ISOPERICHORIC FOCUSING PHENOMENA GENERATED BY COUPLED ELECTRIC AND GRAVITATIONAL FIELD FORCES IN BIDISPERSE MIXTURES OF COLLOIDAL PARTICLES

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The first successful isopycnic focusing generated by the coupled electric and gravitational fields applied to the model bidisperse mixtures of the colloidal silica and polyaniline particles of low size ratio is described. The theoretical analysis and the experimental results show that the density gradient forming liquid should not necessarily behave as a continuum regarding the focused species. This finding confirms the original prediction which was evidenced previously by the focusing under the action of high intensity centrifugal field forces only.
Key words: Isopycnic focusing; Bidisperse colloidal suspension; Colloidal silica density gradient; Colloidal polyaniline composite suspension.

The isoperichoric focusing[1] process, in general, requires the action of a position dependent field force which generates the macroscopic transport phenomena of the focused species. The isopycnic focusing[2], in particular, implies the existence of an effective property gradient of the carrier fluid (the density gradient) which is either created coincidentally with the focusing processes or preformed beforehand due to the action of the gravitational or centrifugal forces. The dispersive processes act against both the density gradient forming and the focusing transports until the steady state is reached. Although they are physically coupled, the density gradient forming and the focusing fluxes can be formally treated as two independent processes. The density gradient is then described by the known exponential law derived already by Einstein[3] and verified experimentally by Perrin[4]. The macroscopic focusing force acting on a single focused species is then given by Archimedes law. This approach, formulated rigorously by the transport differential equations, allows to predict theoretically the conditions under which the focusing phenomena can appear.

A recent theoretical model[5] allowed a new look at the isoperichoric focusing phenomena. The prediction[6], that the density gradient forming complex liquid used in isopycnic focusing should not necessarily behave as a continuum regarding the focused species was, however, controversial with a widespread persuasion. This theoretical prediction was evidenced subsequently[7] by the focusing of the polyaniline nanosize par-

ticles in a density gradient formed by the colloidal silica particles due to the action of the centrifugal forces. The size (average diameter) ratio of the polyaniline to silica particles in the studied bidisperse mixture was low. It has also been postulated theoretically and demonstrated experimentally[8,9] that the electric field instead of the centrifugal forces can be applied to form the density gradient in a suspension of charged colloidal silica particles, and the natural gravitation could be enough to focus the uncharged or slightly charged larger particles. The former experiments were carried out to demonstrate the focusing of the particles whose diameter was 10 000 times larger than the diameter of the density gradient forming colloidal silica. In this communication, the first successful isopycnic focusing generated by the coupled weak electric and gravitational fields applied to the model bidisperse mixtures of the colloidal silica and polyaniline particles of low size ratio is described.

THEORETICAL

The quasi-steady-state concentration distribution in the direction of the density gradient (x-axis) of an i-th focused species in isopycnic focusing is given by[5,8]:

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

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

where $c_i(x)$ and $c_{i,\max}$ are x-coordinate dependent and maximal (at $x_{i,\max}$) concentrations of the i-th focused species within the zone, v_i is the volume of one focused particle, g is the natural gravitational acceleration, $\phi_{\mathrm{m,ave}}$ 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, $U_{\mathrm{m,e}}$ and D_{m} are the transport velocity due to the applied electric field and the diffusion coefficent of the modifier, and w is the width of the liquid layer in focusing cell. The density gradient in the direction of the primary electric field action is described by[5,8]:

$$\rho(x) = \rho_l + \frac{\phi_{\mathrm{m,ave}} \Delta\rho_{\mathrm{m}} w |U_{\mathrm{m,e}}|}{D_{\mathrm{m}}(1 - \exp(-w|U_{\mathrm{m,e}}|\,/\,D_{\mathrm{m}})} \quad . \qquad (2)$$

The velocity of the electrophoretic migration of the charged particles of the density modifier is related to their zeta (ζ) potential[10]:

$$U_{m,e} = I \frac{\varepsilon \zeta E}{\eta} \quad , \tag{3}$$

where ε and η are the permittivity and the viscosity, respectively, of the carrier liquid, E is the electric field strength, and I is a term which can vary from 2/3 to 1 values[10]. The equilibrium state in isopycnic focusing generated by the coupled electric and gravitational field forces is then completely described by Eqs (*1*) to (*3*).

