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Experimental study on the separation of silica gel supports by gravitational field-flow fractionation

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ABSTRACT

The separation and characterization of silica gel particles were investigated by gravitational (1 g) field-flow fractionation. The experiments were performed in a ribbon-like glass-walled channel with a photometric (turbidimetric) detector. Solutions of several surfactants were tested as carrier liquids. Factors affecting the separation process are discussed and the deductions are compared with experimental results. Some aspects concerning the activity of lift forces were confirmed.

INTRODUCTION

The separation and characterization of particles are of great importance for particular products, *e.g.*, silica gel supports for chromatographic columns, where the size distribution, density, porosity, etc., are basic parameters of the support. In order to determine the parameters, chemical methods (chemical affinity) cannot be used, and therefore other methods based on physical principles have to be employed. The determination of support characteristics is commonly performed by expensive and/or slow procedures (*e.g.*, evaluation of photomicrographs, laser optical methods, adsorption analysis). A solution may lie in methods based on hydrodynamic forces which appear intrinsically in shear flows with solid particles. An advantage of this approach is the simple experimental arrangement because the flow works simultaneously as a carrier medium.

Employing the Earth's gravity as the external field, gravitational field-flow fractionation (GFFF) is such a technique, suitable for the separation and/or characterization of particles because the peak dispersion of the fractograms

corresponds to the size distribution of the particles. The technique is effective only for micrometre-sized particles owing to the relatively weak field strength (1 g). GFFF has been used for the separation and characterization of various particulate materials, *e.g.*, glass and latex beads [1–4]. Giddings *et al.* [5] made an attempt to characterize silica gel supports by GFFF but their results were not very satisfactory even after using calibration beads because their calculations were based on a simple steric model without the activity of lift forces that evidently acted there. On the other hand, these forces were utilized by Ratanathanawongs and Giddings [6], who reported a rapid method to characterize silica gel particles by flow/hyperlayer FFF. Giddings and co-workers [7,8] worked out a complete methodology to determine the size distribution, density and porosity of silica gel supports by combining sedimentation FFF (SdFFF) with electron microscopy.

Some effects that play an important role in the separation process have been studied by FFF. Beckett *et al.* [9] were able to detect the adsorption of proteins on polystyrene latex beads with a coverage of less than a monolayer by SdFFF and Li and Caldwell [10] studied the adsorption of polymeric surfactants on cores of

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polystyrene latex particles also by SdFFF. Jones et al. [11] used SdFFF to separate aggregates from doublets to sextuplets in suspensions of poly(methyl methacrylate) latex particles and Barman and Giddings [12] studied the aggregation of polystyrene and poly(methyl methacrylate) latex particles caused by addition of a cationic surfactant to the suspension of an anionic surfactant by SdFFF. Karaiskakis and Koliadima [13,14] investigated changes in the retention of suspensions of submicrometre metal oxide particles caused by reversible adsorption in a centrifugal steel-walled channel, which were in accordance with their calculations involving Hamaker constants and surface potentials; they suggested a new technique called potential barrier FFF (PBFFF). Pazourek and Chmelík [4] studied the elution of polystyrene latex bead mixtures in different carrier liquids containing surfactants by GFFF.

The aim of this work was to investigate the possibility of the separation and characterization of silica gel supports by GFFF. Although a methodology for silica gel support characterization (by SdFFF) has already been reported [7,8], and silica gel supports have been characterized by flow/hyperlayer FFF [6], we carried out this study with a much simpler experimental arrangement: the apparatus for SdFFF consists of a channel built in a centrifuge rotor and the channel for flow FFF must have a rigid frit (frits) with an ultrafiltration membrane (membranes) which are sensitive to pressure changes and fouling, whereas we used a channel made of two glass plates sandwiching a foil (see Experimental). This paper is the first part of a study leading to the size and density characterization of solid particles by GFFF.

EXPERIMENTAL

The experimental arrangement has been described elsewhere [3,4]. We tested five separation channels; all were made by sandwiching a 40-, 80- or 150-μm foil with a channel-shaped cut (spacer) between two 8-mm thick pieces of glass and clamping the latter together between two Lucite bars. The width of all the channel spacer cuts was 2 cm and the lengths were as follows:

channel I, 36 cm; channel IIb, 80 cm; channel III, 108 cm. The dead volumes were 0.52, 1.20 and 1.57 ml (80-μm spacer), respectively, channel IIa 0.60 ml (40-μm spacer) and channel IIc 2.25 ml (150-μm spacer), respectively. Inlet and outlet steel tubes (0.5 mm I.D.) were glued into holes drilled in the glass plates.

