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Phase separation in mixtures of organophilic spherical silica particles and polymer molecules in good solvents

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Introduction

About 25 years ago Asakura and Oosawa (1, 2) pointed to the possibility of the occurence of instabilities leading to flocculation or to phase separation in mixtures of colloidal particles and polymer molecules dispersed in a single (theta) solvent. In proximity of an impermeable (particle) interface the polymer molecules lose configurational entropy. As a result of this "volume restriction" effect (3) the polymer molecules are expelled from the neighbourhood of the particles which thus are surrounded by a depletion zone with a polymer concentration substantially lower than the bulk concentration of polymer. The free energy of the system therefore is increased. The system has the possibility of decreasing its free energy by grouping together the colloidal particles, therewith decreasing the effective depletion area. This can result in phase separation or flocculation of the particles. In 1976 one of us (4) also predicted the phenomenon of instability in mixed colloidal systems, using essentially the same arguments as Asakura and Oosawa, but a somewhat different approach. It was shown that phase separation or flocculation in dilute colloidal dispersions were to be expected at a polymer concentration of a few percent, depending on the molar mass of the polymer used. In the theory the magnitude of the effective attraction between the colloidal particles is proportional to the osmotic pressure exerted by the polymer molecules in solution; the range of the attraction is comparable to the diameter of the macromolecules (about two times the radius of gyration). Recently, instabilities in good solvents were suggested by De Gennes et al. (5,6), who used a mean field theory or, alternatively, scaling concepts.

To date not much direct experimental evidence for the validity of the theories has been published. Vincent et al. (7,8) reported flocculation of polyethylene oxide stabilized latices in aqueous solution (good solvent) containing free polyethylene oxide molecules above some critical concentration of polymer. At very high polymer concentrations a restabilization of the colloidal particles was observed. The results were explained with an approximate theory (9) in which the difference in the interaction free energy (contact energy plus mixing entropy) of the system before and after flocculation was considered. The restabilization could not be explained satisfactorily, however. Very recently Feigin and Napper (10, 11) proposed a theory which accounts for the flocculation of particles at intermediate polymer concentrations, as well as for the restabilization at high polymer concentrations. According to this theory, which is valid for good solvents the restabilization is a kinetic phenomenon caused by the presence of a maximum in the two-particle interaction energy versus distance curve.

In two publications (12, 13) we reported liquid-liquid phase separations in mixtures of organophilic silica particles and polystyrene in cyclohexane at the theta temperature (34.5°C). At a fixed silica concentration (1 or 5% w/v) phase separation was observed above some limiting concentration of polystyrene (1 to 12% w/v) which depended on the molar mass of polymer (mass averaged molar masses from 8×10^3 to 1.9×10^6 g mol^{-1}). It was found that the limiting concentration, c_{lim}, decreased with increasing molar mass of polymer. The results were explained with the theory of Vrij (4) which was worked out numerically (13). In this note we report the results of phase separation experiments on mixtures of organophilic silica and polymers in good solvents at 25 °C.

Materials

We have used three different samples of silica; sample I and sample II are silica particles coated with a chemically bound layer of stearylalcohol molecules and sample III consists of silica particles sterically stabilized with poly-isobutene. Sample I was dispersed in toluene in the presence of polystyrene as a free polymer, and samples II and III were dispersed in cyclohexane in the presence of polyisobutene. Table 1 shows the experimental systems used in this study.

Monodisperse, spherical silica particles coated with stearyl alcohol chains were prepared as described in literature (14–16). Silica particles sterically stabilized with polyisobutene ($\bar{M}_n \approx 1.3 \times 10^3$ g mol^{-1}) were prepared following the procedure described earlier (17). The different silica samples were characterized with light scattering fluctuation spectroscopy. The hydrodynamic radius, obtained from the measured diffusion coefficient using the Stokes-

Table 1. Experimental systems used

System code	solvent	silica sample	particle coating	free polymer
A	toluene	I	stearylalcohol	polystyrene
B	cyclohexane	II	stearylalcohol	polyisobutene
C	cyclohexane	III	polyisobutene	polyisobutene

Table 2. Limiting phase separation concentrations, c_{lim}, obtained with system A

Polymer code	PS 1	PSR 1	PS 3	PS 6	PS 7
$\bar{M}_m$/kg mol^{-1}	8	46	82	637	1900
$\bar{M}_m/\bar{M}_n$	1.0	1.3	1.2	2.8	4.3
c_{lim}/g dm^{-3}	30±2	19±1	12±1	4.1±0.5	4.0±0.5

Table 3. Limiting phase separation concentrations, c_{lim}, obtained with systems B and C

Polymer code		PIB 1	PIB 2	PIB 3	PIB 4	PIB 5	PIB 6	PIB 7
$\bar{M}_m$/kg mol^{-1}		21	78	122	176	490	698	1800
$\bar{M}_m/\bar{M}_n$		3.2	2.1	2.0	2.7	4.5	5.1	5.7
c_{lim}/g dm^{-3}	B	37.3±0.4	16.4±0.2	15.7±0.2	13.0±0.2	9.5±0.1	7.5±0.1	6.4±0.1
	C	not found	106±1	36±1	47±1	19.5±0.5	12.5±0.2	9.8±0.1

Einstein equation proved to be 33 nm for sample I, 27 nm for sample II, and 39 nm for sample III. The angular dependence of the measured diffusion coefficient as well as the angular dependence of the scattered intensity measured with conventional light scattering showed that the particles were reasonably monodispersed.

