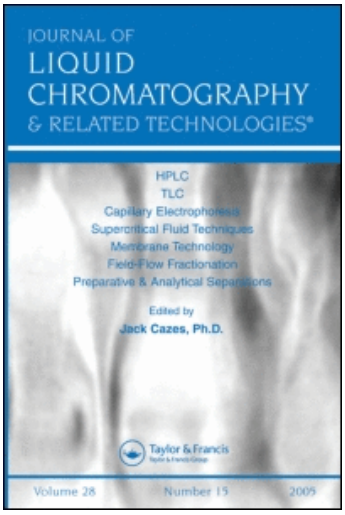

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STUDY OF THE RECOVERY OF COLLOIDAL PARTICLES IN POTENTIAL BARRIER SEDIMENTATION FIELD-FLOW FRACTIONATION

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ABSTRACT

The recovery of particles of the colloidal components subject to separation by the potential barrier sedimentation field-flow fractionation (PBSdFFF) is of great significance in separation science. For the recovery studies in PBSdFFF, monodisperse submicron spherical particles of poly(methyl methacrylate) (PMMA) were used. The extent of the PMMA particles' adhesion and detachment on and from the Hastelloy C channel wall depends on the ionic strength of the suspending medium. The presence of the indifferent electrolyte of $Ba(NO_3)_2$ in the suspending medium, which influences the total potential energy of interaction between the PMMA particles and the channel wall, leads to the partial or total adhesion of the PMMA particles on the channel wall. Finally, the ideal experimental conditions for improving the recovery of the colloidal particles under study in PBSdFFF were investigated.

INTRODUCTION

Potential-barrier sedimentation field-flow fractionation is a new separation method which is based either on particle size differences or on Hamaker constant, surface potential, and Debye-Hückel reciprocal distance differences.[1-9] In

its simplest form, the PBSdFFF technique consists in changing the ionic strength of the carrier solution from a high value, where the attraction between the colloidal particles and the channel wall leads to the total adsorption of the particles at the beginning of the SdFFF channel wall, to a lower value, where the total number of adhered particles is released.

The method has already been applied to the separation and characterization of haematite and titanium dioxide colloidal particles with obvious advantages over the conventional SdFFF technique, such as the possibility of analysing diluted or concentrated colloidal samples even of the same particle size. Necessary presupposition for a good resolution in PBSdFFF is the total recovery of the particles subject to separation. Thus, the recovery studies in PBSdFFF technique should be of great significance in the separation science.

EXPERIMENTAL

The SdFFF system used in this work had the dimensions: $38.25 \times 2.36 \times 0.0174$ cm with a channel void volume of 1.57 cm^3. The outside wall of the channel was bare, polished Hastelloy C alloy, which is principally Ni(56%) with 15% Cr, 17% Mo, 5% Fe, 4% W, and traces of Mn and Si.

The carrier was triply distilled water containing 0.5% (v/v) of detergent FL-70 and 0.02% (w/w) sodium azide as bacteriocide. The electrolyte added to the carrier solution, in order to adjust its ionic strength, was barium nitrate from Riedel-De Haen A. G.

As model samples for the recovery studies in PBSdFFF, monodisperse submicron spherical particles of poly(methyl methacrylate) (PMMA) with nominal diameter of 0.350 μm from Polysciences Inc. were used.

RESULTS AND DISCUSSION

The total potential energy of interaction, *V*, between a spherical particle and the channel wall in PBSdFFF is given by the relation:[2]

$$V = \frac{4}{3}\pi\left(\frac{d}{2}\right)^3 (\rho_s - \rho)\ Gx + 16\varepsilon\frac{d}{2}(kT/e)^2 \tan h(e\psi_1/4kT)$$

$$\tan h(e\psi_2/4kT)\ e^{-\kappa h} - \frac{A}{6}\left[\frac{d(d+2h)}{2h(d+h)} - \ln\left(\frac{d+h}{h}\right)\right] \qquad (1)$$

where *d* is the Stokes particle diameter, ρ_s is the density of the particle, ρ is the density of the solvent, *G* is the sedimentation field strength expressed as

acceleration, x is the coordinate position of the center of particle mass, ε is the dielectric constant of the solvent, e is the electronic charge, ψ_1 and ψ_2 are the surface potentials of the particle and the channel wall, respectively, κ is the reciprocal double-layer ($\kappa^{-1} = BI^{-1/2}$), I is the ionic strength of the suspending medium, A is the effective Hamaker constant, h is the gap width between the planar wall and the closest surface element of the spherical particle, k is Boltzmann's constant and T is the absolute temperature.

