Electronic Supplementary Information (ESI)

Suppression of Self-Stratification in Colloidal Mixtures with High Péclet Numbers

M. Schulz,[a] R. Brinkhuis,[b] C. Crean,[c] R. P. Sear,[a] J.L. Keddie[a]

[a]Department of Physics, University of Surrey, Guildford, Surrey, GU2 7XH, UK

[b]Allnex, Nieuwe Kanaal 7N, 6709 PA Wageningen, The Netherlands

[c]Department of Chemistry, University of Surrey, Guildford, Surrey, GU2 7XH, UK

Materials

We performed experiments using a model system consisting of waterborne colloidal dispersions (*i.e.* latex) with two different mean particles sizes and a thickener. Table S1 provides an overview of the characteristics of the three components. The smaller colloid was a polyurethane latex containing aromatic moieties (provided by Allnex) with a number-average particle diameter of 28 nm. Its as-received solids content was 38 wt.%. The large colloid was an acrylic copolymer latex made from monomers of methyl methacrylate (MMA), butyl acrylate (BA) and methacrylic acid (MAA) in an MMA:BA:MAA mass ratio of 18.3:13.3:1. Its number-average particle diameter was 160 nm, and its initial solids content was 52 wt.%. It was synthesized via emulsion polymerization using an anionic, ethoxylated alcohol surfactant.[1] To avoid negative effects on stratification, we chose a *non-associative* thickener based on an alkali-swellable emulsion (ASE) polymer, which thickens through volume exclusion rather than by forming a gel network.[2,3] This ASE thickener is sold commercially as Acrysol™ ASE-60ER (Dow Chemical). It consists of a copolymer of methacrylic acid and acrylate ester in a near 1:1 ratio. The thickener contained 28 wt.% of the active copolymer component in water, supplied in an acidic state. All three blend components were negatively charged and were colloidally stable when mixed. The hydrodynamic size and polydispersity index (PDI) of the colloids were measured with dynamic light scattering (Malvern Panalytical Zetasizer), as shown in Figure S1. The ASE particles swelled to diameters >300 nm under alkaline conditions.

Table S1. Characteristics of Colloids

Particle type	Chemical composition	Glass transition temperature[a] (°C)	Initial Solids content (wt.%)	Hydrodynamic radius, R_H (nm)	PDI
Large, L	PMMA-BA-MAA	38	52	80	0.02
Small, S	Polyurethane	16	38	14	0.4

[a]Glass transition temperature is the midpoint value obtained from differential scanning calorimetry (Q1000, TA Instruments) on a second heating at 10 °C/min..

Experiments

We prepared a mixture with an initial total volume fraction of colloids of ϕ_{TOT} = 0.3 and a 1:2 volume ratio of the small and large colloid. Thus, the volume fraction of the smaller colloid was fixed at ϕ_S = 0.1. The dispersions were mixed on a tube roller (Cole-Palmer^{TM} Stuart^{TM}) for several hours and then used in some experiments. Two other mixtures were made with thickener added at concentrations of 1 vol.% and 2 vol.% (based on the total volume of the dispersion), with volume fractions of ϕ_T = 0.01 and 0.02, respectively. The volume fraction of the thickener in the continuous phase is given as ϕ_{CP} = $\phi_T/(1 - \phi_{TOT})$. The pH of the thickener solution was raised to 12 with NaOH when mixing with the colloids.

To achieve a range of Pe, the drying temperature was varied from room temperature to 60 °C, by placing the wet film on a heating stage (TP93, Linkam Scientific, UK). The resulting evaporation rates of water at each temperature were measured using a digital balance, as described previously. The initial film thickness, H, was varied between 300 μm and 1 mm by spreading an appropriate volume across the substrate (silicon (100) wafers treated in a UV ozone cleaner (Bioforce Nanosciences Inc.) for 20 min. to increase the hydrophilicity.

For the calculation of D_S, the viscosity of solutions of the ASE thickener in water was measured using a shear rheometer (TA Discovery HR2, Newcastle, DE, USA) fitted with a cone and plate geometry. The cone angle was 2°, and the plate had a 40 mm diameter. Three to five measurements for each concentration were performed, as the shear rates was varied from 0.1 to 100 s^{-1} at a fixed temperature of 30 °C. The pH of the solutions was adjusted by adding concentrated NaOH. The measured viscosity values were used in the calculation of the diffusion coefficient via the Stokes-Einstein equation.