The analysis was performed with an HPP 4001 high-pressure pump (Laboratory Instruments, Prague, Czech Republic) coupled with a UVM 4 spectrophotometric detector (Development Workshops ČSAV, Prague, Czech Republic) operated at 254 nm, or with a Spectra 100 capillary spectrophotometric detector (Spectra-Physics, San Jose, CA, USA) at 200 or 210 nm (Triton X-100). The former detector had a Z-shaped cell with an optical path of 5 mm and the latter had a quartz capillary detection cell of 300 μm I.D. All experiments were performed at 25°C.

The carrier liquids were solutions of Tween 60 (polyoxyethylene sorbitan monostearate) (Fluka, Buchs, Switzerland), Triton X-100 (tert.-octyl phenyl polyoxyethylene ether) (Fluka), solutions of sodium dodecyl sulphate (SDS) (Lachema, Brno, Czech Republic) and benzyldimethylhexadecylammonium chloride (BDHAC) (Fluka), all in distilled water.

The samples were of two types: (i) porous spherical particles (diameters 3, 5 and 10 μm) (Tessek, Prague, Czech Republic) and (ii) nonporous spherical particles 1.43 μm in diameter (a kind gift from Professor E. sz. Kováts). In most of the experiments we used a model mixture of two porous spherical silicas with nominal diameters of 10 and 5 μm (Tessek) with non-porous silica gel particles with the diameter 1.43 μm. The concentration of each type of particle in the mixture was 10 mg/ml.

The experiment consisted of several steps. Initially, after 3 min of ultrasound stirring, 2–6 μl of sample were injected, with a syringe, through a septum into the channel inlet. After the relaxation time, the flow was switched on and the sample was eluted through the channel to the detector. The relaxation time was calculated (for porous and non-porous particles $\Delta\rho$ = 0.5 and 1.2 g/cm^3), respectively, as

$$t_R = 18 \frac{\mu w}{d^2 \Delta\rho g} \qquad (1)$$

where μ is viscosity of the carrier liquid, w is the channel width, d is the particle diameter, $\Delta\rho$ is the density difference between the particle and the liquid and g is the gravitational acceleration constant (9.8 m/s^2).

RESULTS AND DISCUSSION

One factor affecting the separation process in the channel is the smoothness and inertness of the channel walls. An uneven wall surface can mechanically disturb the flow which, together with adsorption on the channel bottom, can cause retardation of the particles and artificial dispersion of the peaks. The adsorption was a more important factor because of the relaxation process performed: in order to force the particles to start from the channel bottom, after injection of a sample the flow was stopped for a sufficient time to allow the particles to sediment through the channel width w. We tested unmodified glass plates which are almost perfectly smooth but particles in the vicinity of the glass could be adsorbed on the surface. According to conclusions of Bories et al. [15], we deduced that the surfactant in the carrier medium covers the channel wall faster and more stably when the glass is modified. We observed that the unmodified glass plates needed about 1 day to condition whereas silicone oil-modified glass plates gave reproducible results earlier. As deduced from the higher retention ratios and sharper peaks, the best results were obtained using glass plates modified with MS200 silicone oil (Midland Silicones, Barry, UK). This was similar to our observations on the separation of polystyrene latex particles by GFFF [4].

Surfactants are added to the carrier medium to reduce the surface tension that exists between the solid surface of the particles and the carrier liquid, between the particles and the channel walls and between the channel walls and the carrier liquid. We tested solutions of surfactants in the concentration range 0.0005–0.5% because at lower concentrations we did not detect retained peaks and at higher concentrations the solutions were too opaque. The surfactants used were cationic (BDHAC), anionic [SDS, critical micellar concentration (CMC) = 0.24%] and two

non-ionic (Tween 60, CMC = 0.005%; Triton X-100, CMC = 0.013%), so in some instances we used surfactants above the CMC. The separation channel then represented a complicated multiphase system [16]. We observed that an increase in surfactant concentration resulted in a slight increase in the retention ratios but in a significant decrease in peak dispersion. We explained this by a decrease in adsorption on the channel walls. Fig. 1 shows the dependence of retention times and peak dispersions on surfactant concentration. It is obvious that the smallest particles (1.43 μm) are mostly affected in this way, probably as they move closer to the channel bottom. The simultaneous increase in density of the surfactant solutions which led to an increase in the buoyant force on the particles was negligible (less than 0.1% for a 0.5% solution of Tween 60).

