EXPERIMENTAL EVIDENCE OF THE ISOPERICHORIC FOCUSING OF NANOSIZE POLYANILINE PARTICLES IN DENSITY GRADIENT FORMED BY COLLOIDAL SILICA

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The isoperichoric focusing transport phenomena were recently described by a rigorous theoretical model. Contrary to the generally accepted supposition that a density gradient forming liquid in isopycnic focusing should behave as continuum regarding the focused species, the model predicts the focusing with no a priori imposed size ratio of the focused to the density gradient forming species. This prediction was evidenced by focusing of the polyaniline nanosize particles in a density gradient formed by colloidal silica particles suspended in water. The size ratio of the polyaniline to silica particles was low.

Key words: Thin-layer isopycnic focusing of polyaniline; Colloidal silica density gradient.

Isoperichoric focusing, thin-layer isoperichoric focusing (TLIF), and the derived separation methods are used for the analysis and characterization or for micropreparative fractionation of macromolecules and particles. The steady-state concentration distribution of the uniform focused species within an individual zone in the direction of the density gradient (x-coordinate) in isopycnic focusing was derived in ref.[1]

$$c_i(x) = c_{i,\max} \exp\left[-\left[\frac{v_i\, g_\mathrm{f}\, \phi_\mathrm{mave} \Delta\rho_\mathrm{m} w}{kT(1 - \exp(-w|U_\mathrm{m}|/D_\mathrm{m}))} \right] . \right.$$

$$\left. . \left[\exp(-x|U_\mathrm{m}|/D_\mathrm{m}) - \exp(-x_{i,\max}|U_\mathrm{m}|/D_\mathrm{m}) \left(1 + \frac{|U_\mathrm{m}|(x_{i,\max} - x)}{D_\mathrm{m}} \right) \right] \right] , \qquad (1)$$

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where $c_i(x)$ is the position dependent concentration of the i-th focused species, $c_{i,\max}$ is its maximal concentration in the focused zone at the position $x_{i,\max}$ where the focusing forces vanish, v_i is the volume of a focused particle, g_f is the centrifugal acceleration, ϕ_mave is the average volume fraction of the density gradient forming species (modifier), $\Delta\rho_\mathrm{m}$ is the density difference between the modifier and the suspending liquid, U_m and D_m are the sedimentation velocity and the diffusion coefficient of the modifier, and w is the width of the liquid layer in centrifugation cell.

The aim of this work was to demonstrate that the above distribution function agrees with the experimental findings and, consequently, the isopycnic focusing of the nanosize particles can appear in a density gradient formed by other type of the colloidal particles. The colored polyaniline (PANI) nanosize particles were focused in a colorless density gradient formed by colloidal silica particles under conditions of TLIF centrifugation. The macrophotograph of the focused zone was taken by using a standard camera and, subsequently, the experimental concentration distribution of the PANI particles within the focused zone was obtained by computer image processing of the scannerized macrophotograph. The experimental concentration distribution was compared with the above described $c_i(x)$ function.

The density and/or the size of the focused species are usually not uniform. According to the above presented distribution function, the density of the focused species determines the position of the zone and the size influences the width of the zone. As a result, the size distribution of the focused species must be taken into account.

EXPERIMENTAL

High speed refrigerated centrifuge, model 4239 R, ALC Milan (Italy), equipped with the swinging bucket rotor was used. The centrifugal acceleration corresponding to 200 G was kept constant during the focusing experiments. The closed all-glass rectangular cross-section cells of the internal size of 10 × 10 × 50 mm were used for centrifugal TLIF. Model Zetamaster, Malvern Instruments, Ltd., Malvern, Worcestershire (U.K.), apparatus was used to measure the average size, the particle size distribution, and the ζ-potential of the PANI and colloidal silica samples. Standard Ubbelohde capillary viscometer with AVS 410 model, Schott (Germany), automatic viscometer was used to measure the viscosities of the silica suspension at different concentrations to determine the effective hydrodynamical particle size and its casual variation within the density gradient. All experiments were performed at 25 °C.

Commercial product Percoll, Pharmacia Fine Chemicals AB (Sweden) consisting of colloidal spherical silica particles coated with poly(vinylpyrrolidone) (PVP) and suspended in water, was used as density gradient forming liquid. The original product was diluted with deionized water to obtain a suitable average density liquid. The size distribution of the silica particles was verified but no aggregate formation was detected in ultrasonically treated Percoll solutions. The density marker beads, Pharmacia Fine Chemicals AB (Sweden), were used to check the shape of the density gradient formed in a reference TLIF cell.