We analysed the films using Raman spectroscopic mapping after cutting cross-sections using an ultra-low angle microtome (ULAM) as described in our previous publication.[4] First, a diamond scribe was used to cut the samples in half to exposed middle region of the samples and to avoid edge-effects. The films were microtomed using a motorized rotary device (MICROM 355S, Optech Scientific Instruments, UK) having a tungsten carbide knife. To prepare sliced surfaces, we followed the procedure by Hinder *et al.*,[5,6] except that we used a slightly larger cutting angle of 2° to broaden the region of observation. According to a simple

geometric calculation, the cross-sectional view was magnified by a factor of $1/\sin(2°) = 28.6$ in comparison to a cross-section cut normal to the surface.

Table S2. Experimental Parameters[a] to Achieve a Range of Pe

Thickener Volume fraction, ϕ_T	T (°C)	H (µm)	η (Pas)[b,c]	Pe	Stratified?
0	60	1000	4.7×10^{-4}	15	yes
0	40	1000	6.5×10^{-4}	8	yes
0	40	750	6.5×10^{-4}	6	intermediate
0	40	500	6.5×10^{-4}	4	no
0.01	60	1000	0.055	1740	intermediate
0.01	40	1000	0.055	630	intermediate
0.01	40	750	0.055	480	no
0.01	40	500	0.055	320	intermediate
0.01	40	300	0.055	190	intermediate
0.01	30	500	0.055	250	yes
0.01	30	300	0.055	150	yes
0.01	20	300	0.055	19	intermediate
0.02	60	1000	1.3	4.2×10^4	intermediate
0.02	40	1000	1.3	1.5×10^4	intermediate
0.02	40	500	1.3	7700	no
0.02	40	300	1.3	4600	no
0.02	30	500	1.3	6000	no
0.02	30	300	1.3	3600	no
0.02	20	500	1.3	780	no
0.02	20	300	1.3	470	no

[a]In all experiments, $\phi_{TOT} = 0.3$ with $\phi_s = 0.1$ and pH = 12

[b]Viscosities for water (for $\phi_T = 0$) as a function of temperature were taken from reference 7.

[c]Viscosities of thickener solutions were measured at a shear rate of 0.1 s^{-1}.

Raman Spectroscopy Mapping

Raman maps were obtained using a microscope (Renishaw inVia, Wotton-under-Edge, UK) using a 50× objective lens and a wavelength of 457 nm with 2400 lines/mm grating. The nodes of a pre-set measurement grid were used to define the points where spectra were obtained for image construction. Static scans were made with spatial distances between the scan spots ranging between 15 and 50 μm. The Raman spectral range was $283 - 2026$ cm^{-1}. The colloidal mixtures show significant peaks at 811 cm^{-1} for the large colloid (CH stretching vibration from the BA and MMA),[8] and at 1635 cm^{-1} for the small colloid (the urethane group's NH stretching vibration[9]). See Figure S1a. In the analysis, these were the two characteristic peaks used to quantify the relative amounts of the two components. The peak for the C=O stretching vibration at 1730 cm^{-1} is characteristic for both the polyurethane and acrylic,[8] and hence it is not a unique identifier for either component.
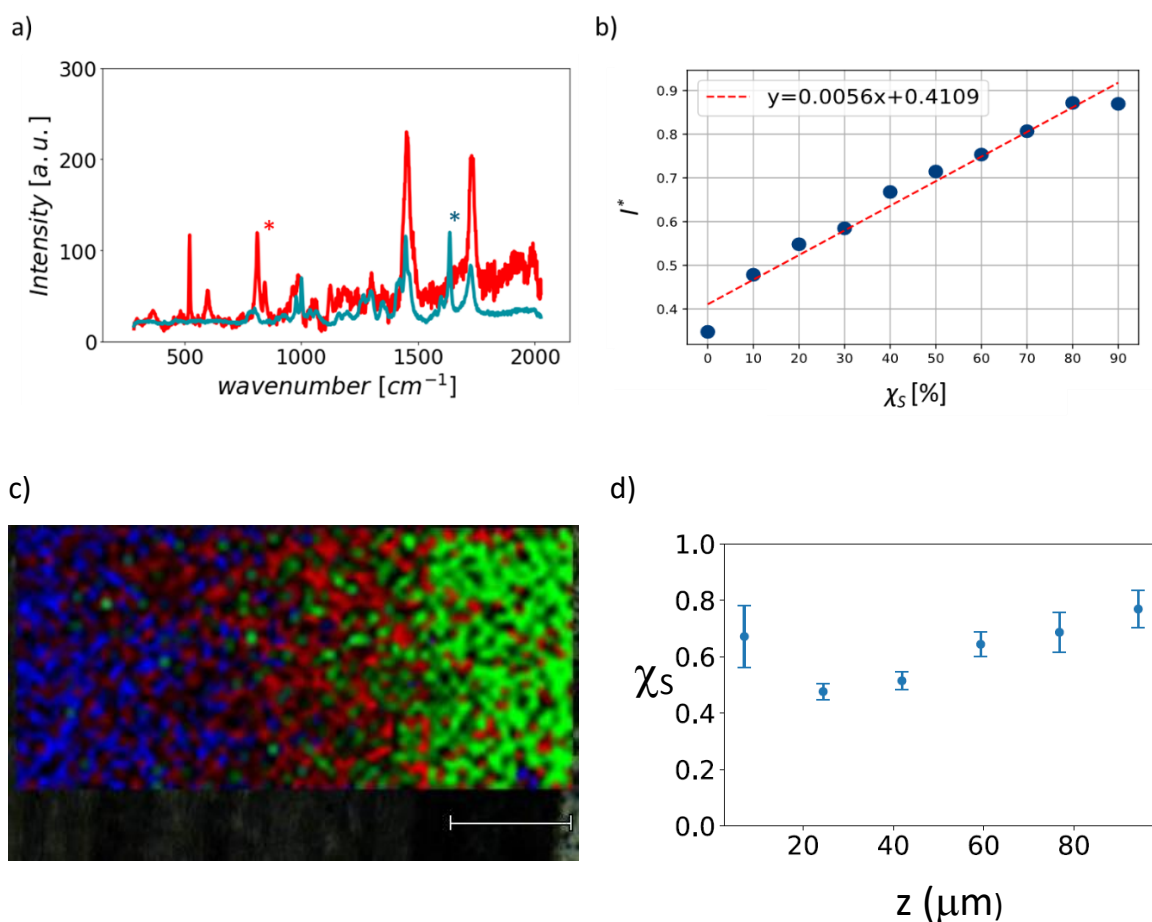
Figure S1. a) Raman spectra showing data for the poly(urethane) (turquoise blue) in the small particles, and the acrylic copolymer (red) in the large particles. Characteristic peaks used for the calibration and quantitative analysis are marked with *. b) Calibration data for the quantitative analysis of large/small mixtures. The normalised peak intensity increases with the volume fraction of the small particles, χ_S. c) An example of a Raman map for an acrylic/polyurethane mixture with 1 vol.% thickener. The film was formed at a temperature of 40 °C with a relative humidity of 45%. The green region represents where the majority is the polyurethane phase, and the red represents where the majority is the acrylic phase. (The majority phase cannot be determined in regions shown in blue.) The scale bar is 200 μm. d) A depth profile obtained from the sample, showing χ_S as a function of depth, z.

