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Rapid Separation of Micron-Sized Particles by Field-Flow Fractionation Using Earth's Gravitational Field

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ABSTRACT

This paper presents the rapid separation of latex particles of diameters 5–20 μm in a simple arrangement of the separation channel. Lift forces, which play an important role in the process, drive particles very quickly from the channel bottom, and they cause a decrease in retention times at first and then a deterioration of resolution when the flow rate increases. The magnitude of the lift forces depends on the flow rate and particle size among others. Several published observations concerning the lift forces are mentioned, and several suggested formulas for these forces are presented. Our experimental data are compared to the lift forces function which seems to be the most relevant: the function suggested by Vasseur and Cox and simplified by Kononenko and Shimkus that originates in inertial effects of the flow. The consequences of such a separation mechanism are discussed with respect to the limitations and advantages of lift forces activity.

INTRODUCTION

The separation of particles is increasingly important among physicochemical separation techniques. For instance, a large number of biological applications require separation of living cells. Many particulate environmental samples and technological products are to be characterized. The chemical affinity cannot be employed in many cases of micron-sized particles, and therefore other separation methods based on physical interactions have to be used.

Field-flow fractionation (FFF) is an analytical method suitable for particle separation (1). It is based on simultaneous actions of physical field

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forces and of the flow velocity profile of a carrier liquid passing through a separation channel. The flow nonuniformity is caused by the viscosity effect and a channel cross-section. The physical field or fields usually act perpendicularly to the flow and can produce three different separation modes: 1) normal mode when the external field forms an exponential concentration distribution of a sample, 2) focusing [hyperlayer (2)] mode when an added physical force acting in the opposite direction to the primary field focuses a solute in a layer with quasi-Gaussian concentration distribution, and 3) steric mode when the external force is so great that all sample particles are compressed on one of the channel walls (the accumulation wall).

Separation and/or characterization of particles can be effectively carried out by FFF. By employing the sedimentation effect, both centrifugal and gravitational (1 *g*) fields can be used. The latter technique, gravitational FFF, has been described theoretically and tested experimentally. Giddings and Myers (3) showed the feasibility of separation of micron-sized glass beads by using the Earth's gravitational field. The same method was used for characterization of silica bead supports. This methodology as a tool for their characterization was recommended (4). However, calibration was necessary because the dependence of the retention ratio on the flow rate exhibited a significant nonlinearity at higher flow rates. Caldwell et al. (5) reported the separation of silica gel particles and latex beads of the same diameters due to the high retention ratios of the latex beads. The cause of such an anomalous behavior of latex particles was assigned to the lift forces. Although the lift forces have not been quantitatively well characterized, gravitational FFF was also used to characterize residues from coal (6) or fine coal particles (7). Cardot et al. (8) recently examined retention of red blood cells under similar conditions. The use of equations deduced for the ideal steric FFF process for the determination of particle diameter did not yield satisfactory results. Therefore, Peterson et al. (9) verified a semiempirical function describing the dependence of the retention ratio on the radius of a particle in order to bridge the lift forces troubles and to create a direct calibration curve formula. Kononenko and Shimkus (10) studied the lift forces in a channel with integral Doppler anemometry detection.

Lift forces can be either employed or suppressed in order to achieve particle separation. Ratanathanawongs and Giddings (11) employed lift at higher flow rates in flow/hyperlayer FFF for faster separation combining the cross-flow field with the lift forces orientated in the opposite direction. On the other hand, a possible way to reduce the effect of the lift forces is an increase in the size of a physical field. Giddings et al. (12) and Chen et al. (13) achieved separation using a cross-flow field that pressed particles toward a porous accumulation wall. An increase in the centrifugal field can also be utilized. Using this, Koch and Giddings (14) separated particles with diameters >1 μm and Caldwell et al. (15) separated red blood cells. Giddings et al. (16) eliminated the influence of the lift forces on calibration by using a centrifugal force that pressed calibration particles of lower density more strongly toward the channel bottom so that the density differences were compensated. To characterize the lift forces, Williams et al. (17) investigated the retention of latex particles in a centrifuge and suggested a semiempirical formula for a near-wall lift force on the basis of lubrication phenomena.

Generally, the lift forces (the tubular pinch effect or sigma effect) drive particles laterally to the streamline direction and thus cause the anomalous retention ratios. These hydrodynamic forces were first examined in 1922 when Jeffery (18) published his paper concerning small ellipsoidal particle behavior under shear flow. The rheological properties of suspensions have been investigated by many workers, unfortunately with both controversial observations and conclusions (19–28). For a review, see Ref. 29.

