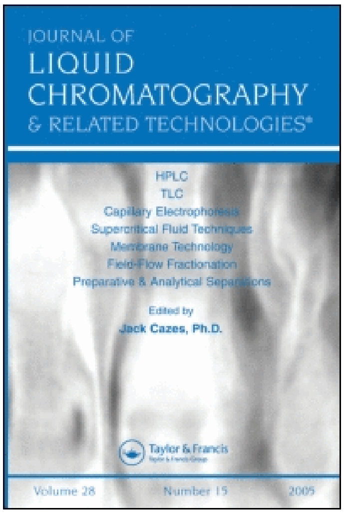

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INFLUENCE OF DENSITY OF ZEOLITE PARTICLES ON THEIR RETENTION IN GRAVITATIONAL FIELD-FLOW FRACTIONATION

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ABSTRACT

Gravitational force is one of main forces necessary for separation of particles in gravitational field-flow fractionation. It is proportional to particle size and density. The influence of density on the elution behavior was studied using zeolites containing varying amounts of platinum. The other properties of the zeolite samples (e.g., size, shape, particle size distribution) were the same as those of the original zeolite sample without platinum. We proved that retention of particles was related to their densities. However, densities could not be calculated from elution data because we found that zeolites were eluted in a focusing elution mode. This mode was induced by hydrodynamic lift-forces and their nature has not been fully understood yet; this excludes exact calculation of density. The effects of sample preparation, amounts of sample injected, and flow rates of a carrier liquid are described.

INTRODUCTION

Gravitational field-flow fractionation (GFFF) is the experimentally simplest member of the family of field-flow fractionation (FFF) techniques. GFFF utilizes Earth's gravity as an external force field, which causes settlement of particles towards the channel bottom (accumulation wall).[1,2] However, there are also other forces acting on particles in the carrier liquid flow-hydrodynamic lift forces.[3,4] In contrast to the gravitation, they tend to drive particles away from the channel accumulation wall and focus them into narrow zones. The position of the zones in the flow velocity profile is determined by the particle size and density.

There are several other particle properties that may significantly influence retention of particles in GFFF, e.g., shape,[5,6] plasticity,[7] and surface charge.[8-10] GFFF has been used successfully for separation of glass beads,[1] chromatographic silica gel supports,[4,11-13] polystyrene (PS) latexes,[14] and blood cells.[5-7,15-17]

The density of particles was studied by several FFF techniques, e.g., sedimentation FFF (SFFF),[18-26] sedimentation-flotation focusing FFF (SFFFFF),[27,28] and GFFF.[3,6] Various samples were studied: PS latexes,[18-20,22-24,26,27] polyvinylchloride,[16,22] and polybutadiene latexes,[21,25] polyglycidylmethacrylate latexes,[27] and red blood cells.[6] For density measurements by SFFF, a method was developed in which density of polystyrene latex particles was determined by a series of runs using carrier liquids of different densities.[18] In SFFFFF, Percoll-based density gradients were used.[27]

Zeolites are a group of crystalline hydrated aluminasilicates of group I and II elements, such as sodium, potassium, magnesium, and calcium. Their structure is composed of an infinitely extending three-dimensional network of AlO_4 and SiO_4 linked through shared oxygen atoms.[29]

The paper describes behavior of various kinds of zeolites containing 0%, 3%, and 9% of platinum, respectively. The goal of this work was a description of the influence of particle density on the elution behavior of particles in GFFF. It is known that platinum is distributed inside zeolite particles, and it means that all samples used have the same average particle size and its distribution. This is an important advantage to previous studies dealing with the influence of particle density on retention in FFF, where particles made of different materials were used. Contrary to zeolites, those particles differed not only in density, but also in other properties (size, shape, etc.).

EXPERIMENTAL

Materials

All zeolite samples (a kind gift from Dr. Nováková) were prepared at the Institute of Physical Chemistry in Prague. Their average particle diameter was 1 μm. The samples were resuspended at the concentration of 2-10 mg/mL in redistilled water which was also used in all measurements as a carrier liquid. The samples were wetted either under vacuum or by sonication.

Methods

The experimental set up was described elsewhere.[4,6] The separation channel used in this work was cut in an 80 μm thick spacer, which was placed between two mirror-quality float glass plates. The channel had dimensions 20 mm x 360 mm, including the inlet and outlet triangles with a height of 30 mm (dead volume 0.53 mL). The pump was an HPP 4001 (Laboratory Instruments, Prague, Czech Republic). A spectrophotometric detector, Spectra 100 (Spectra-Physics), with a capillary cell (I.D. of 300 μm) was used at 254 nm.

Aliquotes (1 μL) of samples were injected with a syringe through a septum directly into the channel inlet. The injected sample was transported for 6 s at a flow rate of 200 μL/min. After 60 s without the carrier-liquid flow (for settlement of particles), the flow was switched on (the range of flow rates was 400-2000 μL/min), and the sample was eluted through the channel to the detector.

