Characterisation of polymers and particles by asymmetrical flow field-flow fractionation

van Bruijnsvoort, M.

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Summary

Flow field-flow fractionation (FFF) is one of today’s most universal separation methods for macromolecules and particles. It can cover a size range from a few nm’s up to ca. 100 μm. Flow FFF is at its most powerful when combined with multi-angle light scattering (MALS) detection, that enables the on-line determination of molar mass and conformation. Flow FFF is an ideal tool to study the diffusional behaviour of macromolecules and particles, due to the possibility for analytes to freely diffuse in solution at relatively low concentrations.

In Chapter 1, the principles of flow FFF in an asymmetrical flat channel and tubular channel (hollow-fiber flow FFF) are introduced. The retention in the normal mode, which allows for a direct translation of retention time to diffusion coefficient and hydrodynamic size, and steric/hyper layer mechanisms are described.

Chapter 2 is an introduction to the application of hollow-fiber membranes in analytical chemistry. An overview is given of the applications in which hollow-fiber membranes are used for separation, amongst which hollow-fiber flow FFF (HF5) can be reckoned. Hollow-fiber membranes can be placed in front of the separation channel for sample preparation, or after the separation channel to enhance the detectability. The preparation of organic and inorganic hollow-fiber membranes is described, with several methods to deposit membrane films onto a porous surface and modify the films to gain specific selectivity.

Chapter 3 shows the application of a polyacrylonitril hollow-fiber membrane for the separation of synthetic polymers in hydrophobic organic solvents. Multiple polymer standards are successfully fractionated in organic solvents, illustrating the resistance of the system towards such solutions. The repeatability of the calculated diffusion coefficients, separation efficiency and recovery for polystyrene standards in ethyl acetate was satisfactory. From the peak dispersion of a monodisperse protein, it followed that non-equilibrium band broadening was the sole source of dispersion and instrumental side-effects were negligible. It is deduced from general theory that a HF5 system performs optimally with long fibers (to reduce side effects) with a small inner diameter.

In Chapter 4, the diffusional behaviour of a model polyelectrolyte, polystyrene(sulfonate), is studied with a home-built HF5 system. The (apparent) diffusion coefficient of four polystyrenesulfonate standards is measured at varying injected mass and at different ionic strengths of the carrier liquid. A sharp increase of the apparent diffusion coefficient above a certain critical concentration of the polyelectrolyte at the accumulation wall is witnessed. The dependence of this critical concentration on the ionic strength is following the trend predicted by a model based on Debije-Landau-Verwey-Overbeek theory, that describes the repulsion of hard, incompressible spheres. Also, the velocity of overloaded zones is following the theoretical predictions for hard spheres. Results from standards with a molar mass of above ca. 100 kDa deviate from the model, which may be caused by intermolecular interactions.
In Chapter 5, asymmetrical flow FFF-MALS is applied for the characterisation of several polymethylmethacrylate core-shell latices. Hydroxylated core-shell latices appeared to be unaffected by a varying pH. The carboxylated core-shells displayed strong swelling with increasing pH in the range from 5 to 10. By contrast, a much milder increase of the root-mean-square (r.m.s.) radius was observed with MALS detection, which indicates that the scattering plane is moving relatively inwards during the swelling process due to a decreasing density of the outer shell. From the comparison of the swelling of two carboxylated core-shells under varying ionic strengths with a Donnan model, it appeared that a significant amount of counter-ion condensation takes place in the shells.

In Chapter 6, the retention mechanism of four different amylopectins in asymmetrical flow FFF is studied with MALS detection. Amylopectins were dissolved under mild conditions, in a 1 mol l\(^{-1}\) sodium hydroxide solution. With an injected mass below overloading conditions, the apparent hydrodynamic radius was observed to decrease with increasing inlet flow rate. In addition, the root-mean-square radius trace measured with MALS decreased with the retention time, in contrast to the retention order in normal mode. This anomalous retention behaviour points towards the occurrence of steric/hyperlayer effects. However, combination of MALS data with the retention showed that the amylopectins behave as macromolecules with a considerably larger hydrodynamic radius than expected on basis of the radius of gyration.