On the other hand, the retention ratio can be increased by adsorption of a surfactant on the particle surface (a decrease in apparent density and an increase in hydrodynamic size [10]) or by aggregation of the particles. This would explain our observation that small particles (about 3 μm)
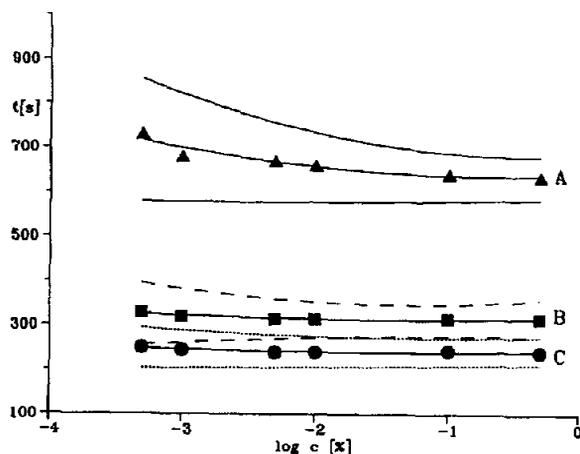

Fig. 1. Dependence of retention times on concentration of Tween 60 in the carrier liquid. In each instance the central curve with symbols shows the retention time of the peak mass centre, and the two lines above and below define the time width of the peak base. The top three curves A (▲) are for 1.43-μm particles, the middle three curves B (■) for 5-μm particles and the bottom three curves C (●) for 10-μm particles. Data were obtained with the model mixture in channel III at a flow-rate of 0.96 ml/min; 2 μl of suspension were injected.

exhibited at low flow-rates the same retention ratio as 10-μm particles. We tried to confirm the presumed aggregation by optical microscopy, trapping a drop of the eluted liquid on a microscope slide, but unfortunately we were not able to distinguish between the primary aggregation in the channel and the secondary aggregation at the liquid drop/air interface.

Pores of the particles influence the apparent density. The porosity of silica gel supports can decrease the apparent density down to 1.5 g/cm^3 [8]. Moreover, the particles can contain gas bubbles not released even after a 6-h sonication [8]. Another consequence of the particle porosity relating to interfacial effects could be higher sensitivity of the porous particles to changes in experimental conditions with respect to the type
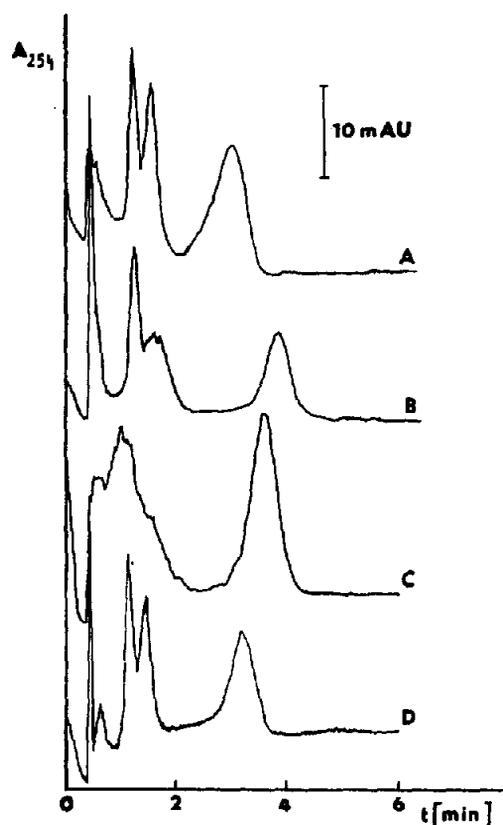
and concentration of surfactants used. We observed different retention ratios of the same sample in different surfactants, which can be explained by different physico-chemical interactions between the particle surface and the carrier liquid. The surfactant influences the particle-wall interaction (adsorption) and particle-particle interaction (aggregation). We deduced that the former effect results in a shift of the retention ratio (the lower the retention ratio the more intensive is the adsorption) and the latter affects resolution (the poorer the resolution the more intensive is the particle-particle interaction). This is illustrated in Fig. 2, which compares four fractograms obtained in different carrier liquids. The first sharp peak (its left-hand edge retention ratio is 1.5) corresponds to light fragments or microbubbles, the second (clear in D, overlapped with the first in A–C) is the dead volume peak [3]. Based on these observations, we chose 0.1% Tween 60 solution as the best carrier liquid, (Fig. 2A).