RESULTS AND DISCUSSION

Sample preparation is very important for porous particles in FFF. A suitable procedure should be able to remove contingent air cavities inside the particles. As a result, the particles are better wetted, and the apparent density of the particles is unified. In the case of porous silica gel particles, we found that sonication for several minutes was sufficient as a sample preparation procedure for samples in detergent solutions.[12] However, in the case of zeolites in pure water, sonication was inefficient, and peaks measured by GFFF were irregular and broad (data not shown). For this reason, zeolites were first wetted in water, under vacuum, and sonicated for 1 min just before injection.

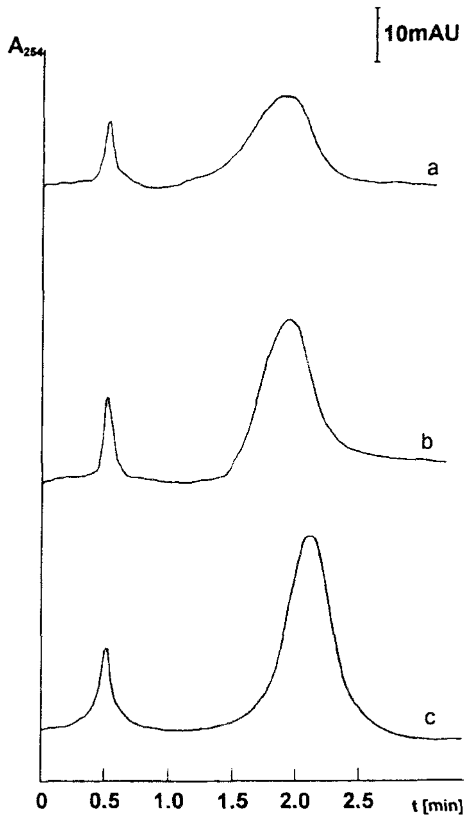

Figure 1. The fractogram of the zeolites with different contents of platinum (a - 0%, b - 3%, c - 9%). The experimental conditions: flow rate = 1000 μL/min, zeolite concentration = 5 mg/mL, injected volume = 1 μL.

Fractograms of all three kinds of zeolites used are shown in Figure 1, where one can see that elution times increase with increasing amounts of platinum in the zeolites. The observed retention ratios do not correspond to the steric elution model, where particles are rolling on the channel bottom.[1] Because the retention ratios are also dependent on the flow rate of the carrier liquid (see Figure 2), we can conclude that the elution mode is the focusing (hyperlayer) one.[30,31] Focusing of the particles above the channel bottom is caused by the influence of lift forces.[3,4,9] However, the nature of lift forces has not been fully understood yet and, therefore, we are not able to calculate the density of zeolites from their retention data.

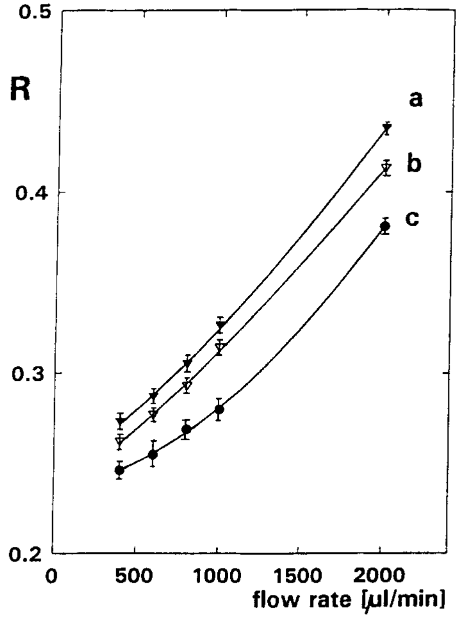

Figure 2. The dependence of the retention ratios of three zeolite samples with different platinum contents (a - 0%, b - 3%, c - 9%) on the flow rate. The experimental conditions: zeolite concentration = 5 mg/mL, injected volume = 1 μL.

Nevertheless, the influence of the particle density on retention of particles is evident. The samples used were prepared from the same original zeolite, which was identical with the sample without platinum. The particles of all three samples have identical sizes, particle size distributions, and shapes because platinum is located on the surface of the pores inside the zeolite particles and, therefore, it does not change the particle volume (V_0). From the shapes of fractograms of the different zeolites (see Figure 1), which are similarly broad, we can conclude that platinum does not block the pores. Blocked pores could not be completely wetted, and cavities containing air would cause appearance of broad peaks, as a result of a broad density distribution of samples with the same platinum content. This means that the samples differ only in density, which is based on the platinum content. This is the main advantage of zeolites with different platinum content to particles made of different materials used in previous studies.[3,4,27] Those particles differed also in size, shape, particle size distribution, etc. It is clear, from Figures 1 and 2, that zeolite samples without platinum are eluted first, which means that the position of their focused zones is the highest one above the channel bottom. On the contrary, zeolite samples containing 9% of platinum are eluted as the last ones, which means that they are eluted near the channel bottom where are lower velocities of the carrier liquid. The exact density of the original zeolite sample is not known (the approximate value is 1.5 g/cm^3). However, we know exactly the amounts of platinum in particular samples. Thus, we can express their relative densities. The relative density is defined as a ratio of a particular zeolite sample density (ρ_p) to a density of the original zeolite without platinum (ρ_0). It is based on the identical particle volume (V_0) of all zeolites samples:

