

Supporting Information for:
“Colloidal aggregation in mixtures of partially miscible liquids
by shear-induced capillary bridges”

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1 Supporting data

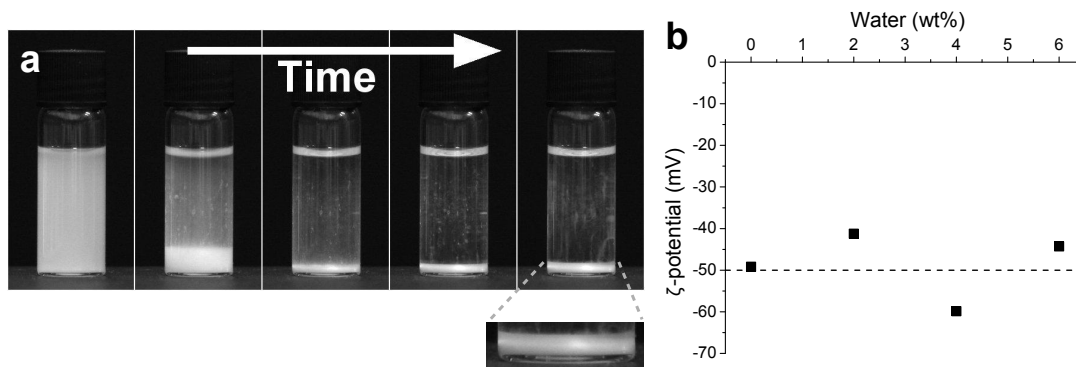


Figure S1: (a) Warming a sample of 1 vol% silica particles in a water/propanal mixture (25 wt% water, 75 wt% propanal) to room temperature (21°C) after it being cooled in ice-water. Frames 2, 3 and 4 are taken respectively 10, 15 and 35 minutes after the first image. At the bottom a part of the final image is shown in more detail to make the liquid-liquid interface more clearly visible. (b) ζ -potential of the silica particles in propanal/water mixtures as a function of the water concentration in the solvent.

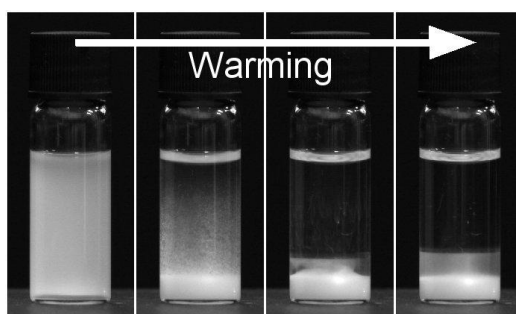


Figure S2: Sample of a 50/50 (w/w) 2-butanol/water mixture containing silica particles (1 vol%) warming up to room temperature after being cooled in ice-water: 1st image was taken approximately 5 minutes after removal from ice-water, and frames 2, 3 and 4 were taken, respectively, 5, 10 and 20 minutes after the 1st image.

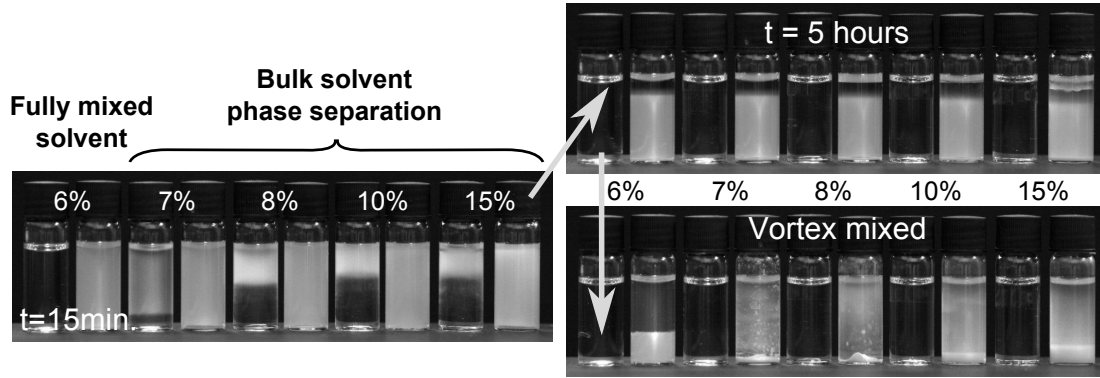


Figure S3: Samples of varying ethylene glycol concentration (sets of two vials: blank on the left and containing 1 vol.% particles on right) dispersed/mixed at approximately 50°C and then left to cool to room temperature while taking photographs. The image on the left shows vials 15 minutes after having started imaging the hot samples. The images on the right show (top) the vials after 5 hours, (bottom) which were subsequently vortex mixed.