The last equation shows that the total potential energy V depends upon a variety of properties of the particle, the suspending medium, and the channel wall, including particle diameter, particle and medium densities, particle and wall surface potentials, temperature, ionic strength, and Hamaker constant. Of the various quantities which affect the V value, none is as accessible to empirical adjustment as I, which depends on both the concentration and the cationic or anionic charge of the indifferent electrolyte added to the carrier solution. When the concentration of the electrolyte exceeds a given value, called critical electrolyte concentration (*CEC*), total adhesion of the colloidal particles occurs at the beginning of the SdFFF channel wall.

While, the addition of indifferent electrolytes to the carrier solution at concentrations lower than the *CEC* value does not influence the retention volume and hence the Stokes diameter of the particles under study in PBSdFFF, the same addition strongly influences the recovery of the colloidal particles, as it is dependent on the interaction energy between the particles and the channel wall (cf. Table 1 and Figure 1). In the present work the recovery, R_i, is measured by the ratio of the area, S_i, of the sample peak eluted from the channel by using as carrier that, with the given electrolyte concentration to the total area, S_{tot}, which is the sum of the area S_i and that corresponding to the peak eluted when the carrier solution is changed to one in which no adhesion occurs and the field strength is reduced to zero.

$$R_i = \text{Recovery} \quad (\%) = \frac{S_i}{S_{tot}} \times 100 = \frac{S_i}{S_i + S_i'} \times 100 \qquad (2)$$

At concentrations higher than the critical electrolyte concentration in which total adhesion of the colloidal particles occurs at the beginning of the SdFFF channel wall, the recovery is zero, as $S_i = 0$. At intermediate electrolyte concentrations, partial adhesion of the particles occurs and the recovery values vary between 0 and 100 (cf. Table 1 and Figure 1). As reference, a sample peak for the 100% recovery was taken that was obtained, by using as carrier, triple distilled water with 0.5% v/v detergent FL-70 and 0.02% w/w NaN_3, without any amount of electrolyte. It must be pointed out, that the total recovery of the injected into the column particles after their detachment, was verified by the fact that the area under the curve of the eluted peak, after the detachment of

Table 1

Recoveries , R_i, of the PMMA Particles from the SdFFF Channel Wall at Two Different Field Strengths* Versus the Electrolyte $Ba(NO_3)_2$ Concentration, as well as the Corresponding PMMA Particle Diameters, *d*

C $Ba(NO_3)_2$ (M)	Field Strength (rpm)	R_i (%)	*d* (μm)
0	717	100.0	0.358
	1000	100.0	0.354
1×10^{-7}	717	97.3	0.358
	1000	97.3	0.351
1×10^{-6}	717	95.1	0.354
	1000	94.0	0.351
1×10^{-5}	717	89.6	0.371
	1000	86.3	0.359
3×10^{-5}	717	87.4	0.369
	1000	84.2	0.344
6×10^{-5}	717	86.3	0.367
	1000	83.1	0.347
1×10^{-4}	717	75.4	0.343
	1000	75.4	0.344
2×10^{-4}	717	67.8	0.358
	1000	64.5	0.352
4×10^{-4}	717	0 (Total adhesion)	---
	1000	0 (Total adhesion)	---

* Different field strengths = 717 and 1000 rpm.

the adhered particles, was exactly the same with that obtained by PBSdFFF using a carrier solution in which the particles are not adhered at the channel wall.

From the previous it is concluded that during the adhesion step in PBSdFFF the carrier solution must contain an indifferent electrolyte at concentration higher than the *CEC*, so as to assure the total adhesion of the colloidal particles at the beginning of the SdFFF channel wall. On the other hand, during the elution step, a carrier solution with or without any electrolyte, in which the recovery of the particles will be 100%, must be used. Both concentrations of the electrolyte are critical, as, during the adhesion step, the concentration must be higher than the *CAC*, while during the detachment (elution) step this concentration must be zero or too low to assure the total (100%) recovery of the colloidal particles subject to separation by PBSdFFF. These concentrations depend on both the nature of the colloids and the indifferent electrolyte used.