The PANI spherical nanoparticles were prepared by Dr J. Stejskal from the Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, by polymerization of aniline in the presence of PVP in the reaction mixture to stabilize the resulting suspension[2]. The raw sample was fractionated by large scale isopycnic focusing to narrow the density distribution of the original unfractionated sample. The fractions were washed by multiple centrifugation in deionized water to remove free PVP stabilizer and Percoll.

RESULTS AND DISCUSSION

The PANI is green or blue suspension whose color varies with the pH value of the suspending liquid while Percoll is transparent light-yellow liquid. The grayscale intensity of the scannerized macrophotographs was found to be a linear function of the PANI concentration within the relevant range of concentrations when the convenient yellow filter and black and white film were used to take the pictures.

The particle size distribution of the PANI fraction chosen for focusing experiments is shown in Fig. 1*a*. The average particle diameter of this fraction is 274 nm and the polydispersity characterized by standard deviation of the particle size distribution is 138 nm. A low ζ-potential of the PANI dispersion is of the order of ±10 mV and it does not vary significantly with pH, within the relevant range, as can be seen in Fig. 1*b*. The density of the PANI particles of this fraction, measured by TLIF is 1.1022 g cm^{-3}. As the density difference between the first and the last of 24 fractions obtained by large-scale isopycnic focusing was about 0.07 g cm^{-3}, concerning the density, each individual fraction can reasonably be regarded as uniform.

The particle size distribution of the silica in Percoll is shown in Fig. 1*a*. Its average particle diameter is 28 nm and the polydispersity characterized by standard deviation of the particle size distribution is 22 nm. The ζ-potential of the Percoll silica particles is of the order of –40 mV and does not vary with pH within the relevant range (see Fig. 1*b*). The average effective hydrodynamical size was calculated from the concentration

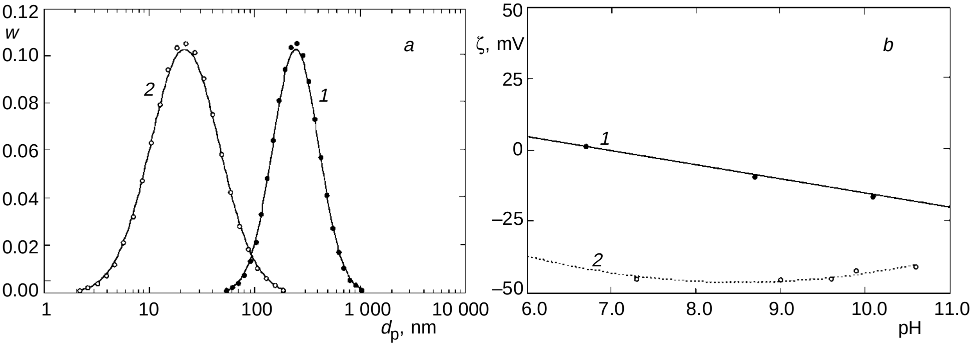

FIG. 1

Characterization of the colloidal particles: (*1*) PANI, (*2*) Percoll; *a* particle size (d_p) distribution of the PANI fraction A17 and of the Percoll silica; *b* dependence of the ζ-potential on the pH value of the unfractionated PANI sample and of the Percoll silica dependence of the relative viscosity of Percoll. The experimental dependence was fitted by non-linear regression to the viscosity versus volume fraction relationship for hard sphere model[3],

$$\eta_r = 1 + \frac{5}{2}\varphi + (4 \pm 2)\varphi^2 + (42 \pm 10)\varphi^3 \ , \tag{2}$$

which is valid for volume fractions within $0.0006 \leq \varphi \leq 0.6$. The results are shown in Fig. 2. The average hydrodynamical size of the silica particles calculated from viscometry data is 42 nm. As can be concluded from the ζ-potential measurements, the effective sizes of the PANI and Percoll silica particles do not vary with the pH within the relevant range.

A section of the scannerized macrophotograph of the steady-state focused zone of the PANI fraction (after 528 h of centrifugation) is shown in Fig. 3 together with a section of the scannerized macrophotograph of the reference TLIF cell displaying the focused layers of the density marker beads used to determine the shape of the established density gradient in a simultaneous experiment performed under identical conditions.

The experimental concentration distribution of the PANI particles within the focused zone is shown in Fig. 4 together with two theoretical shapes of the focused zone calculated by using the above Eq. (*1*) and the actual experimental parameters as the adjustable input data. The particle size distribution of the PANI fraction was taken into account and two normalized theoretical concentration distribution functions were calculated. The curve *3* in Fig. *4b* corresponds to a hypothetical uniform particle size sample