Phase separation in ethylene glycol/nitromethane mixtures

Some suspensions of silica particles in ethylene glycol/nitromethane mixtures were made to undergo a temperature quench by leaving them to cool down to room temperature after having been heated. Samples at varying ethylene glycol concentration were monitored as they cooled down (Figure S3). Liquid mixtures without silica particles (blanks) demonstrated that bulk phase-separation has taken place after 15 minutes (Figure S3, left), as observed by turbid regions that cream towards the top of the samples (ethylene glycol-rich phase separates out, which has a slightly lower density than the nitromethane-rich phase). However, this leaves colloidal stability unaffected with the particles slowly sedimenting as evidenced by a sharp sedimentation front (Figure S3, top right). Some particles, however, do appear to be collected in C_w -rich droplets at the top of the sample. Collecting all the particles in the bulk ethylene glycol-rich phase is achieved by vortex mixing (Figure S3, bottom right).

2 Processing fluorescence spectroscopy data

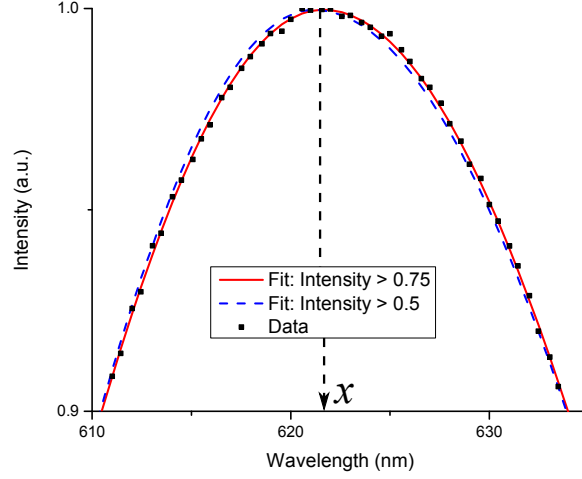


Figure S4: Example fits for different intensity cut-offs aimed at finding peak center x .

Fitting

To find the peak center, the peaks were first normalized and then intensities below a specified value were cut off for fitting by an asymmetric Gaussian

$$I(\lambda) = A \exp\left(-\frac{(\lambda - x)^2}{2\sigma^2}\right) \begin{cases} \sigma = \sigma_L, A = A_L & \text{if } \lambda < x \\ \sigma = \sigma_R, A = A_R & \text{if } \lambda > x \end{cases}$$

where fit parameters A , x and σ are, respectively, peak height, peak center and peak width (subscripts L and R indicate left and right of x , respectively). The quality of the fit depends on the part of the data that is used. An example where the data with $I > 0.5$ and $I > 0.75$ was fitted (Figure S4) shows that the former already gives a reasonable fit, while clearly a better fit is obtained for a larger threshold. In order to carefully determine the peak center position the threshold is set at 0.8 for all data.

Determining \bar{x}

Spectra were recorded in series of, typically, 5 sequential measurements of a sample (Figure S5a). Measurements of supernatants were always preceded and succeeded by measurements of a stock solution of Nile Red in propanal/water into which the particles were dispersed. This provided a guide to the reproducibility of measuring x , and established a baseline. Displaying x of individual measurements for a particular liquid composition in the sequence in which they were obtained, reveals that often the first measurement in a series is a clear outlier. These were discarded, consistently over all data, and the remaining averaged to get \bar{x} . Finally, the \bar{x} of the samples were shifted to take into account the variability of the baseline, which becomes apparent from the blanks (Figure S5b). This was done by assuming that they were shifted with respect to the baseline by the same amount as the average of the 2 sandwiching blanks.

To convert the \bar{x} values into compositions, a calibration curve was constructed, and fitted to a quadratic equation (Figure S6).