COMPUTER SIMULATION

Our theoretical approach[5,6], which resulted in Eqs (*1*) to (*3*), was used to calculate the concentration distributions of two species in various bidisperse mixtures of the colloidal particles undergoing the effect of the electric and gravitational field forces. The electric field forces, whose intensity can be expressed as a multiple of the equivalent of gravitational acceleration, were assumed to affect only the density gradient forming charged particles in our model calculations. On the other hand, the large size uncharged particles undergoing the focusing were supposed to be affected only by the gravitational field forces. The range of the validity of these assumptions was discussed previously[8,9]. In any case, the charge of the large focused particles influences only the position of the focused zone but not the appearance of the focusing phenomenon proper.

Software Mathematica™ and our program written in Quick Basic™ were used for the computer simulation. The result is shown in Fig. 1. The curve *1* represents an exponential concentration distribution of the density gradient forming charged species described by Eq. (*2*). The curves *2* to *4* show the concentration distributions of the

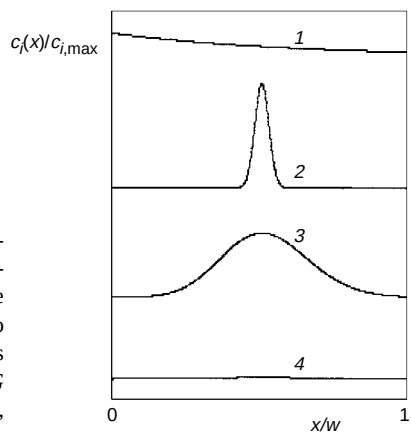

FIG. 1
Theoretical concentration distributions of the density gradient forming species (curve *1*) and focused species (curves *2* to *4*) in bidisperse mixtures of colloidal particles; particle size ratio d_i/d_m: 33 (*2*), 10 (*3*), 1 (*4*). Input parameters: E is equivalent to centrifugal acceleration of 200 G (G = 9.81 m sec^{-2}), $\phi_{m,ave}$ = 0.1, $\Delta\rho_m$ = 1 g cm^{-3}, d_m = 30 nm, w = 1 cm

focused uncharged species calculated by using Eq. (*1*) for different particle size ratios of the focused to the density gradient forming species. The curves in Fig. 1 are not normalized and, consequently, the dimensionless x/w and $c_i(x)/c_{i,\max}$ axes are without numerical scales that, in fact, have no meaning for this model case.

As can be seen in Fig. 1, the width of the concentration distribution of the focused species (curves *2* to *4*) increases with the decreasing particle size ratio and the focusing phenomenon disappears only when this ratio approaches to 1. This conclusion is independent of the position of the focused zone within the established density gradient or, in other words, it is independent of the density of the focused species, as can easily be verified from Eq. (*1*). The input parameters for the model calculations shown in Fig. 1 are given in the figure legend and correspond approximately to the conditions applied in real experiments. However, the main conclusion concerning the increasing of the width of the focused zone with decreasing particle size ratio is independent of these parameters.

The density gradient evidently does not change at constant electric field strength (see Eqs (*2*) and (*3*)) and its slope has no effect on a general tendency of the focused zone to be larger with the decreasing particle size ratio of a bidisperse suspension. A detailed study of the effect of other operational variables (not relevant for the main objective of this work) was published recently[11].

When the focused particles are charged they can be displaced from their isopycnic position to another equilibrium position where the force due to the electric field is balanced by the buoyant forces. This displacement has no meaning regarding the main objective of this work to demonstrate the occurrence of the focusing phenomenon in a bidisperse mixture of the colloidal particles undergoing the coupled action of the electric and gravitational fields and, moreover, it can be easily calculated[8,9].

EXPERIMENTAL

A simple apparatus for thin-layer isoperichoric focusing (TLIF) described in ref.[8] was used in this work. Its principle is shown in Fig. 2. The focusing experiments were carried out in square (10 × 10 mm) cross-section TLIF cells made of transparent polystyrene walls, closed at both ends by the electrodes. A low and constant voltage of 300 mV was applied in TLIF cell on a distance of 10 mm between the electrodes.