The goal of this paper is to present a possibility for the simple and fast separation of micron-sized particles by FFF using the Earth's gravitational field and to explain our observations on the lift forces equation published by Kononenko and Shimkus (10).

THEORY

In dealing with the separation and/or the characterization of particles in FFF, the first important characteristic of the process is the transition point where the diffusive motion of the particles is comparable to that caused by the physical field used. This border between Brownian and sedimentation behavior can be derived from trivial equations. The critical diameter of the particle can be obtained as a function of the density difference between the carrier liquid and the particle:

$$d_{crit} = \sqrt[4]{12kT/\pi g \Delta\rho} \tag{1}$$

where k is Boltzmann's constant, T is the thermodynamic temperature, g is the gravitational acceleration constant, and $\Delta\rho$ is the difference between the density of the particle and that of the carrier liquid.

Expressions for the lift forces usually come from a solution of the Navier–Stokes equations. Authors usually started at the general form (symbolically):

$$\mu \cdot \nabla^2 \mathbf{u} - \nabla p = \rho(\mathbf{u} \cdot \nabla \mathbf{u}) \tag{2}$$

which holds together with the equation of continuity $\nabla \cdot \mathbf{u} = 0$ and boundary conditions: $\mathbf{u} = \omega \times r$ on the sphere surface and $\mathbf{u} = 0$ at infinity. $\mathbf{u}$, p, μ, and ρ denote, respectively, vector of the linear velocity, pressure, viscosity, and density of the liquid; and ω is the angular velocity of the particle with radius r (the origin of a coordinate system is in the center of the particle).

Saffman (30) reported that an explanation of the lateral migration of spheres in shear flow cannot be based on a solution of the Navier–Stokes equations without the inertia term (the right-hand side of Eq. 2). As a consequence of this term, he found an expression for a constant lateral velocity driving spheres in the direction of the smaller velocity gradient. If we use the simple Stokes resistance formula $F = 6\pi\eta\rho v$, the magnitude of the lift forces can be expressed by

$$F = 93\pi\rho u^2\alpha^5 w^2 \tag{3}$$

which is valid provided that $\alpha \ll 1$. Here u is the mean linear velocity of the flow, and α is defined as r/w (r is the particle radius and w is the channel height).

Later, Saffman (31, 32) presented an equation for the lift forces in a uniform simple shear of unbounded flow (or shear with a small curvature) derived when the Reynolds number of the sphere is $\ll 1$ and the Reynolds number of the tube is $\gg 1$ ($\delta \leq 0.5$):

$$F = 15.82\alpha^2 V\sqrt{(1 - 2\delta)\mu\rho u w^3} \tag{4}$$

where V is the difference in velocity between the center of the particle and the streamline at this point, and δ is the dimensionless distance of the particle center from the channel bottom.

Rubinow and Keller (33) solved the Navier–Stokes equations with the inertial term and obtained a formula that can be written for small values of the Reynolds numbers and an unbounded nonshear flow as

$$F = 3\pi V r^3 \rho u(1 - 2\delta)/w \tag{5}$$

Williams et al. (17) made many experiments in a centrifugal channel. On the basis that the particles lag the flow in the vicinity of the walls, they (34) presented the following equation for a near-wall lift force:

$$F = 1.72 \times 10^{-6}\, r^3 \mu s_0/h \tag{6}$$

where s_0 is the undisturbed shear rate at the channel wall, and h is the distance of closest approach of the sphere to the wall $\delta w - \alpha w$.

The most important fact following from Eqs. (3)–(6) is that the functions exhibit only one focusing point in the tube axis (in the channel half-height, respectively), presuming that V (function of δ) does not alter its sign.

On the other hand, there are solutions of the Navier–Stokes equations with the inertial term that are in accordance with the Segre–Silberberg effect where spheres flowing under shear in a tube are concentrated in an annular region. For example, Ho and Leal (35) found that

$$F = 36\rho u^2\alpha^4 w^2[(1 - 2\delta)^2\Delta_1 - (1 - 2\delta)\Delta_2] \quad (7)$$

where Δ_1 and Δ_2 are tabled functions of δ.