To calibrate the Raman intensity, several films with a random particle distribution (made using a very low evaporation rate) and with varying amounts of the small colloid were used as standards. We found for each calibration standard the intensity ratio fraction, $I^* = \frac{I_{small}}{I_{small}+I_{large}}$, with I_{small} and I_{large} being the intensities of the characteristic peaks corresponding

to the polyurethane (in small particles) or the acrylic copolymer (in large particles). The calibration spectra were taken from the surfaces, rather than cross-sections, of the standards. We plotted I^* against the known volume fraction of the polyurethane component (small particles) in the dry state, χ_s. We fit a linear regression to the data (see Figure S1b) to find:

$$I^* = 0.0056 \pm 0.0006 \ \chi_s + 0.411. \tag{S1}$$

This equation was used subsequently to determine χ_s from the I^* values measured from a sample with an unknown variation in composition.

The cross-sectioned samples were placed in the Raman spectrometer, with the samples still on the microtome sectioning block, so that the exposed interface was level. We performed 2D map measurements over a few mm^2 of the microtomed area in a grid pattern with one edge of the map on the border between the cut interface and the original top surface. An example Raman map is shown in Figure 1c. Equation S1 was used to convert the measured Raman intensities at each point to χ_s. Then the values of χ_s, averaged across the width of the area of a sample, were compared to the value obtained for a random mixture (film formed with a very low Pe) to determine the extent of the stratification. The percent excess was determined from the difference in χ_s of the random mixture and the analysed sample. Figure 1d shows the depth profile obtained from the sample that was mapped.