The polyaniline (PANI) spherical particles of the tailor-made average diameter and narrow particle size distribution[12] (PSD) stabilized by the poly(vinyl alcohol) (PVA) or by the poly(*N*-vinylpyrrolidone)[13,14] (PVP) and dispersed in a colloidal silica suspension of spherical particles stabilized also by the PVP, were used in this study. The silica is a commercial product Percoll, Pharmacia Fine Chemicals AB (Sweden). Its average particle diameter measured by the quasi-elastic light scattering[7] (QELS) is 28 nm, however, the average effective hydrodynamic size calculated from the viscometry data[7] is 42 nm. Four bidisperse PANI–silica mixtures were studied. The mixture I was the same PANI–PVP composite (PANI I) with the silica–PVP composite (Silica) as used in our previous centrifugal experiment[7]. The mixture II was composed of the same silica–PVP composite but the second component was a complex PANI–silica–PVP composite (PANI II). The mixtures III and IV were

composed of the same silica–PVP composite but the second components were the PANI–PVA composites (PANI III and PANI IV) of different average particle sizes.

The PSDs of the PANI–PVA, PANI–PVP, PANI–silica–PVP, and silica–PVP composites were measured by the QELS. The PSDs of all studied samples are shown in Fig. 3 from which the bidisperse character of the mixed suspensions (PANI I + Silica), (PANI II + Silica), (PANI III + Silica), and (PANI IV + Silica) can be easily deduced. The average particle diameters of all studied PANI composite samples are given in Table I. The ratio of the average particle diameter of the PANI based composites to the average effective particle diameter of the silica–PVP in mixtures I and III is roughtly 6.5 and 6.1, respectively, while it is 31 for the bidisperse mixture II of the PANI–silica–PVP with silica–PVP and 30 for the bidisperse mixture IV of the PANI–PVA with silica–PVP. The volume fractions of the silica–PVP particles in bidisperse suspensions were around $\phi_{m,ave} = 0.1$ while the volume fractions of the PANI composite particles were about 0.00001, thus roughly 10^4 times lower.

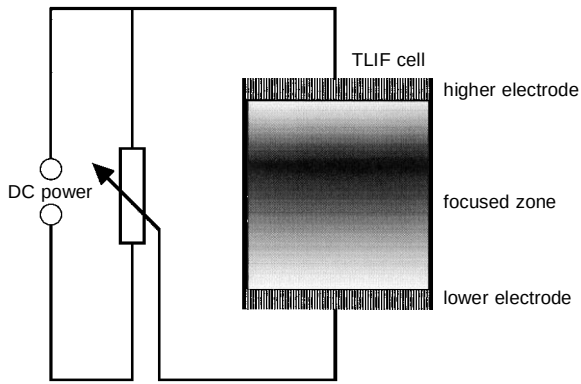

FIG. 2
Schematic representation of the apparatus for thin-layer isopycnic focusing

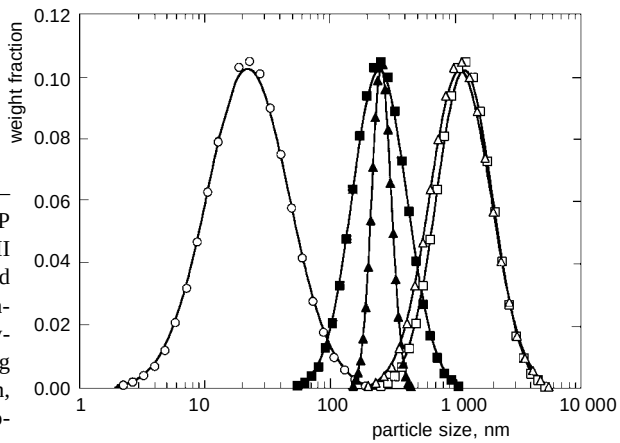

FIG. 3
Particle size distributions of PANI–PVP (PANI I ■), PANI–silica–PVP (PANI II ❒), PANI–PVA (PANI III ▲), PANI–PVA (PANI IV Δ), and silica–PVP (Silica ❍) colloidal composite particles. Average hydrodynamic size of silica–PVP (including the electric double-layer) is 42 nm, average diameters of PANI composites are given in Table I