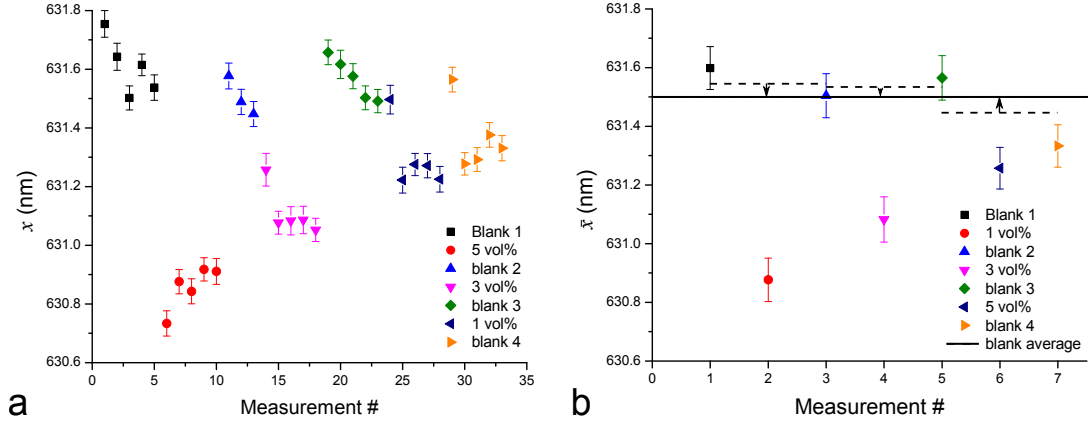


Figure S5: (a) All x obtained from a single series of measurements at fixed water concentration (12 wt%). (b) Averaged and adjusted (as indicated by dashed lines and arrows) values of x from the measurement series in (a).

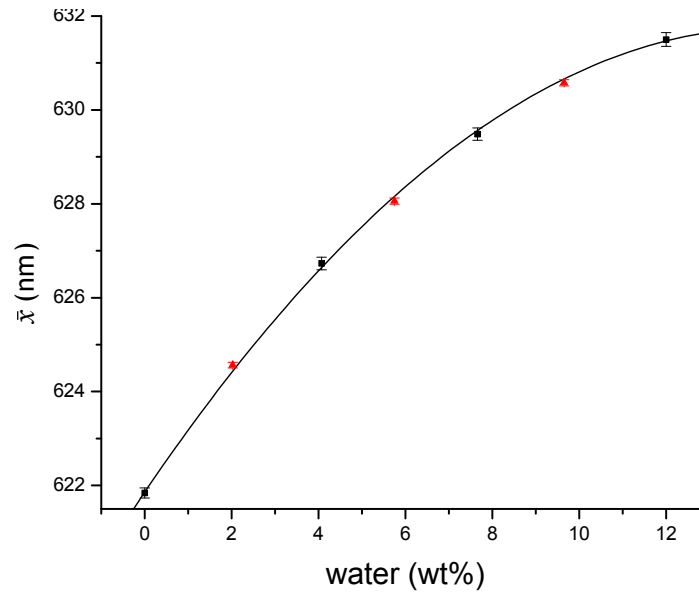


Figure S6: Calibration curve used to extract water concentration from values plotted in Figure 5d. The red triangles are measurements performed at a different time, but were not used for the fit and included only for reference.

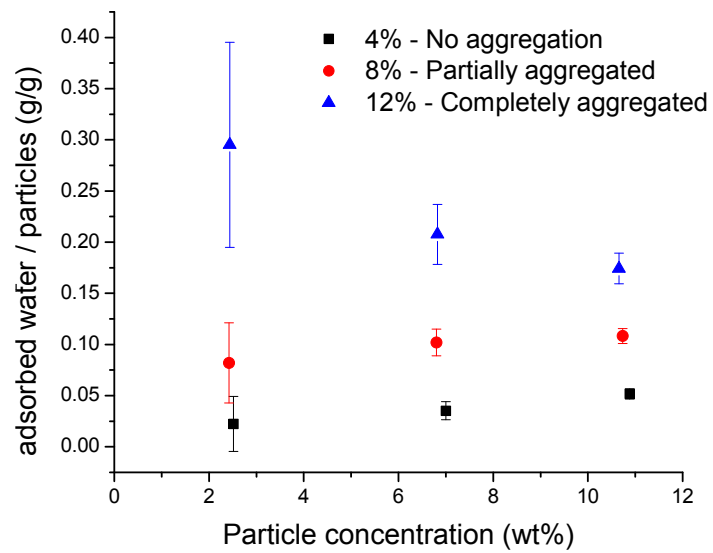


Figure S7: Plots of the mass ratio of adsorbed water to particles against the particle concentration.