Cox and Brenner (36) also solved the Navier–Stokes equations with great generality, and an explicit interpretation of their results was intro-

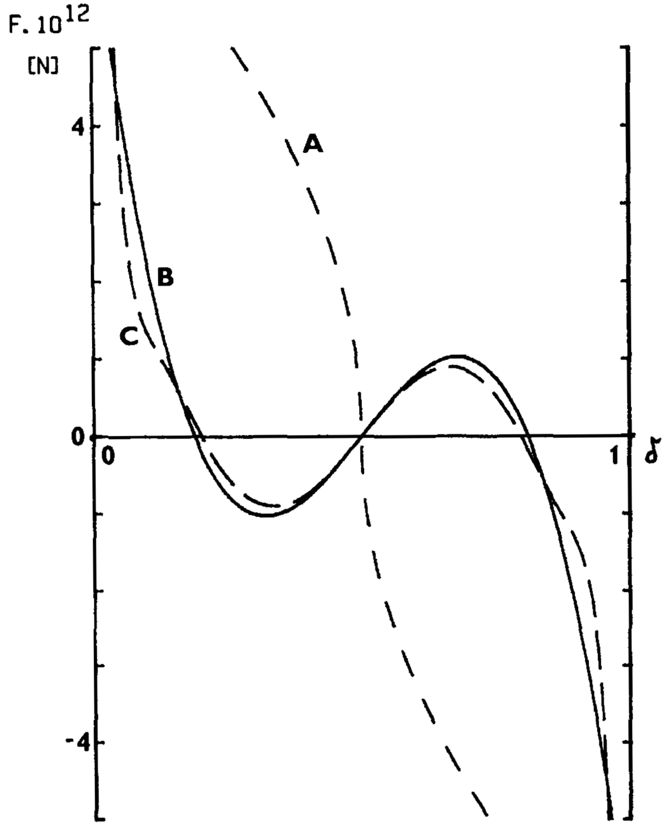

FIG. 1 Graphs of Eqs. (4), (8), and (7) as functions of δ (Curves A, B, and C, respectively). In the case of Eq. (4) (Curve A), we substituted an approximate expression $\frac{4}{3}u\alpha^2$ (38) for V in order to show the focusing point of Eqs. (3)–(6) at $\delta = 0.5$ clearly. Parameters were selected to correspond to our experimental conditions: $u = 50$ cm/min, $r = 10$ μm, $w = 80$ μm, $\rho = 0.998$ g/cm^3.

TABLE 1
Comparison of Particle Archimedes Weights with Calculated Functional Values of Lift Forces[a]

d (μm)	G (N)	F_1 (N)	F_2 (N)	F_3 (N)
5	3.5e−14	3.9e−15	2.0e−14	2.9e−14
7	9.7e−14	2.1e−14	6.9e−14	7.3e−14
10	2.8e−13	1.2e−13	2.3e−13	1.6e−13
20	2.3e−12	4.0e−12	1.5e−12	1.0e−12

[a] d = nominal diameter. $G = \pi d^3 g \Delta\rho/6$. F_1 was calculated according to Eq. (3) (Ref. 30). F_2 was calculated according to Eq. (8) (Ref. 10). F_3 was calculated according to Eq. (7) (Ref. 35). The functional values are calculated for $\delta = \alpha$ (the position of a sphere on the channel bottom). Selected values: w = 80 μm, ρ = 0.998 g/cm^3, $\Delta\rho$ = 0.055 g/cm^3, u = 50 cm/min, g = 9.80665 m/s^2.

duced by Vasseur and Cox (37). A simplification of this formula was presented by Kononenko and Shimkus (10):

$$F = -81/4\pi\rho u^2\alpha^4 w^2(1 - 2\delta)[k^2 - (1 - 2\delta)^2]/(1 - k^2) \qquad (8)$$

where $k = 0.62$.

We rewrote all these expressions in accordance with our notation and applied them to the horizontal Poiseuille flow between two planes. Keeping in mind the conditional validity of some of these equations, we can at least compare the courses of them (number of focusing points) and the order of those expressions to the Archimedes weights of particles (see Table 1). The curves of Eqs. (4), (7), and (8) are displayed in Fig. 1.

EXPERIMENTAL

A schematic representation of the experimental arrangement is shown in Fig. 2.