The absorption spectra in the visible range and the ζ-potential of the nanosize PANI particles vary with the pH value[7,11–14], while the colloidal silica–PVP suspension is transparent light-yellow liquid whose absorption in the visible range does not vary with the pH but the ζ-potential depends on the pH value. As the focusing experiments were carried out under conditions of almost constant pH (lying between 9.00 to 9.15) the variations of the above mentioned PANI properties with the pH are within the range of experimental errors of their determination and are negligible regarding their effect on the studied focusing phenomenon. Under these conditions (low ionic strength and constant pH), the effective sizes of all particles in the mixture are also constant[7,12].

The colour difference between the PANI and silica based colloidal particles allows to determine the concentration distribution of the PANI composites within the focused zone formed in silica–PVP density gradient. The macrophotographs of the steady-state focused zones of the coloured PANI composite particles in the transparent and colourless silica–PVP suspension were taken by using a standard camera and a black and white film. The acquired images were computer processed by using a standard software Adobe Photoshop™, Color It™, and Aldus Super Paint™ to obtain the experimental concentration distribution of the focused species. The most important data on the TLIF experiments relevant for this study are summarized in Table I, more details can be found elsewhere[7].

RESULTS AND DISCUSSION

According to the numerical calculations whose results are shown in Fig. 1, which were performed by using Eqs (*1*) to (*3*) and the input data corresponding to the real characteristics of the studied particles, the samples PANI I and PANI III should exhibit the focused zones much larger than the curve *3* in Fig. 1, while the focused zones of the samples PANI II and PANI IV could be comparable with the curve *2* in Fig. 1. The scanned and computer processed images of a section of the TLIF cells, representing the initial uniform PANI distributions and the quasi-steady-state focused zones of samples PANI I, II, and IV, are shown in Fig. 4.

The images a and b in Fig. 4 correspond to the initial uniform distribution of the sample PANI I and the final quasi-steady state reached after 268 h, respectively. Although some subtle concentration distribution of the PANI I can be seen in Fig. 4, image b, the zone is very large and the position of its maximum and its width cannot be

TABLE I
Operational parameters in TLIF focusing experiments; applied voltage 300 mV

Focused sample	Average diameter of focused particles, nm	Initial density of Silica suspension g cm^{-3}
PANI I	274	1.0848
PANI II	1 314	1.1087
PANI III	257	1.0490
PANI IV	1 244	1.0490

correctly determined. The sample PANI III which has almost the same average particle diameter exhibited similar behaviour, a large zone difficult to identify.

On the other hand, distinct focused zones of the large particle size PANI II and PANI IV samples were formed. The focused zone of the sample PANI II (image d in Fig. 4) was stable starting at about 142 h from the initial state shown on the image c in Fig. 4. The focused zone of the sample PANI IV was stable after about the same time from the initial state shown on the image e in Fig. 4. The image f in Fig. 4 shows the steady-state focused zone after 278 h.

The scanned images of the initial uniform colour distribution of the PANI II sample and of the steady-state focused zones of the PANI II and PANI IV samples were computer processed to obtain the experimental concentration distribution within the focused zones. The grayscale intensity of the scanned macrophotographs of the focused zones was found previously[7,11] to be a linear function of the PANI concentration within the investigated range of concentrations when a convenient yellow filter and a black and white film were used to take the pictures. The results are shown in Fig. 5. The Fig. 5a shows a constant intensity of the colour across the TLIF cell corresponding to the initial uniform distribution of the PANI particles. The Figs 5b and 5c show the concentration distributions within the steady-state focused zones of the PANI II and PANI IV samples. The widths of the experimental concentration distributions within the focused zones lie between those calculated theoretically and shown in Fig. 1, curves *2* and *3*.