$$\rho_0 = \frac{m_0}{V_0} \qquad (1)$$

$$\rho_p = \frac{m_p}{V_0} = \frac{m_0 + p_p m_0}{V_0} = \frac{m_0(1 + p_p)}{V_0} \qquad (2)$$

and, thus,

$$\frac{\rho_i}{\rho_0} = 1 + p_p \qquad (3)$$

where m_0 is the mass of a zeolite particle containing no platinum, m_p is the mass of a zeolite particle containing platinum, p_p is the ratio of a platinum amount to the mass of a zeolite particle. The influence of relative densities on the retention ratio of zeolite samples at different flow rates is shown in Figure 3. This effect is more expressed at higher flow rates, which phenomenon is probably connected with the flow rate dependence of lift forces.

Recently, it was described that retention ratios in GFFF in the focusing elution mode are influenced by the number of injected particles.[13] Too large amounts of injected samples induce overloading effects, which cause an increase in the observed retention ratios with increasing amounts of injected silica gel particles. Similar results were observed, also, in the case of the zeolites used in this work (Figure 4). This observation complicates interpretation of the particle density from the elution data, because higher injected amounts of particles result in lower apparent densities than follows from the elution data obtained from the injection of lower amounts of particles. In order to obtain reasonable results, it is necessary to inject the same number of particles, as small as possible for a reasonable detection, in each experiment.

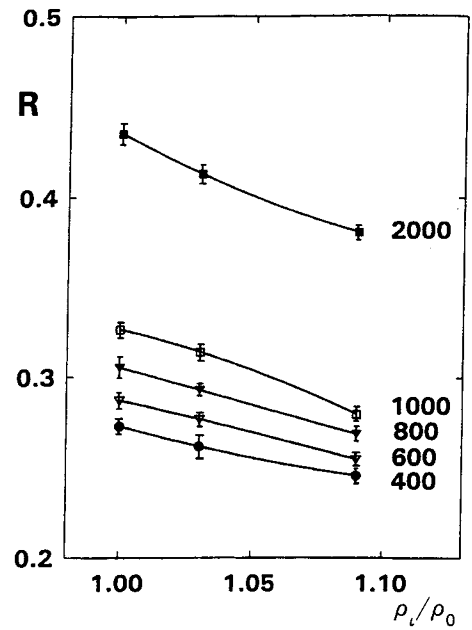

Figure 3. The dependence of the retention ratio on the relative densities of the zeolites at different flow rates ranging from 400 μL/min to 2000 μL/min. The experimental conditions: zeolite concentration = 5 mg/mL, injected volume = 1 μL.

Our results show that GFFF can be used for comparison of densities in the case of particles which differ only in their densities. Provided that certain conditions (e.g., sample preparation, injection of the same amounts of particles, application the same flow rate, and carrier liquid), are fulfilled, densities can be determined by using calibration curves.

In the case of particles with different shapes or sizes, other techniques have to be used, e.g., SFFFFF.

Although present knowledge of GFFF suggests that gravitational force and hydrodynamic lift forces are the most important forces affecting the samples, it is known that other forces (e.g., electrostatic and van der Waals forces) influence behavior of the particles.[8-10] Therefore, our future work will deal with an influence of these forces on the determination of the zeolite density by GFFF.

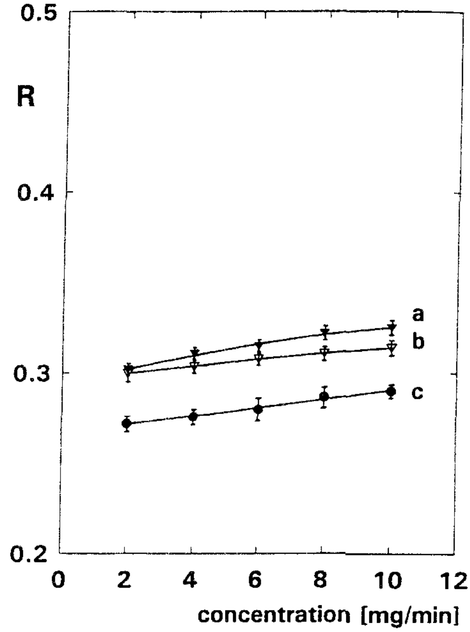

Figure 4. The dependence of the retention ratio on the amount of injected zeolite samples with different platinum content (a - 0%, b - 3%, c - 9%). The experimental conditions: flow rate: 1000 μL/min, injected volume = 1 μL.

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