PHASE SEPARATION OF STERICALLY STABILIZED COLLOIDS AS A FUNCTION OF TEMPERATURE

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Colloidal dispersions of sterically stabilized silica spheres in toluene are found to separate into two layers when the temperature drops below a certain threshold. The phase diagram shows a dependence on the overall concentration. The behaviour of the dilute phase compares with theoretically calculated binodals using polydispersity in the polymer-like attraction. For the concentrated phase no agreement is obtained.

1. Introduction

In previous papers we reported on the "hard-sphere" properties of colloidal silica particles in non-polar solvents [1,2]. The particles are sterically stabilized by a protective layer of octadecyl chains, attached terminally to the surface [3]. The solvents used were cyclohexane, cycloheptane and chloroform. These solvents are "good" solvents; the dispersions are stable at temperatures ranging from 5 to 40°C and some of them have already been stored for several years.

The quality of the solvent is connected with the fact that it has a tendency to solvate the octadecyl chains on the particle surfaces. When the octadecyl chains prefer contacts with solvent molecules to contacts with other chains (from different particles), the free energy will increase when two particle surfaces approach each other and both layers of protective chains attempt to interpenetrate. This results in a repulsive potential which, because of the small interpenetration depths, will be steep and therefore mimic a so-called "hard-sphere" interaction. Similar mechanisms work in polymer solutions and in dispersions of colloids stabilized with polymers [4,5].

On the other hand, it can be expected that less good solvents will induce attractive forces upon inter-particle contacts, i.e. the octadecyl chains prefer contacts with each other to contacts with solvent molecules and are thus less soluble. Examples of "bad" solvents are the lower alcohols and acetone.

Another way of influencing the quality of the solvent is to change the temperature. In some solvents in fact we found that the dispersions became unstable and showed a strong increase in turbidity when the temperature was decreased below a certain threshold. For the following solvents these temperatures were approximately (for a dispersion of 5% w/w): benzene 40°C, toluene 10°C, and xylene less than −10°C. The phenomenon is reversible, i.e. increase of temperature results, after mixing, in restabilised dispersions. Polymer systems behave in a similar way: poly-isobutylene, e.g., a polymer with alkane groups, is perfectly soluble in cyclohexane, but becomes insoluble in benzene below room temperature. The solvation balance can be a very delicate matter because the interaction (free) energy per particle should be compared with the thermal energy kT. In the case of large colloidal particles the number of interchain contacts may be large, so slight differences in the chemical nature of the solvent may already lead to differences in stability.

We think that the London–van der Waals forces between the silica cores of the particles play a minor role, for large particles with a diameter of 300 nm are stable in cyclohexane (for such a system even colloidal crystals were observed). The weakness of this force is probably connected with the fact that the refractive

index of the silica particles (n = 1.45) is comparable to the refractive index of many non-polar solvents [6].

2. Theory

As a result of lowering the temperature the original dispersion separates into a dilute and a concentrated phase. An equilibrium between these phases can be described by the thermodynamic potential of the particles, μ_2, and of the solvent, μ_1. Instead of the thermodynamic potential of the solvent the osmotic pressure can be used. For spheres with a small attraction we use for the osmotic pressure Π as a function of volume fraction ϕ:

$$\Pi \frac{V_{\mathrm{HS}}}{kT} = \frac{\phi + \phi^2 + \phi^3}{(1-\phi)^3} - \gamma\phi^2 . \tag{1}$$

This is an equation analogous to the "van der Waals equation". The first term of the right-hand side is the hard-sphere contribution in the Percus–Yevick approach. The second term describes the attraction via the dimensionless parameter γ. V_{HS} is the volume of the hard sphere, k the Boltzmann constant and T the absolute temperature. The thermodynamic potential μ_2, at constant μ_1, can be derived from eq. (1) ‡

$$\mu_2/kT = \mu_2^{\theta}/kT + \ln\left(\frac{\phi}{1-\phi}\right) + \frac{\frac{5}{2} - \frac{1}{2}\phi + \phi^2}{(1-\phi)^3} - 2\gamma\phi . \tag{2}$$

In the same way as is done for polymers we write for γ [8]:

$$\gamma = A(\theta/T - 1), \tag{3}$$

where θ depends on the type of chains on the particle, and on the solvent used. The value of A will depend on the size of the particles and on the interpenetration depths of the protecting layers.

If polydispersity (that can refer not only to size but also to the attraction parameter γ) is introduced the relations become more complex [9].