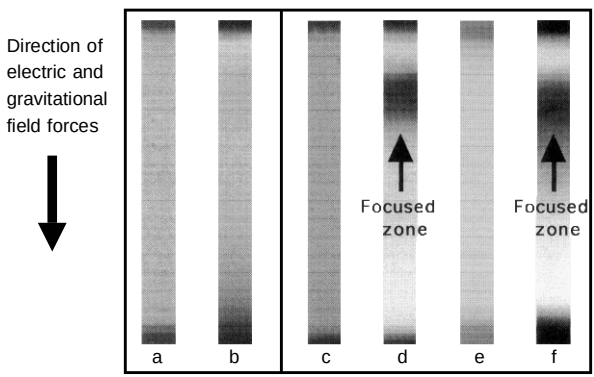

FIG. 4

Computer processed images of the macrophotographs of the initial uniform mixture and of the focused zone of PANI I (a, b), PANI II (c, d), and PANI IV (e, f) nanosize composite particles in bidisperse mixture with colloidal Silica particles in focusing experiments with coupled electric and gravitational field. a Initial homogeneous bidisperse mixture PANI I–Silica; b quasi-steady-state distribution of PANI I–Silica after 268 h; c initial homogeneous bidisperse mixture PANI II–Silica; d quasi-steady-state distribution of PANI II–Silica after 142 h; e initial homogeneous bidisperse mixture PANI IV–Silica; f quasi-steady-state distribution of PANI IV–Silica after 278 h

The main conclusion that can be drawn from the described experiments is that the proposed isopycnic focusing principle exploiting the coupling of the electric and gravitational fields is reliable even for the effective focusing and thus the separation of the particles whose size is not very different compared with the size of the density gradient forming colloidal particles. The principal objective of this study was then achieved. The intended refinement of the theoretical approach, by including the effect of the interparticle interactions, as well as of the experimental technique, should allow a quantitative comparison of the theory with the experimental results.

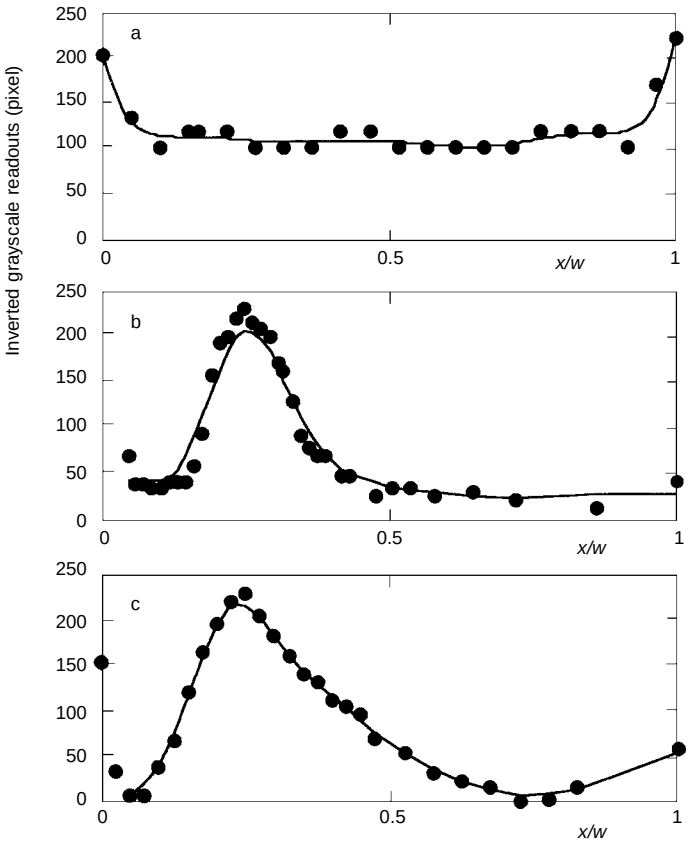

FIG. 5

Experimental concentration distributions of the PANI II and PANI IV samples obtained by computer processed images of the scanned macrophotographs. a Initial homogeneous bidisperse mixture PANI II–Silica; b quasi-steady-state distribution of PANI II–Silica after 142 h; c quasi-steady-state distribution of PANI IV–Silica after 278 h

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