

## Phase Separation in Bimodal Dispersions of Sterically Stabilized Silica Particles.

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**Abstract.** – Binary mixtures of suspended, nearly hard-sphere, sterically stabilized colloidal silica particles of diameter ratio 6 were observed to phase-separate at comparable volume fractions of the two particle species. The occurrence of phase separation as a function of the particle concentrations was studied visually and by small-angle light scattering. The results support recent predictions by Biben and Hansen.

*Introduction.* – Until recently it was generally believed that hard-sphere mixtures do not phase-separate into two fluid phases. Indeed at least within the Percus-Yevick closure of the Ornstein-Zernike equation and using the compressibility theorem to calculate the thermodynamic quantities this is true [1,2]. However Biben and Hansen have shown [3] that starting from the Rogers-Young closure, which is known to be more accurate for hard spheres than the Percus-Yevick closure [4], such mixtures do seem to become unstable for  $r_{\text{large}}/r_{\text{small}} > 5$  at sufficiently high volume fractions. A direct experimental test of the predictions of Biben and Hansen [3] is obviously not an easy task as hard-sphere atoms do not exist in reality. However, nowadays one can prepare (almost) monodisperse spherical colloidal particles whose short-ranged harshly repulsive interparticle forces closely approximate that of hard spheres [5,6]. It can be shown that the thermodynamic properties of such suspensions are the same as those of the hypothetical hard-sphere atomic system [7]. A detailed discussion of colloid-atom analogies has been given recently by Pusey [8].

The purpose of this letter is to investigate experimentally the limits of stability of a binary hard-sphere mixture as a function of the two particle concentrations using a bimodal dispersion of colloidal particles. So far experiments on binary mixtures of colloidal particles have focused mainly on the fluid-solid phase separation. In particular the structure of the solid phase has been studied for size ratios  $r_{\text{large}}/r_{\text{small}} < 3$  as a function of concentration [9,10]. Even though not directly pertaining to hard-sphere mixtures, we mention that a strong fluid-solid phase separation indicating an effective attraction between the large particles has been observed in mixed aqueous dispersions of surfactant micelles as the small spheres and latex particles [11] or oil droplets [12,13] as the large particles. Here the size ratio is of order 100. Recently Sanyal *et al.* [14] specifically addressed the stability of binary

hard-sphere fluids using aqueous dispersions of charged latex particles with  $r_{\text{large}}/r_{\text{small}} = 5$ . After the samples had been left for a few days to settle, they observed flocculation of the large particles using an optical microscope. From this observation they conclude that a phase separation had occurred.

In this study we use a bimodal dispersion ( $r_{\text{large}}/r_{\text{small}} = 6$ ) of silica particles sterically stabilized with octadecyl alcohol in cyclohexane. In monodisperse suspensions of this kind the behaviour of the particles can be modelled with a hard-sphere interaction [6]. At volume fractions  $\phi_{\text{small}}$  between 0.25 and 0.35 and  $\phi_{\text{large}}$  between 0.05 and 0.20 both visual observations and small-angle light scattering experiments provide evidence that a phase separation occurs. Whereas the upper phase, rich in small particles, definitely has a fluid character, it could not be determined unambiguously whether the lower phase, rich in large particles, is fluid or solid. The results are compared with theoretical predictions [3].

*Experimental.* – Two batches of silica particles were prepared and subsequently coated with octadecyl alcohol using the method described in ref. [15]. Purification was carried out by repeated centrifugation of the particles followed by redispersing in cyclohexane (analytical grade). The particles were characterized by static and dynamic light scattering and by electron microscopy. The results are summarized in table I.

Static-light-scattering measurements of dilute dispersions (about 0.1 per cent by weight) were made on a FICA 50 photometer (Société Française d'Instruments de Contrôle et d'Analyse). For the small particles the data could be analysed using a Guinier fit [16]. The radius of the large particles could not be easily measured because they have nearly refractive index matched in cyclohexane, so the form factor becomes distorted due to optical inhomogeneity of the particles [17]. We therefore determined the radius of the uncoated particles in ethanol, from the location of the first minimum of the form factor. This value, which is presented in table I, is expected to be a few nm smaller than that of the coated particles.

Dynamic-light-scattering measurements were made using a Spectra Physics Model 2025 argon ion laser ( $\lambda = 514.5$  nm) and a Malvern K7025 correlator (128 channels). The data were analysed using the method of cumulants [18].

Electron microscopy was carried out using carrier grids covered with a formvar film coated with carbon in a Philips Model CM 10H transmission electron microscope. An image analysis system was used to obtain particle size distributions from the micrographs. The particle radii as determined by electron microscopy are seen to be significantly smaller than those determined by light scattering. This phenomenon is quite common. It can be explained in part by the fact that different moments of the particle size distribution are probed by the different techniques [19]. Furthermore the particles are thought to shrink under the conditions present in the microscope. Using the radii obtained with static-light scattering, the size ratio  $r_{\text{large}}/r_{\text{small}} = 6.1$ .