The samples were styrene–divinylbenzene copolymer particles made by Seradyn, Inc. (Indianapolis, Indiana, USA) with nominal diameters of 2, 5, 10, and 20 μm and by Dow Diagnostic (Indianapolis, Indiana, USA) with a diameter of 7 μm. The density of all the latex particles (1.055 g/cm^3) was checked in our laboratory by the standard procedure in the gradient medium Percoll (Pharmacia AB, Uppsala, Sweden). This density was used not only because of the ideal spherical shape of the latexes but also because this density is comparable to the density of biological macromolecules that we plan to separate in the near future. Silica gel beads of 5 and 10 μm diameters (Tessek, Prague, Czechoslovakia) with

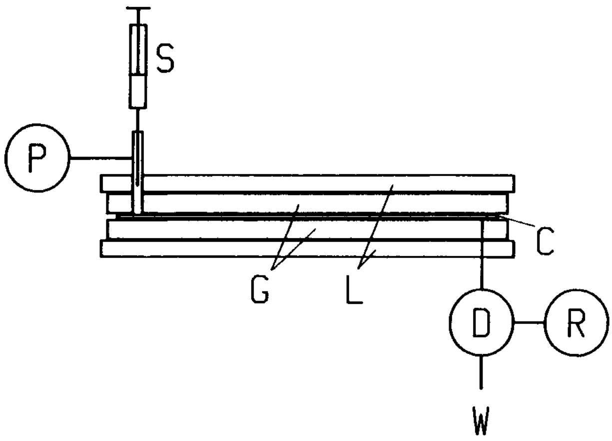

FIG. 2 Schematic representation of the experimental arrangement. P is the pump, S is the syringe that injects through the inlet capillary into the channel, L is the Lucite blocks, G is the two glass plates gripping the channel spacer C, D is the detector, R is the recorder, and W indicates the waste.

densities of about 2.2 g/cm^3 were also used in order to examine the influence of the particle density on retention. All the samples were of about 0.1% concentration. Before injection, each sample was stirred by ultrasound for about 30 seconds in order to destroy any contingent aggregates.

Two separation channels were constructed, both by sandwiching a 80-μm celluloid spacer between two 8-mm thick pieces of glass and clamping them together between two Lucite bars 2-cm thick. The dimensions of the spacer of Channel I were 20 mm × 1157 mm and gave a channel volume of 1.80 mL. Channel II had dimensions of 20 mm × 360 mm and a volume of 0.52 mL. Inlet and outlet steel tubes were glued into drilled holes in the glass plates. For Channel I they were of inner diameter 1.0 mm and were used to carry out direct injection of samples by a syringe through a septum into the inlet tube. Both capillaries of Channel II had an inner diameter of 0.5 mm. The carrier liquid was a 0.1% solution of Tween 60 (Fluka AG, Buchs) in distilled water. The pump was an HPP 4001 high pressure pump (Laboratory Instruments, Prague, Czechoslovakia). A UVM 4 spectrophotometric detector (Development Workshops ČSAV, Prague, Czechoslovakia) was used at 254 nm. All experiments were made at 20°C, and the flow rate was controlled by a flowmeter.

Because the injection did not place the particles directly on the channel bottom and we wanted them to start from there, we had to wait till all the particles in the sample sedimented through the channel height distance before the flow was switched on. This relaxation time was usually 3 minutes (except for experiments with 2-μm latex particles). The experiment consisted of several stages. First, after the ultrasound stirring, 10–25 μL of a sample was placed in a syringe and injected 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.

RESULTS AND DISCUSSION

Equation (1) yields a critical diameter (d_{crit}) value of 2.32 μm according to the density differences between latex particles and the carrier medium. It is shown in Fig. 3 that the fractogram of latex particles with a smaller diameter (2 μm) exhibits an extremely broad peak which does not correspond to the size and size distribution guaranteed by the producer (σ_{rel} < 3%). In order to avoid the problems due to Brownian motion, and thus

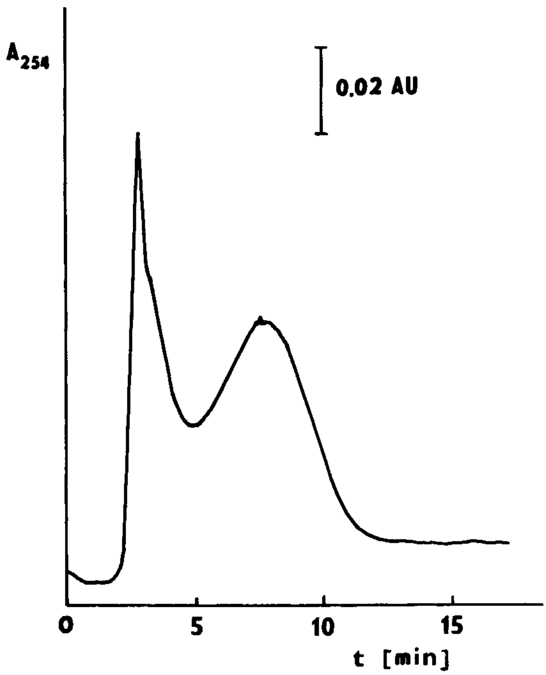

FIG. 3 Fractogram of latex particles of 2 μm diameter in Channel II. Experimental conditions: relaxation time t_r = 15 minutes, flow rate Q = 205 μL/min.