Fig. 3 compares fractograms obtained under optimized conditions (the carrier liquid is a 0.1% solution of Tween 60 and the channel bottom is modified with MS200 silicone oil) at different flow-rates in channel III. There is an increase in the retention ratio with increasing flow-rate for all three sizes of particles in the mixture. This is
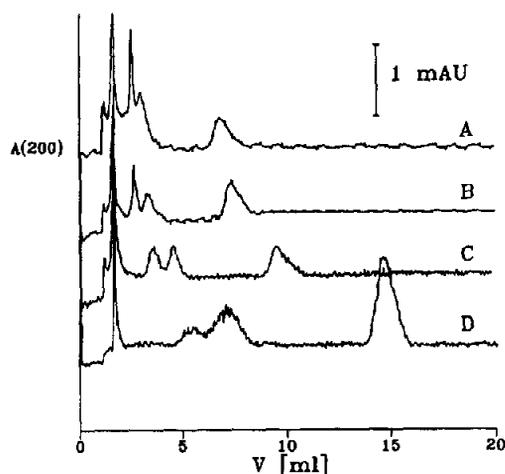

Fig. 2. Comparison of fractogram of the model mixture of silica gel particles (10, 5 and 1.43 μm) in different surfactants (0.1% solutions): (A) Tween 60; (B) SDS; (C) BDHAC; (D) Triton X100. The flow-rate was 0.95 ml/min and 1 μl of the model mixture suspension was injected into channel I.

Fig. 3. Fractograms of the model silica mixture at different flow-rates: (A) 2.87; (B) 1.94; (C) 0.96; (D) 0.212 ml/min. A 4-μl volume of the suspension was injected into channel III.
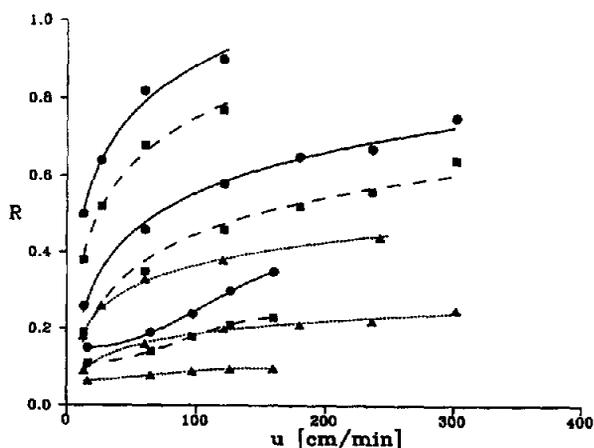
Fig. 4. Dependence of retention ratio R on linear flow velocity u in channels with different heights w (length $l = 80$ cm). Solid lines are for channel IIa ($w = 40$ μm, 0.5 μl injected), dashed lines for channel IIb ($w = 80$ μm, 1 μl injected) and dotted lines for channel IIc ($w = 150$ μm, 2 μl injected). Particle size in the model mixture: $\bullet = 10$ μm; $\blacksquare = 5$ μm; $\blacktriangle = 1.43$ μm. The carrier liquid was a 0.1% solution of Tween 60.

Fig. 5. Dependence of retention ratio R on linear flow velocity u in channels with different lengths l (height $w = 80$ μm). Solid lines (with closed symbols) are for channel I ($l = 36$ cm, 0.5 μl of suspension injected), dotted lines (with open symbols) for channel II ($l = 80$ cm, 1 μl injected) and dashed lines (with half-closed symbols) for channel III ($l = 108$ cm, 2 μL injected). The three curves A (circles) represent silica gel particles of nominal diameter 10 μm in the model mixture, B (squares) those of nominal diameter 5 μm and C (triangles) those of diameter 1.43 μm.

in accordance with the activity of lift forces and a similar increase was observed with all kinds of supports tested. Moreover, the retention ratios increased with a decrease in the channel width w.