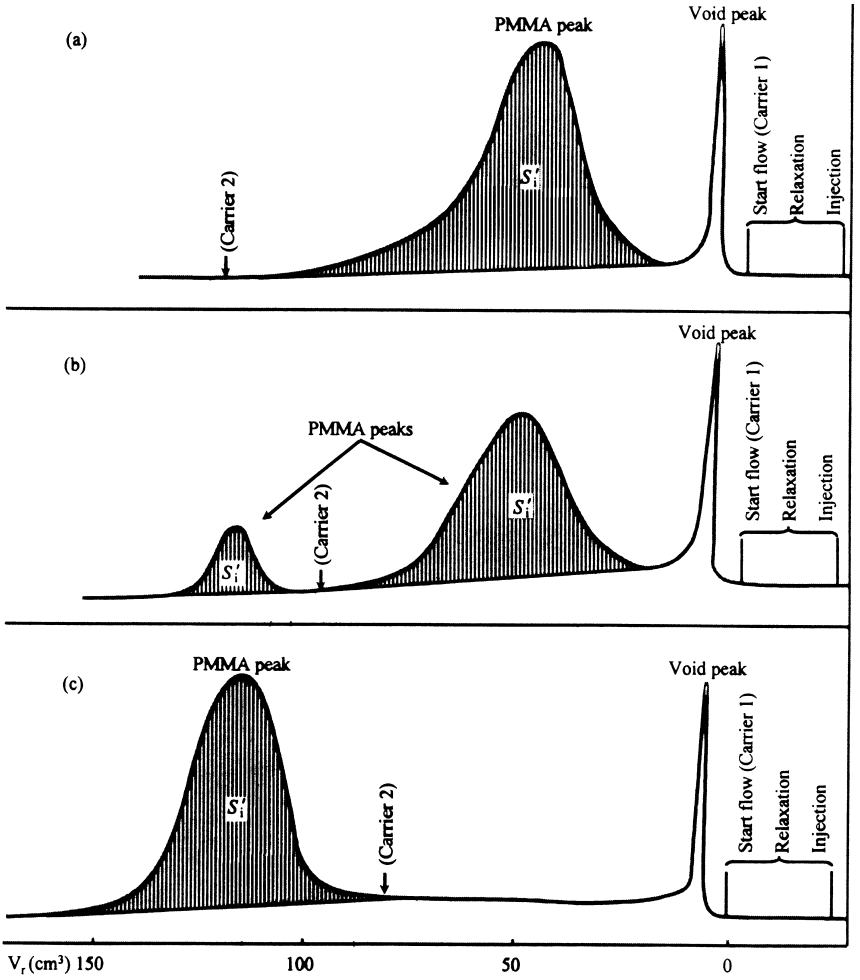

Figure 1. Fractograms (detector response versus retention volume V_r) of monodisperse PMMA spherical particles obtained by SdFFF. The carrier 1 contains 0.5% v/v FL-70 + 0.02% w/w NaN_3 with various amounts of barium nitrate: (a) $c_{Ba(NO_3)_2} = 0$ M; (b) $c_{Ba(NO_3)_2} = 3 \times 10^{-5}$ M; (c) $c_{Ba(NO_3)_2} = 4 \times 10^{-4}$ M, while the carrier 2 contains only 0.5% v/v FL-70 + 0.02% w/w NaN_3; sample = 100 µL; flow-rate = 106 $cm^3 h^{-1}$; relaxation time = 10 min;

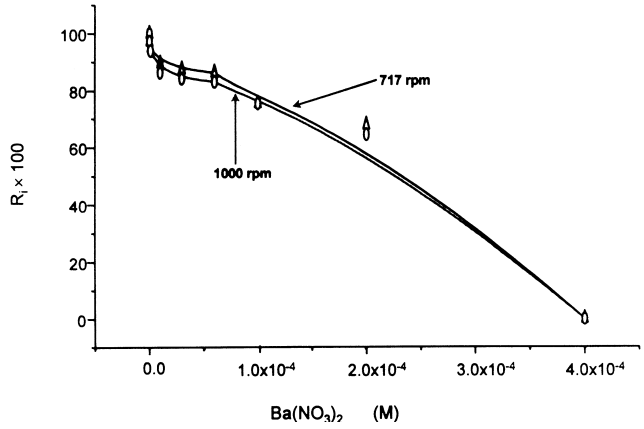

Figure 2. Recoveries (R_i) of PMMA particles in PBSdFFF vs the barium nitrate concentration at two different field strengths (717 and 1000 rpm).

The results (cf. Table 1 and Figure 2) also show that the adhesion of the colloidal particles at the beginning of the SdFFF channel wall, and hence, their recovery from the channel, is not dependent on the acceleration rate as the recoveries are almost identical at two different field strengths (717 and 1000 rpm). This is reasonable as the adhesion/detachment processes are dependent on the potential energy of interaction between the colloidal particles and the channel wall (cf. Eq. (1)) and not on the acceleration rate. In support of the above prediction is the fact that the critical electrolyte [$Ba(NO_3)_2$] concentration for the total adhesion of the PMMA particles on the Hastelloy C channel wall is identical (4×10^{-4} M) at the two different acceleration rates used.

As a general conclusion one could say that the appropriate adjustment of the experimental conditions in the PBSdFFF technique, so as to assure the total recovery of the colloidal particles under study, should be of great significance in the separation science.

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