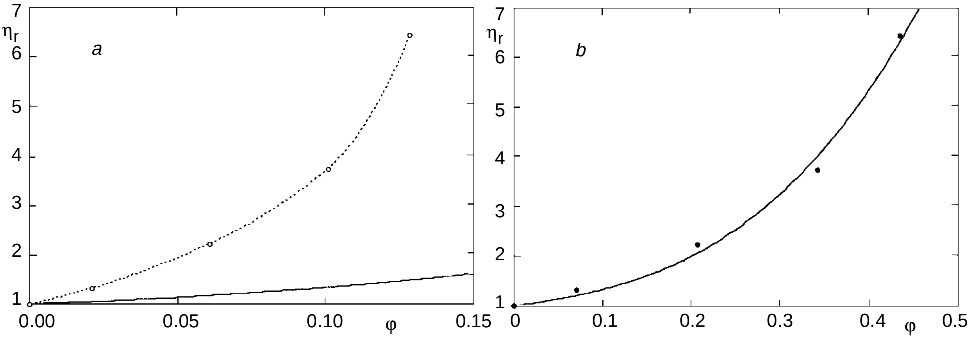

FIG. 2

Relative viscosity of Percoll colloidal silica as a function of the volume fraction (φ); *a* comparison of experimental data (○) with a theoretical relationship (——) for a suspension of the uniform hard spheres (Eq. (*2*)); *b* nonlinear regression fit of the experimental viscosity data for Percoll to the curve for hard sphere model to obtain the effective hydrodynamical dimensions of the silica particles of the given average particle diameter and the curve *4* takes into account the real particle size distribution of the PANI sample. It is clear from Fig. 4 that the normalized concentration distribution calculated from the experimental data lies well between two theoretical curves. The shape of the theoretically calculated and experimentally found density gradient is also shown in Fig. 4. Both shapes agree quite well. To give an idea

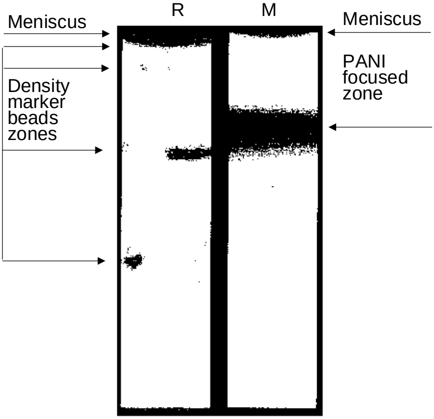

FIG. 3
Scannerized macrophotograph images of the focused zone of PANI particles in the measuring TLIF cell (M) and of the four density marker beads in the reference cell (R) taken at 528 h of the centrifugation

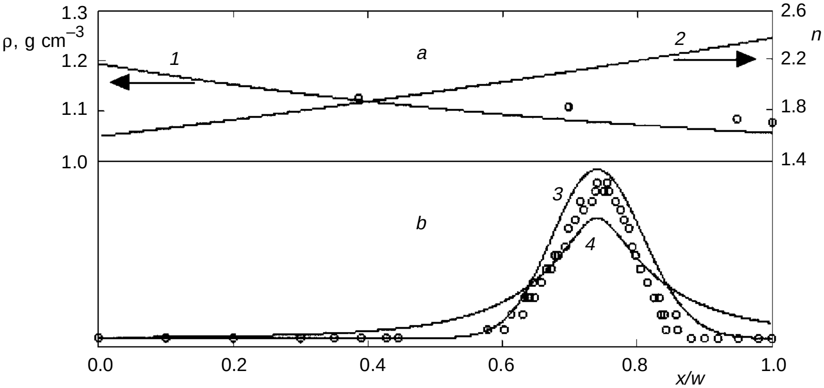

FIG. 4
Theoretical and experimental steady-state concentration distributions of PANI fraction within the focused zone in the direction of the dimensionless *x/w*-coordinate correlated with the theoretical and experimental density distributions within the TLIF cell and with the corresponding silica interparticle distances; *a* steady-state density distributions found experimentally from the positions of the density marker beads at 528 h of centrifugation (❍) and calculated theoretically (curve *1*) and interparticle distance expressed as a multiple, *n*, of the average size of silica particles, d_p (curve *2*); *b* physical model applied to hypothetical monodisperse PANI fraction (curve *3*), physical model applied to real polydisperse PANI fraction (curve *4*), and experimental concentration distribution (❍)

about the silica interparticle distances within the established density gradient, this calculated parameter is represented in Fig. 4 as a function of the position in the direction of the *x*-coordinate.

The model focusing experiment described in this study demonstrates that the isopycnic focusing appears is a suspension mixture of the two different but close sizes colloidal particles and that this phenomenon is correctly described by our theoretical model[1]. The size ratio of the focused PANI particles to the density gradient forming silica particles is roughly 6.5. Another experimental work in progress has clearly demonstrated analogous results but for a binary mixture of the colloidal polypyrrole and silica particles of lower size ratio. The results of a recent Monte Carlo simulation indicate similar conclusions[4].

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