We have used five samples of polystyrene, three of which were obtained from Pressure Chemical Company (PS 3, PS 6, and PS 7). Two samples (PS 1 and PSR 1) were prepared in our laboratory with anionic polymerization. Seven polyisobutene samples were used. Four samples (PIB 3, PIB 4, PIB 6, and PIB 7) were kindly supplied to us by Dr. A. Schuller of BASF and two samples (PIB 1 and PIB 2) by Dr. E. L. Neustadter of British Petroleum. One sample (PIB 5) was obtained from Aldrich Chemical Company. All polymer samples were characterized with gel permeation chromatography in tetrahydrofuran. The results (mass averaged molar masses and $\bar{M}_m/\bar{M}_n$ values) can be found in tables 2 and 3.

Methods

Solutions of silica and polymer were pipetted accurately from stock solutions into a specially shaped test tube with a narrow lower part facilitating the detection of small amounts of demixed fluid phase at the bottom. The silica concentration was kept constant at 1% (w/v) whereas the polymer concentration was varied. The concentrations of silica and polymer were calculated from the densities and concentrations (determined by drying until constant weight at 60°C and 1 Torr) of the stock solutions and the amount of dilution. After pipetting the required amounts of silica, polymer and solvent, the tube was tightly closed and the

solution was thoroughly mixed. The solutions were allowed to stand at 25 °C and were visually inspected for at least 72 hr.

Results and discussion

Immediately after mixing, the solutions of polymer and silica were transparant with the exception of solutions having a polymer concentration much higher than the limiting concentration (defined below). These solutions were turbid. After some time depending on the polymer concentration used (usually within two hours), solutions with a polymer concentration above the limiting concentration became turbid. The turbidity, which was hardly or not visible at polymer concentrations very close to c_{lim} (defined below), increased with increasing polymer concentration. All turbid solutions eventually separated into two fluid phases. The lower phase was rich in silica and the upper phase rich in polymer. The volume of the lower phase initially increased with increasing polymer concentration but was constant at higher polymer concentrations (about one tenth of the total volume). Phase separation in these systems is a reversible phenomenon: upon gentle shaking the two fluid phases readily mixed, yielding a transparent solution provided that the initial polymer concentration was not too much above the limiting phase separation concentration. With higher polymer concentrations mixing yielded a turbid solution as could be expected from the observations made in preparing the silica-polymer mixtures. On standing the solutions again showed phase separation.

The limiting phase separation concentration, c_{lim}, was defined as the concentration of polymer above which phase separation could be observed 24 hr after mixing. It was

determined accurately by preparing several series of silica-polymer mixtures with polymer concentrations very close to each other. The experimental results are given in tables 2 and 3. It is evident that in all cases c_{lim} decreases with increasing molar mass of the polymer, which was also found in our previous experiments (12, 13). The c_{lim} values of polystyrene, obtained with the stearylalcohol coated silica sample I dispersed in toluene (System A) can directly be compared with the c_{lim} values obtained earlier in the system silica, polystyrene and cyclohexane at the theta temperature (12, 13). In the good solvent toluene the limiting phase separation concentrations prove to be lower by a factor of about 3. This can probably be attributed to the increase in the osmotic pressure (positive second virial coefficient) and in the effective size (swelling) of a polymer in a good solvent. As a result both the magnitude and the range of the effective attraction between colloidal particles in a dispersion of polymer molecules in a good solvent is increased compared with a theta system. The results obtained with polyisobutene as free polymer (systems B and C) can not be directly compared with the results of our previous studies (polystyrene in cyclohexane). The very strong molar mass dependence of the c_{lim} obtained with the polyisobutene stabilized silica sample III (system C) however, was also found with polystyrene as the free polymeric component (13). Silica particles stabilized with relatively long polymer chains thus seem to be more stable than particles coated with short stearylalcohol molecules.

Feigin and Napper (10, 11) predicted another limit concentration of polymer above which the stability of the colloidal particles is *kinetically* restored. We have performed some experiments with silica sample II at high (10 to 20% w/v) polyisobutene (PIB 3) concentrations in cyclohexane in order to verify their prediction. Because of the high viscosity the concentrated polymer solutions were difficult to handle and final concentrations could not be calculated accurately. Contrary to the findings of Vincent et al. (7, 8) we did not observe a restabilization; in all cases the system showed phase separation.

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