due to a different separation mechanism, in all the following experiments we used polystyrene latexes in the 5–20 μm diameter range.

As mentioned in the theoretical section, the lift forces play a crucial role in the following experiments performed in an FFF channel. The functional values of the three lift forces equations are compared in Table 1. It can be seen that only one functional value of F_1 (Eq. 3) exceeds the particle Archimedes weight. However, Eqs. (3)–(6) exhibit only one focusing point in the channel half-height ($\delta = 0.5$) (cf. Curve A in Fig. 1), and our experimental results (presented below) prove that another focusing point exists. These observations are in agreement with the curves of Eqs. (7) and (8), respectively, drawn in Fig. 1 (Curves B and C), and the proper functional values (F_2 and F_3) are of the same order as the Archimedes weight G. Equation (8) is presented in a simpler mathematical form than Eq. (7). Therefore, Eq. (8) (Curve B) was considered to be the most useful equation for our purposes.

On Curve B (see Fig. 1) there are three points between the channel walls where the lift forces are zero: in the channel center ($\delta = 0.5$), at $\delta = 0.19$, and at $\delta = 0.81$. Consequently, it is to be expected that the particles influenced only by the lift forces (very light particles) during elution are concentrated in these positions and thus exhibit retention ratios of 1.5 (for $\delta = 0.5$) and ~1 (for $\delta = 0.19$ and 0.81), respectively. (The positions $\delta = 0.19$ and $\delta = 0.81$ are not resolvable because of the symmetry of the carrier velocity profile.) However, in the usual arrangement of an FFF channel, the Archimedes weight of particles acts, and the resulting retention ratio is smaller than 1 when the particles start from the channel bottom. All these considerations are reflected in Fig. 4. Fractogram A shows a typical result of the fractionation of silica gel particles dissolved in the carrier liquid. There are three peaks in this fractogram: The left edge of the first one corresponds to the retention ratio 1.5 and indicates particles with a similar density as the carrier liquid, e.g., particular light fragments or microbubbles which can stay in the meta-stable position ($\delta = 0.5$). The second peak (the dead volume peak with a retention ratio equal to 1) can also contain low molecular weight additives which cannot be in the first peak. The third peak represents the retained silica gel particles (the retention ratio < 1). Fractogram B was obtained after two decantations of the original sample. It is apparent that the amount of both low density particles and low molecular weight additives decreased because of the sample preparation procedure. The compounds removed in the supernatant are shown in Fractogram C. A similar pattern of peaks can be seen in Figs. 5 and 7, respectively, as the first two peaks. However, in the case of latex particles, the dead volume peak is usually much

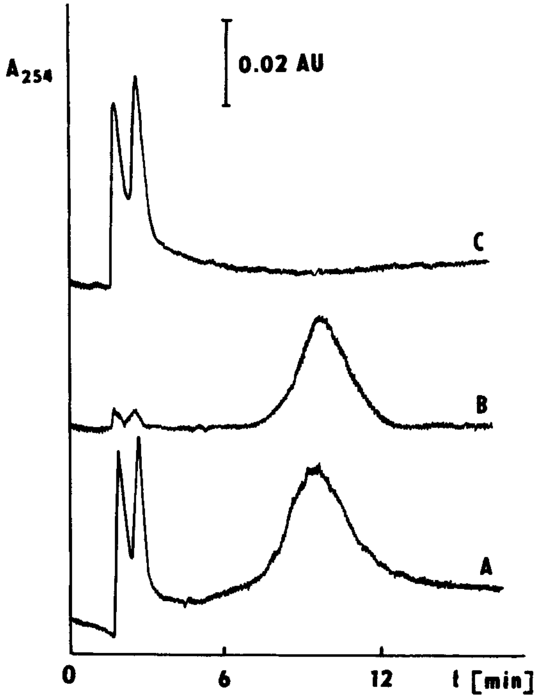

FIG. 4 Fractograms of 10-μm silica bead samples obtained in Channel II. Fractogram A shows the characterization of the original sample in 0.1% Tween 60 solution. Fractogram B shows the characterization od the sample after two decantations. The experiment with the supernatant from the sedimented sample yields Fractogram C. Experimental condition: Q = 210 μL/min, t_r = 20 seconds.

broader and the small peak with the retention ratio of 1.5 can be overlapped.

