycnic layers.[7]

dominate over the particle-particle interactions. Figure 2 shows clearly that the increase in ionic strength resulted in much steeper concentration distribution of the particles in sedimentation equilibrium and the center of gravity of the concentration distribution of the silica particles was closer to the bottom of the sedimentation cell. Since these experiments were carried out in a sedimentation cell of much larger size than the thickness of a FFF channel, the interactions of particles and the bottom wall of the cell cannot explain the observed effect.

Figure 3 demonstrates an increase of the ratio of sedimentation velocity U to diffusion coefficient D of silica particles with increasing concentration of NaCl. The dependence $U/D = f(c_{\mathrm{NaCl}})$ was calculated from the experimental data shown in Figure 2. Figure 3 shows that the mobility (the diffusion coefficient D as well as the velocity of the transport U generated by the external field force) of the particles is higher at higher ionic strength because the repulsive electrostatic interactions

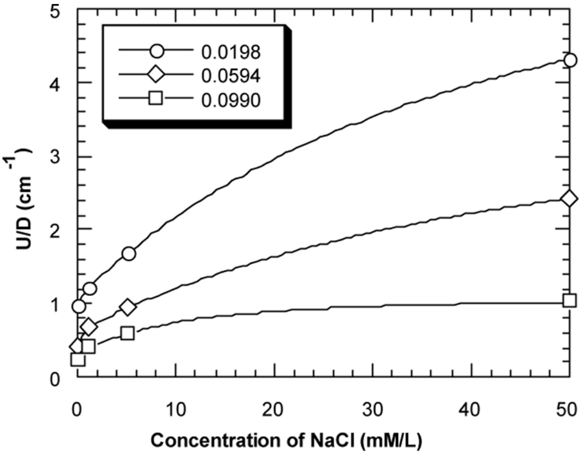


Figure 3. Dependence of the experimental U/D ratio on the concentration of NaCl measured in sedimentation experiments for three different volume fractions of the silica in suspension.[1]

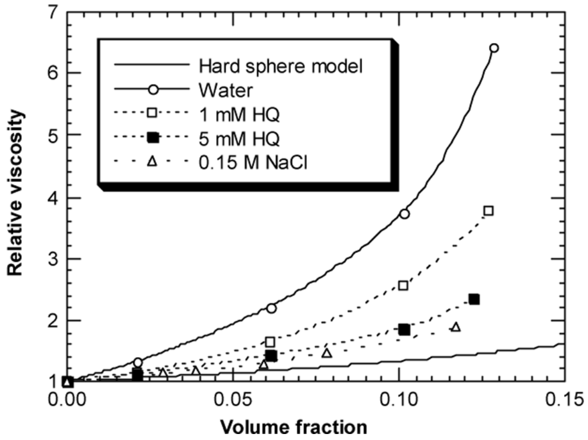


Figure 4. Relative viscosity of a suspension of silica particles as a function of volume fraction at different ionic strengths modified by the addition of the NaCl or hydroquinone compared with the theoretical relationship, Equation (4).[8]

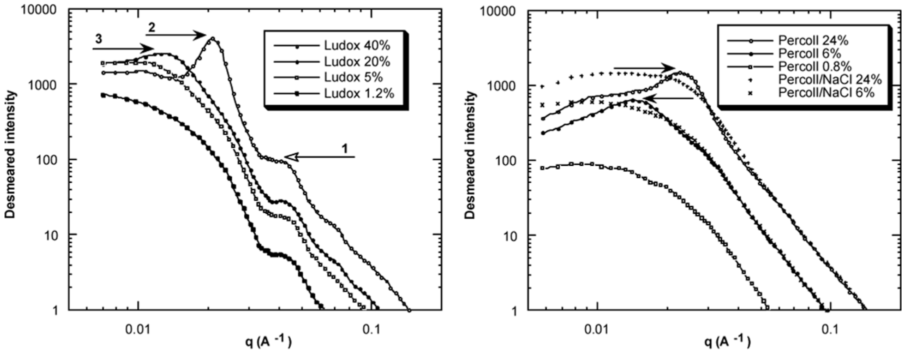
are screened; that the positive slope of the $U/D = f(c_{\mathrm{NaCl}})$ dependence indicates that the increase in U prevails over the increase in D; and that the impact of the screening is more important for the diluted suspension.

Screening effect causes a measurable reduction of the apparent size of the charged particles. This effect is not minor, as already proved by our former viscometry measurements.[8] Figure 4 demonstrates a strong variation of the relative viscosity of the charged silica particles suspended in water containing different concentrations of NaCl. Only at very high ionic strengths, the dependence of the relative viscosity, η_{rel}, on the volume fraction, ϕ, of silica particles approaches the behavior of an ideal suspension of hard spheres, described by Einstein relationship:

$$\eta_{rel} = 1 + 2.5\phi \tag{5}$$

The consequence of the electrostatic repulsive interactions at relatively high concentrations of the retained particles near the accumulation wall or in a focused zone is that organized structures like colloidal crystals may be formed. Since such a hypothesis is difficult to verify by FFF experiments, the measurements by small-angle X-ray scattering were performed with the use of the suspensions of pure silica (Ludox) and silica covered by poly(vinylpyrrolidone) (Percoll) particles at different concentrations of the particles and at 0 and 50 mmol/L of the NaCl added to the suspensions. The results are shown in Figure 5.

The plateaus on the curves of the desmeared intensity as a function of the inverse value of the scattering vector, q, for Ludox, pointed out by arrow 1, correspond to the size of the particles, and the maxima, pointed out by arrows 2 and 3, correspond to the characteristic distance between the particles, and, in this case, they indicate the presence of an organized structure in the suspension. The maxima are shifted to lower q values with decreasing concentration of the silica and thus with increasing distance between the particles in an organized structure and also when



(a) (b)

Figure 5. Small angle X-ray scattering measurements of the suspensions of (a) pure silica particles (Ludox) and (b) silica covered by poly(vinylpyrrolidone) (Percoll) of different concentrations in water and in a solution of 50 mmol/L NaCl.

the repulsive electrostatic interactions between the particles are screened by high ionic strength (NaCl). The same observation holds true for Percoll but the maxima are less pronounced, which is probably due to the layer of the poly(vinylpyrrolidone). As a result, the formation of colloidal crystals should be taken into account when considering the secondary effects that contribute to the retention of the charged species in all FFF techniques.

CONCLUSIONS

The analysis of our experimental data obtained in the course of several years' experience by various field-flow fractionation techniques but also by other analytical methods was realized. Our experimental results were critically compared with the experimental findings and conclusions published by other authors. In some cases, our conclusions agree with previous published studies. However, substantially different opinion, based on this analysis, exists especially as concerns particle-particle interactions, which, according to our findings, dominate over other interactions that can occur in field-flow fractionation experiments. A new effect, a possible formation of organized structures of the type of colloidal crystals that can be generated by the external physical fields applied in field-flow fractionation experiments, is described. This study is part of a series of detailed investigations of the separation mechanisms, of the "secondary" effects and related phenomena, occurring in FFF experiments.[9]

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