‡ For μ at constant pressure, see ref. [7].

$$\Pi \frac{\pi}{6kT} = \frac{\xi_0}{1-\xi_3} + \frac{3\xi_1\xi_2}{(1-\xi_3)^2} + \frac{3\xi_2^3}{(1-\xi_3)^3} - \sum_{i,j} \gamma_{ij}\phi_i\phi_j(d_i d_j)^{-3/2} . \tag{4}$$

$$\mu_i/kT = \mu_i^{\theta}/kT + \ln\left(\frac{\phi_i}{1-\xi_3}\right) + \frac{d_i^3\xi_0 + 3d_i^2\xi_1 + 3d_i\xi_2}{1-\xi_3} + \frac{3d_i^3\xi_1\xi_2 + \frac{9}{2}d_i^2\xi_2^2}{(1-\xi_3)^2} + \frac{3d_i^3\xi_2^3}{(1-\xi_3)^3} - 2\sum_j \gamma_{ij}\phi_j(d_i/d_j)^{3/2} . \tag{5}$$

$$\xi_\nu = \sum_i \phi_i d_i^{\nu-3} , \tag{6}$$

$$\gamma_{ij} = (\gamma_{ii}\gamma_{jj})^{1/2} . \tag{7}$$

Here d_i is the diameter and ϕ_i is the volume fraction of the spheres i. Polydispersity in the value of A may not only be caused by polydispersity in particle size. Because the interpenetration depth of the protecting layers is very small with respect to the average particle radius, the value of A becomes sensitive to the local variations in interpenetration in the mutual contact area. Therefor the magnitude of A may vary from particle to particle due to small local dents and hillies on the particle surface. In order to study the effect of polydispersity we consider for simplicity's sake two types of particles with the same radius but with a different prefactor A (namely A_{11} = 150 and A_{22} = 266). The temperature θ is taken as 300 K. Equal volume fractions of both types of particles are taken. Some calculated phase diagrams are presented in fig. 1. Also plotted in fig. 1 are the cloud-point curve (i.e. the temperature at which the onset of separation occurs when a dispersion of given volume fraction is cooled, plotted against this volume fraction) and the so-called shadow curve [10] (i.e. the cloud-point temperature plotted against the volume fraction that separates at the cloud-point curve).

From fig. 1 it can be seen that the phase diagrams in a polydisperse system are a function of the total volume fraction, in contrast to a one-particle system. For a given total volume fraction eqs. (4), (5), (6) and (7) can lead to solutions for which the volume of one

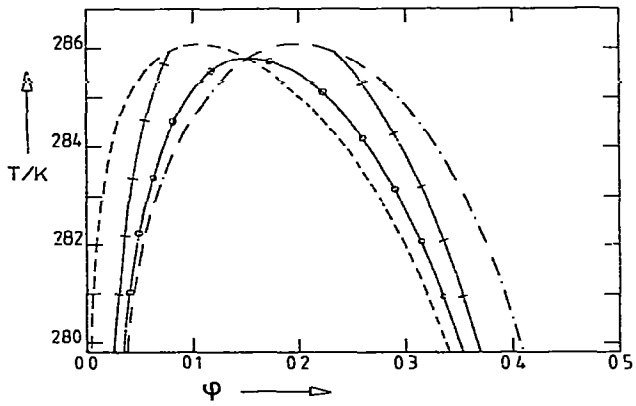

Fig. 1. Theoretical phase diagrams for the overall volume-fractions of 0.08 (+—+) and of 0.155 (–o–o–). The cloud-point curve (– – –) and the shadow curve (-.-.-) are plotted also.

of the phases is negative. This is merely a result of keeping the overall volume fraction constant. If the solution will be realistic, then it is impossible for both phases to have volume fractions greater than the overall volume fraction. Therefore the calculated phase line ends where it crosses the abscissa value of the given overall volume fraction.

3. Characterization

Phase separations in a dilute and a concentrated phase were measured using a system of particles which have been characterised as follows: The particles have a radius of 48 ± 1 nm measured with P.C.S. in cyclohexane (a good solvent) and a standard deviation in size of 13% (measured with electron microscopy). From elemental analysis we calculate that the particle is coated with 10.4% organic material and from that we calculate that the surface coverage is 0.15 nm^2 per octadecyl chain. The specific interaction volume q ($\phi = qc$) lies in the range 0.6–0.8 $cm^3\ g^{-1}$ [1,2].