It follows from the lift forces function (Eq. 8) that an increase of the flow rate evokes an increase in the magnitude of the lift forces and thus the particles drift up. The lift forces activity is displayed by an increase of the retention ratios. This effect is clearly shown in Fig. 5. At low flow rates (Fractograms A), the peaks of the four different-sized latex samples are almost baseline separated while at high flow rates (Fractograms C) this good resolution is almost lost.

The dependence of the retention ratio on the flow rate is illustrated in Fig. 6. In the case of latex particles, there is a plateau at the beginning of the curves (A–D). The two curves for silica gels (E, F) do not exhibit any plateau; they have an almost linear course with a smaller slope within

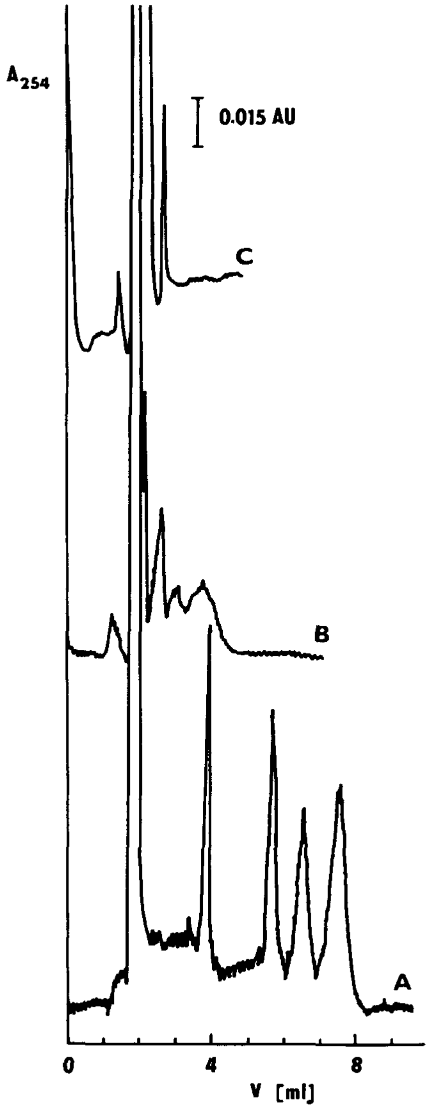

FIG. 5 The influence of a flow rate increase on the resolution of the separation of latex particles with diameters of 20, 10, 7, and 5 μm in Channel I. Fractogram A was obtained at Q = 200 μL/min, Fractogram B at Q = 1000 μL/min, and C at Q = 3000 μL/min, t_r = 3 minutes.

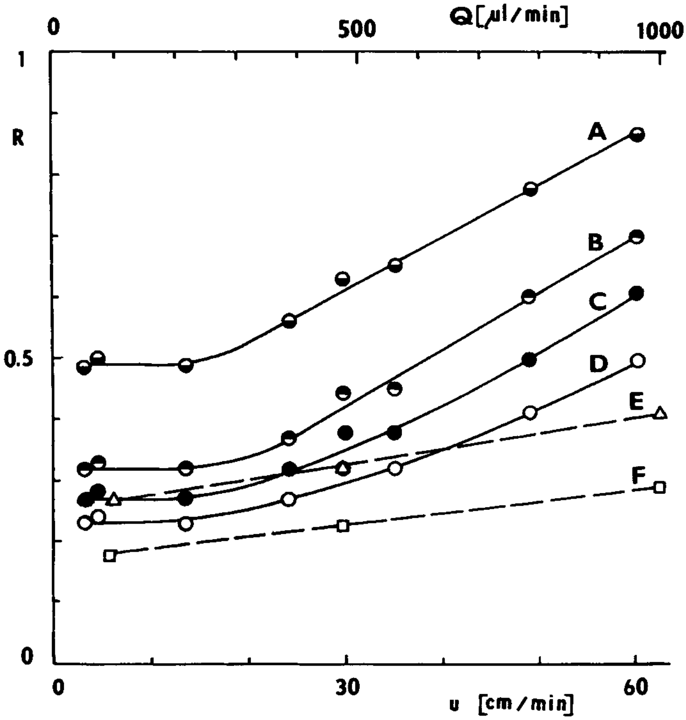

FIG. 6 The dependence of the retention ratio on the linear velocity u and the flow rate Q. The full-line Curves A, B, C, and D apply for latex particles with diameters of 20, 10, 7, and 5 μm, respectively. The dashed Curves E and F show the analogous dependence for the silica gel particles with nominal diameters of 10 and 5 μm, respectively. t_r = 3 minutes.