TABLE I. – *Particle characterization.*

Property	Unit	Small particles	Large particles
Laboratory code		SV25	SHE3(0)S
Particle density	g/ml	$1.59 \pm 0.02$	$1.807 \pm 0.004$
Radius – static-light scattering	nm	35	212
– dynamic-light scattering	nm	$32 \pm 4$	$231 \pm 9$
– electron microscopy	nm	19	186
Polydispersity		0.14	0.05

Dispersion densities were determined by weighing 25 ml in a volumetric flask calibrated against cyclohexane. The concentration (dry mass) of both dispersions was about 0.2 g/g, as determined by drying a known amount of dispersion under a dry nitrogen flow at 90 °C until constant weight. From these data the particle densities and volume fractions were calculated.

Samples were prepared in tubes of 1 cm diameter and 5 cm height closed with a screw cap. After the preparation samples were concentrated by forced evaporation of the solvent under a nitrogen flow. The moment particles started to dry against the cell wall, the evaporation was interrupted, and the sample shaken vigorously.

Eleven samples were prepared at different volume fraction ratios  $\phi_{\text{small}}/\phi_{\text{large}}$ . Two caveats should be made here. First, the uncertainties in the densities amount to uncertainties in the volume fractions of a few per cent. Second, various ways exist to estimate the particle volume fraction and the results may differ significantly. For instance, one may also use the specific volume as determined from rheological measurements [20]. However, this will not alter the overall shape of the phase diagram that is obtained here.

For small-angle light scattering measurements, some samples were transferred into rectangular quartz cuvettes 1 cm wide with an optical path length of 2 or 5 mm. A simple set-up was made to probe the intensity scattered at small angles. Light from a 10 mW He-Ne laser ( $\lambda = 632.8$  nm) was expanded to illuminate about 1 cm<sup>2</sup> of the sample. The transmitted light was focused and a 1.5 mm pinhole in the focal plane of the lens was used to block the primary beam and select light scattered at small angles. This light was focused again onto a photo diode, the output of which was recorded. In this set-up the scattering angle is ill-defined. A typical angle would be 0.5°, corresponding to a scattering vector  $q = 10^5$  m<sup>-1</sup>.

*Results.* – Most samples were studied only by visual inspection. When the large particles cluster, either in a floc or in a droplet of the concentrated phase, the resulting aggregate of particles will sediment more quickly than in the case where the system remains stable. A sudden change of sedimentation velocity with sample concentration therefore signals an instability. However, in some cases it was very difficult to discern the sedimentation boundary. Small-angle light scattering was then used to study the clustering of large particles. Since particle scattering in the forward direction is proportional to  $r^6$  [16], small-angle scattering is mainly due to large particles and it will increase when these particles aggregate. Indeed this method proved to be very useful in discriminating stable samples from unstable ones.

The observations are summarized in fig. 1. For clarity a division into three regions is made: region *A* with  $\phi_{\text{small}}/\phi_{\text{large}} > 7$ , region *B* with  $1.4 < \phi_{\text{small}}/\phi_{\text{large}} < 7$  and region *C* with  $\phi_{\text{small}}/\phi_{\text{large}} < 1.4$ . In regions *A* and *C* the large particles are seen to sediment very slowly (typically less than 1 mm/day) and light scattering shows no evidence for instability. In region *B* the behaviour is similar at low concentrations. At higher concentrations the samples become unstable as can be concluded from the large increase of small-angle light scattering within an hour. Depending on the concentration this is accompanied either by a rapid formation of a sediment on the bottom of the sample or by a rapidly moving sedimentation boundary (about 1 mm/hour) leaving the supernatant almost clear. At still higher concentrations two samples seemed to become stable again. The sequence of phenomena observed on increasing concentration is illustrated in fig. 2 for a sample with  $\phi_{\text{small}}/\phi_{\text{large}} = 4.3$ . In some cases we observed that a sample that was unstable at first became stable after a few days. Sonicating the sample for a few minutes then sometimes brought back the instability.

When phase separation occurs it would be very interesting to know the nature of the different phases and their respective concentrations. Experimentally it is very difficult to