4. Experimental

Solutions are made and experiments performed as follows. Dried (80°C in an N_2 atmosphere) silica particles are weighed in calibrated cylindrical cuvettes and a weighed amount of toluene is added. The cuvettes are closed with a screw-cap with a teflon-coated liner. The cuvettes are cooled in a thermostatically controlled waterbath to the desired temperature at a rate of 1°C/h. When the temperature is low enough the samples are found to have separated into two parts with a more or less sharp interface between the two phases. After a few hours phase separation is complete and the samples are allowed to attain room temperature (25°C) outside the waterbath. It was observed that up to 5°C above the phase-separation temperature (i.e. still in the stable region) the turbidity of the samples was much higher than at 25°C. This effect is attributed to the still considerable attraction of the particles. The two phases do not mix unless they are shaken and their respective concentrations are determined as follows. The turbidity of the dilute phase is measured (at 25°C) and with the aid of a calibration curve (measured at 632 nm; $\tau_{max} \approx 300\ m^{-1}$) the concentration of this phase is found. The height of the concentrated phase is measured and from this the volume is obtained. Knowing this volume, the total amount of silica and the concentration of the dilute phase one can calculate the concentration in the concentrated phase. This concentration cannot be measured by turbidity, since the calibration curve at these concentrations is too flat and shows a maximum. It was observed that in the dilute phase some of the silica stuck to the wall of the cuvettes but upon warming became detached and settled. It is likely that some of this silica was dissolved in the dilute phase, although it

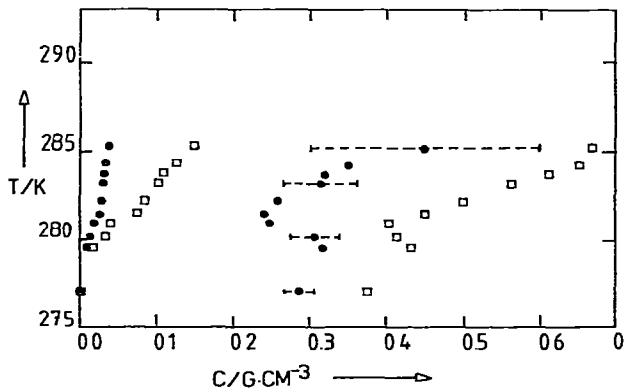

Fig. 2. Experimental phase diagrams for the concentration 0.05 (•) and 0.21 g cm^{-3} (□). Note the large errors in the concentration of the concentrated phase (drawn in a few points only).

apparently belongs to the concentrated phase. Therefore the samples were cooled a second time. When this was done the concentrated phase decreased in volume, reflecting the fact that this phase had not reached its equilibrium after one cooling cycle. A third cycle did not cause a further decrease in the volume of the concentrated phase. The measured concentrations of the dilute phase did not change (within experimental error) after the second cooling cycle. Some results for total concentrations 0.05 and 0.21 g cm^{-3} are presented in fig. 2.

5. Discussion

From fig. 2 it can be seen that the phase diagrams for the two overall concentrations (and for the other concentrations measured also) do not coincide. This is thought to be an effect of polydispersity, such as is found with polydisperse polymers [10]. The dilute phase behaves more or less as expected from the theoretical calculations (fig. 1). In spite of the large errors in the determination of the concentration of the concentrated phase it is clear that this branch of the phase diagrams is rather dissimilar to the theoretical curves. At a given overall concentration the concentration at high temperatures is higher than at low temperatures. Also the order of the curves is reversed (high overall concentration gives a higher concentration than a low total concentration).

One of the reasons for this observed behaviour may be that fractionation by size occurs and therefore turbidity does not give the correct concentration. In principle our calibration curve cannot be used to determine the concentration because the degree of fractionation is dependent on the temperature and on the total concentration. Calculations (including fractionation) of the phase separation can be used to estimate the errors that arise if turbidity is used as an estimate of concentration. Only if it is assumed that the larger particles are more soluble than the smaller ones, can the observed behaviour be explained. But we have observed that the dilute phase is enriched with the smaller particles.

Another reason for the observed behaviour of the concentrated phase may be the strong attractions between the particles at low temperature. When the attraction is larger than say a few kT the particles adhere to each other rather strongly. In the concentrated phase they build a loose (gel-like) structure which attains equilibrium only very slowly. The volume of this phase is therefore too large and the concentration too low compared with the equilibrium values. This is also reflected in the decrease of the volume of the concentrated phase during the second cooling cycle.

It will be clear that several problems remain to be solved. We thought however that it is worthwhile to report the observed phenomena at an early stage.

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