Viscosity Measurements

The viscosity of solutions of ASE thickener in water was measured using a shear rheometer (TA Discovery HR2, Newcastle USA) fitted with a cone and plate geometry. The cone angle was 2°, and the plate had a 40 mm diameter. Three to five measurements for each concentration were performed, as the shear rates was varied from 0.1 to 100 s^{-1} at a fixed temperature of 30 °C. The pH of the solutions was adjusted by adding concentrated NaOH. Results for viscosity measurements at pH of 12 are presented in Figure S2.
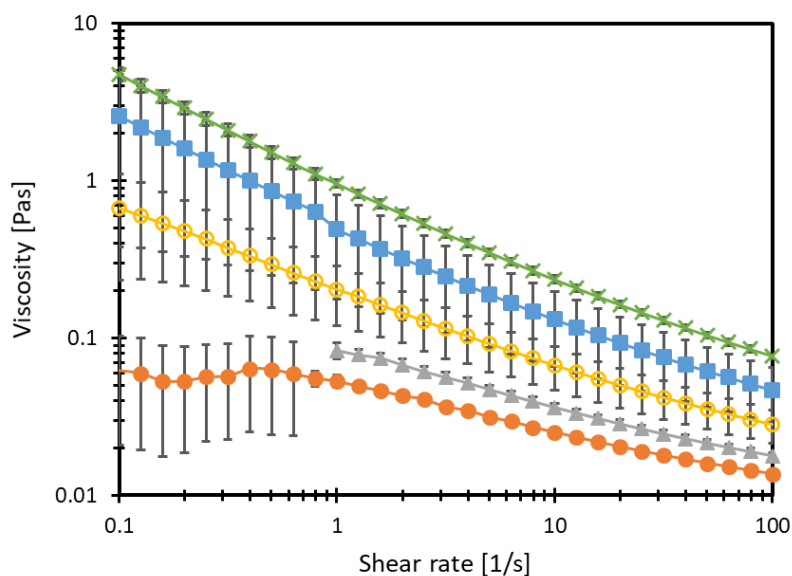
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Figure S2. Shear-rate dependence of the viscosity of solutions of ASE thickener in aqueous solutions at a pH of 12 obtained over a range of volume fractions: $\phi_{CP} = 0.015$ (●); $\phi_{CP} = 0.02$ (▲); $\phi_{CP} = 0.025$ (○); $\phi_{CP} = 0.03$ (■); and $\phi_{CP} = 0.04$ (x).

For calculations of the colloidal diffusion coefficient, values of the viscosity are needed in the limit of zero shear rate. For the lowest thickener concentration ($\phi_{CP} = 0.015$), the viscosity reaches a constant plateau value below shear rates of 1 s^{-1}, and there is a shear thinning at higher rates. With the higher concentrations, the solutions show shear thinning. However, the viscosity does not reach a plateau value at lower shear rates. The measurements were unreliable at lower shear rates. Therefore, the value of viscosity at the lowest shear rate of 0.1 s^{-1} was used in the calculations of the diffusion coefficient. The results are summarized in Table S1. The value for a solution with $\phi_{CP} = 0.01$ (at a shear rate of 0.1 s^{-1}) was interpolated from the other measurements.

Table S3. Viscosity of solutions of non-associative thickener at pH 12 and shear rate of 0.1 s^{-1}

ϕ_{CP}	η (Pas)
0.015	0.06
0.025	0.67
0.03	2.57
0.04	4.78

The viscosity of the thickener solutions did not vary significantly when the temperature was raised by 10 or 20 °C.
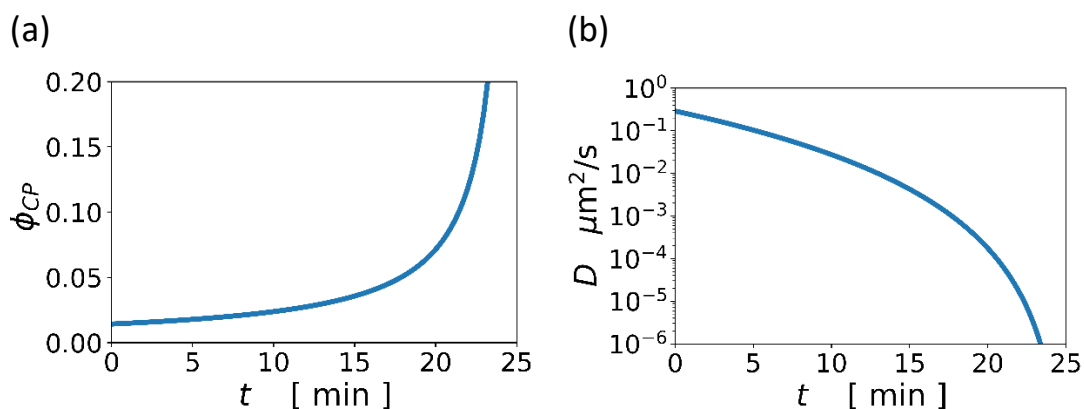
Figure S3. Calculations of the time evolution of a) the volume fraction of the thickener in the continuous phase; b) self-diffusion coefficient, D_S, of the small particles. The initial $\phi_T = 0.01$ and $H = 300$ μm.

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