our experimental range. All the retention ratios rise at higher flow rates. However, the retention ratios did not increase boundlessly. In our experiments we found a retention ratio limit according to Eq. (8); the retained peak never exhibited a retention ratio > 1. This means that at the highest flow rates the particles reach the same vertical position in the channel, whatever size they have, and the peak resolution is lost. Note that the retention ratios obtained in both channels at the same linear velocities were identical. This means that the lift forces carried particles very quickly from the channel walls.

Figure 7 shows the optimized separation of latexes of 5, 7, 10, and 20 μm in Channel I. The fractograms of the individual samples (A–D), drawn above the fractogram of their mixture (E), prove there was no interaction among the particles and indicate that the larger particles are eluted before

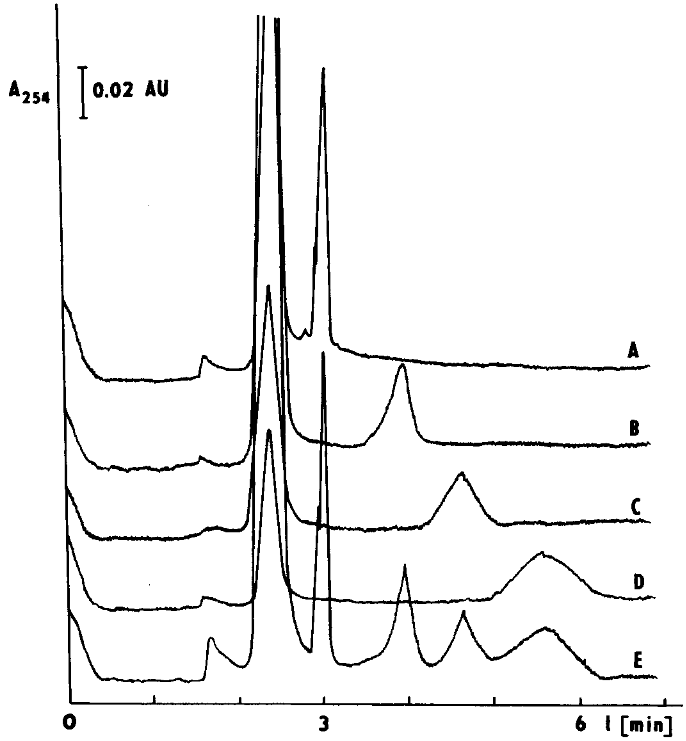

FIG. 7 Characterization of individual latex samples and separation of their mixture in Channel I. Fractograms A, B, C, and D show characterizations of particles with diameters of 20, 10, 7, and 5 μm, respectively. Fractogram E displays the separation of their mixture. Experimental conditions: t_r = 3 minutes, Q = 782 μL/min.

the smaller ones. The small peaks appearing before the dead volume peak had a retention ratio at its left edge equal to 1.5.

CONCLUSIONS

The qualitative agreement of our experimental results with the lift forces function published by Kononenko and Shimkus (10) (Eq. 8) supports the theory explaining the origin of the lift forces in inertial effects of flow. An approach based on this function involves one methodological limitation: At high flow rates there is a retention ratio limit of $R \approx 1$ since particles reach the same vertical position independently on their diameters. Two other natural restrictions are given by the value of d_{crit}, which defines the lower border of particle sizes at the given density because smaller particles are affected by the comparable diffusion. The upper natural limitation is the height of the channel because particles with a diameter $d > 0.21w$ exhibit the retention ratio $R > 1$ given by simple steric exclusion.

The simple arrangement of the channel makes it possible to carry out the separation of micron-sized particles in a few minutes and at low cost. Moreover, this experimental arrangement is promising for further studies of the lift forces. The optimizing of the arrangement and the examination of the separation mechanism will go on.