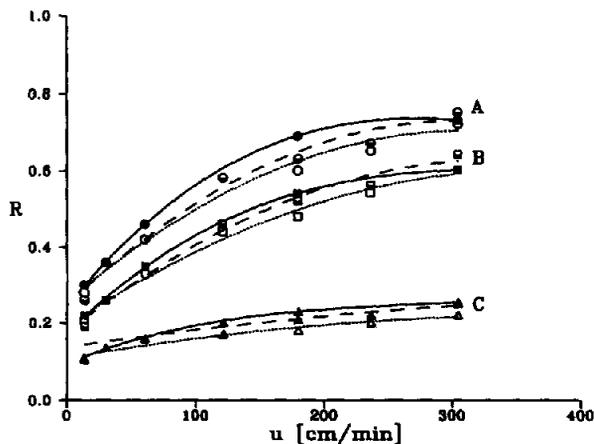Fig. 4 shows the dependences of the retention

ratio on the linear velocity for three different channel widths w. One can see that the smallest retention ratios were obtained in the channel with the highest w (150 μm).
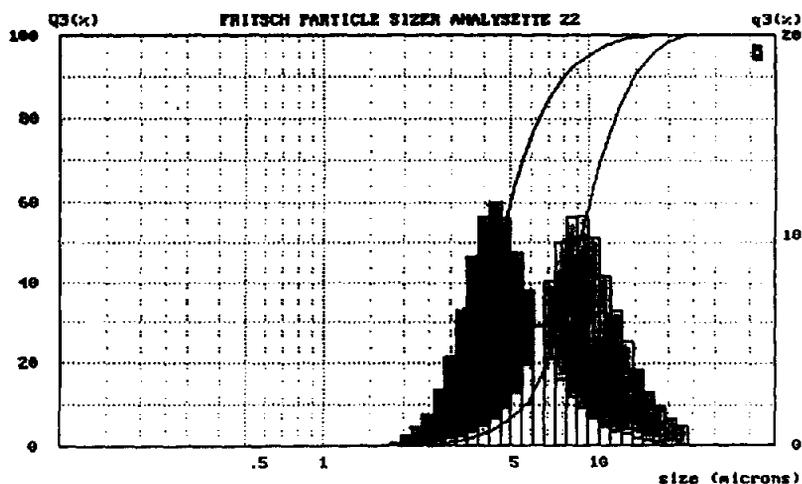

Fig. 6. Size distribution curves of silica gel particles of nominal diameters 5 and 10 μm (in the model mixture) measured on a Fritsch Analysette 22 particle sizer. The black histogram holds for the 5-μm silica and the grey histogram for the 10-μm particles in the model mixture. To distinguish the two histograms, their common part is shown in white. The histograms were obtained separately (not from a mixture) and were overlapped graphically.

Fig. 5 demonstrates that the lift forces acted very rapidly as the retention ratios were almost identical in channels I–III with lengths of 36, 80 and 108 cm, respectively. The plateau on the curves is in qualitative agreement with the lift force function [4].

The peaks in all the fractograms are relatively broad because their dispersions correspond to the size distributions which are relatively broad for silica gel particles (20–50%) compared with, e.g., standard latex particles (usually <2%). This is illustrated in Fig. 6 by two overlapped size distribution histograms of samples that we tested. The histograms were obtained separately by light-scattering measurements on a Fritsch (Idar-Oberstein, Germany) Analysette 22 particle sizer. There is a broad distribution of the two silica gel particles used, which prevent complete separation and also the total resolution of GFFF peaks in fractograms.

CONCLUSIONS

The separation process is influenced by the quality of the channel wall surface and by the quality and concentration of the surfactant used. Under particular experimental conditions, GFFF enables a mixture of silica gel particles to be separated. The GFFF technique is performed with an extremely simple experimental arrangement, in contrast to other FFF techniques (flow FFF, SdFFF). The channel height w is a natural parameter of the separation defining the particle sizes that can be effectively separated.

With respect to the separation mechanism we can conclude that the lift forces drive particles in the vertical equilibrium position δ_F very quickly.

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