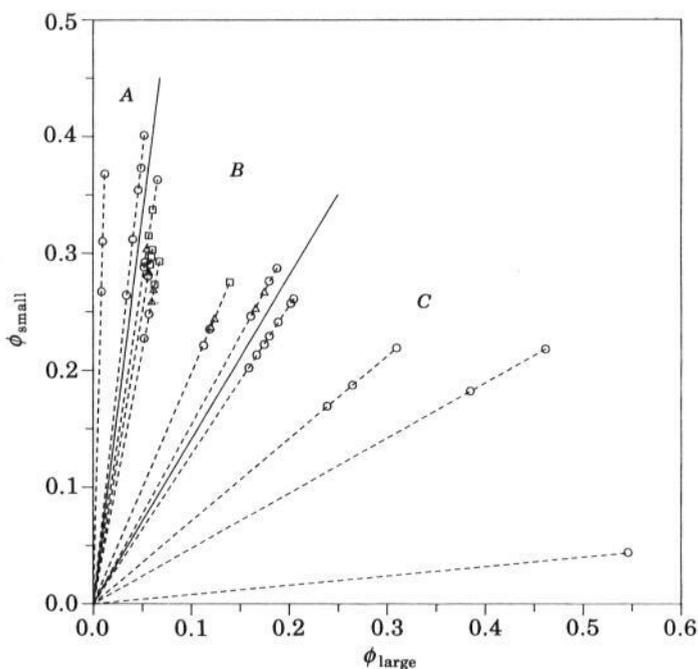


Fig. 1. - Phase behaviour of mixtures of large spheres and small spheres with  $r_{large}/r_{small} = 6$ . Meaning of the symbols: ○ slow sedimentation of the large spheres, △ a sediment is formed rapidly but the supernatant remains turbid, □ rapid sedimentation leaving the supernatant almost clear. The dashed lines connect experiments done on the same sample, by dilution or concentration. The regions A, B and C, separated by full lines, are discussed in the text.

obtain such information, as the large particles always sediment and the equilibrium situation is modified by the gravity field. However, a few remarks can be made. The sediment that was obtained was always rather fluid. Even after a few days it would be more easier to redisperse than a sediment in a sample without small spheres. The presence of small spheres in the sediment could account for this phenomenon [21, 22]. In a sample without small spheres

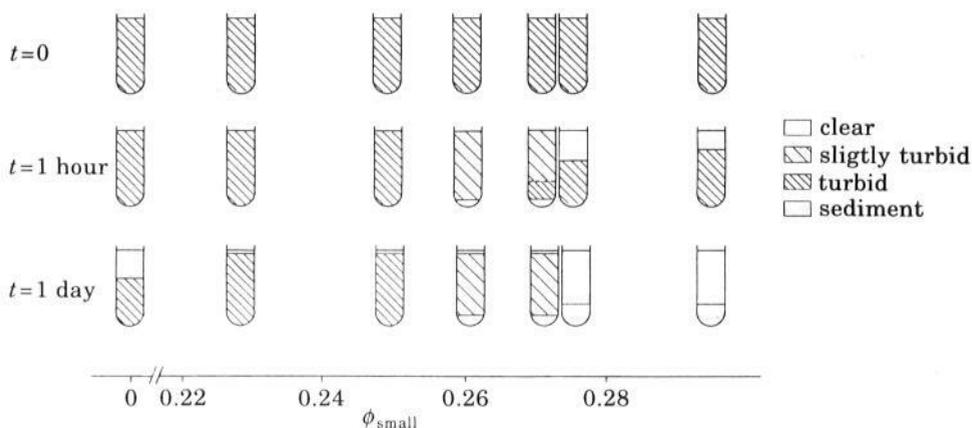


Fig. 2. - Sedimentation behaviour at  $\phi_{small}/\phi_{large} = 4.3$  as a function of concentration and time. At  $\phi_{small} = 0$  a sample with large spheres only is sketched.

an amorphous sediment is formed first, from the top of which crystallites start to grow after a few days. In the sediment formed in the presence of small spheres crystals grow in the course of a few weeks. The crystallization then proceeds to fill the whole sediment. This is probably due to the increased fluidity of the sediment. In all samples the supernatant was found to contain a large number of small particles, since a cake of particles was formed quite rapidly against the cell wall as soon as a sample was concentrated by evaporation of solvent.

*Discussion.* – The data we present here suggest that a phase separation is actually occurring. The fact that dilution of the sample is always seen to result in a sudden disappearance of the instability indicates that it is not due to an irreversible aggregation.

The instability occurs in a fairly narrow concentration range, at volume fractions  $\phi_{\text{small}}$  between 0.25 and 0.35 and  $\phi_{\text{large}}$  between 0.05 and 0.20. These figures agree qualitatively with the available predictions of Biben and Hansen [3] for a diameter ratio of 10. However, from their work it is expected that the instability would extend both to low and to high values of  $\phi_{\text{large}}$ , which is clearly not the case here. It should be stressed that our experiments are concerned with the behaviour of the samples during the first few hours. After this, sedimentation becomes important even in stable samples. Therefore we only observe instabilities that manifest themselves within a few hours. It may be that the phase separation kinetics becomes slow outside region *B* where  $\phi_{\text{small}} = \phi_{\text{large}}$  and within region *B* at larger concentrations. We were unable to determine whether the initially formed concentrated phase is a stable colloidal fluid or a metastable fluidlike or glassy suspension. The crystallization observed over a few weeks could be either the result of the slow concentration-dependent kinetics of formation of colloidal crystals from a supersaturated fluid [23] or could be caused by densification to the freezing point due to sedimentation.

As was mentioned above, we sometimes observed that a sample which initially showed an instability became stable after a few days. We hypothesize that this may have been due to some of the small particles sticking to large particles. Similar particle mixtures have been observed to show a slight attraction between unlike particles [24]. From electron micrographs we conclude that irreversible aggregation of particles does not take place in our mixtures. However, the presence of attractions should be expected to modify the phase diagram to some extent.

In summary we claim to have observed a phase separation in bimodal dispersions of sterically stabilized silica particles. This supports the prediction of an instability in hard-sphere mixtures [3]. Further work is needed to establish why the instability is observed only in a narrow concentration range.

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