REFERENCES

1. J. C. Giddings, M. N. Myers, K. D. Caldwell, and S. Fisher, in *Methods of Biochemical Analysis*, Vol. 26 (D. Glick, Ed.), Wiley, New York, 1980, p. 79.
2. J. C. Giddings, *Sep. Sci. Technol.*, *18*, 765 (1983).
3. J. C. Giddings and M. N. Myers, *Ibid.*, *13*, 637 (1978).
4. J. C. Giddings, M. N. Myers, K. D. Caldwell, and J. W. Pav, *J. Chromatogr.*, *185*, 261 (1979).
5. K. D. Caldwell, T. T. Nguyen, M. N. Myers, and J. C. Giddings, *Sep. Sci. Technol.*, *14*, 935 (1979).
6. H. Meng, K. D. Caldwell, and J. C. Giddings, *Fuel Process. Technol.*, *8*, 313 (1984).
7. K. A. Graff, K. D. Caldwell, M. N. Myers, and J. C. Giddings, *Fuel*, *63*, 621 (1984).
8. P. J. P. Cardot, J. Gerota, and M. Martin, *J. Chromatogr.*, *568*, 93 (1991).
9. R. E. Peterson II, M. N. Myers, and J. C. Giddings, *Sep. Sci. Technol.*, *19*, 307 (1984).
10. V. L. Kononenko and J. K. Shimkus, *J. Chromatogr.*, *520*, 271 (1990).
11. S. K. Ratanathanawongs and J. C. Giddings, *Ibid.*, *467*, 341 (1989).
12. J. C. Giddings, X. Chen, K-G. Wahlund, and M. N. Myers, *Anal. Chem.*, *59*, 1957 (1987).
13. X. Chen, K-G. Wahlund, and J. C. Giddings, *Ibid.*, *60*, 362 (1988).
14. T. Koch and J. C. Giddings, *Ibid.*, *58*, 994 (1986).
15. K. D. Caldwell, Z. Q. Cheng, P. Hradecky, and J. C. Giddings, *Cell Biophys.*, *6*, 233 (1984).
16. J. C. Giddings, M. H. Moon, P. S. Williams, and M. N. Myers, *Anal. Chem.*, *63*, 1366 (1991).
17. P. S. Williams, T. Koch, and J. C. Giddings, *Chem. Eng. Commun.*, *111*, 121 (1992).
18. G. B. Jeffery, *Proc. R. Soc. London*, *A101*, 169 (1922).
19. G. I. Taylor, *Ibid.*, *A138*, 41 (1932).
20. H. L. Goldsmith and S. G. Mason, *Nature*, *190*, 1095 (1961).
21. G. Segre and A. Silberberg, *Ibid.*, *189*, 209 (1961).
22. G. Segre and A. Silberberg, *J. Fluid Mech.*, *14*, 136 (1962).
23. H. L. Goldsmith and S. G. Mason, *J. Colloid Sci.*, *17*, 448 (1962).
24. D. R. Oliver, *Nature*, *192*, 1259 (1962).
25. A. Karnis, H. L. Goldsmith, and S. G. Mason, *Ibid.*, *200*, 159 (1963).
26. R. V. Repetti and E. F. Leonard, *Ibid.*, *203*, 1346 (1964).
27. C. D. Denson, E. B. Christiansen, and D. L. Salt, *AIChE J.*, *12*, 589 (1966).
28. J. S. Hallow and G. B. Wills, *Ibid.*, *16*, 281 (1970).
29. H. Brenner, *Adv. Chem. Eng.*, *4*, 287 (1966).
30. P. G. Saffman, *J. Fluid Mech.*, *1*, 540 (1956).

31. P. G. Saffman, *Ibid.*, *22*, 385 (1965).
32. P. G. Saffman, *Ibid.*, *31*, 624 (1968).
33. S. I. Rubinow and J. B. Keller, *Ibid.*, *11*, 447 (1961).
34. A. J. Goldman, R. G. Cox, and H. Brenner, *Chem. Eng. Sci.*, *22*, 653 (1967).
35. B. P. Ho and L. G. Leal, *J. Fluid Mech.*, *65*, 365 (1974).
36. R. G. Cox and H. Brenner, *Chem. Eng. Sci.*, *23*, 147 (1968).
37. P. Vasseur and R. G. Cox, *J. Fluid Mech.*, *78*, 385 (1976).
38. R. Simha, *Kolloid Z.*, *76*, 16 (1936).

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