Stabilization of Pickering emulsions with oppositely charged latex particles: influence of various parameters and particle arrangement around droplets

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Supplementary Information

Table S1. Characterization details of particles

Particle type	Mean diameter/μm	Surface charge density/ μC cm^{-2}	Functional groups	Zeta potential/mV (1 mM NaCl at 25 ºC)	Contact angle/° (decane-water)[a]
Polystyrene	0.5	19.7	amidine	+ 50.29	103.1 ± 4.0[*]
Polystyrene	2.2	22.7	amidine	+ 27.7	103.1±4.0[*]
Polystyrene	0.5	1.8	sulphate	- 90.24	116.1 ± 12.3[*]
Polystyrene	3.0	6.7	sulphate	- 57.3	116.1 ± 12.3[*]
Polystyrene	9.0	-	sulphate	- 100.0	116.1 ± 12.3[*]
Silica	4.0	-	carboxylic acid	- 48.0	55[**]
Polymer-based magnetite	3.0	-	carboxylic acid	- 74.3	-

[a] Measured through water at a decane-water interface.

[*]Contact angles of amidine and sulphate polystyrene latex particles are from Isa, L.; Lucas, F.; Wepf, R.; Reimhult, E., Measuring single-nanoparticle wetting properties by freeze-fracture shadow-casting cryo-scanning electron microscopy, *Nature Commun.* **2011,** *2*, 438.

[**]Contact angle of silica particles is measured in-house using the gel trapping technique.

Figure S1. Heteroaggregation of aqueous dispersions of oppositely charged polystyrene latex particles of diameter 2.2 μm (+) and 3.0 μm (-), initially and one and two days later. From left to right, ϕ_p = 0, 0.013, 0.020, 0.048, 0.063, 0.091, 0.167, 0.200, 0.250, 0.333, 0.500, 0.667, 0.750, 0.800, 0.833, 0.909, 0.938, 0.952, 0.980, 0.987 and 1.000 respectively. Total particle concentration is 0.1 w/v% (≈ 6.7×10^7 per mL of water phase), pH = 7. Aggregation leading to significant sedimentation is observed at intermediate compositions $0.333 < \phi_p < 0.833$.

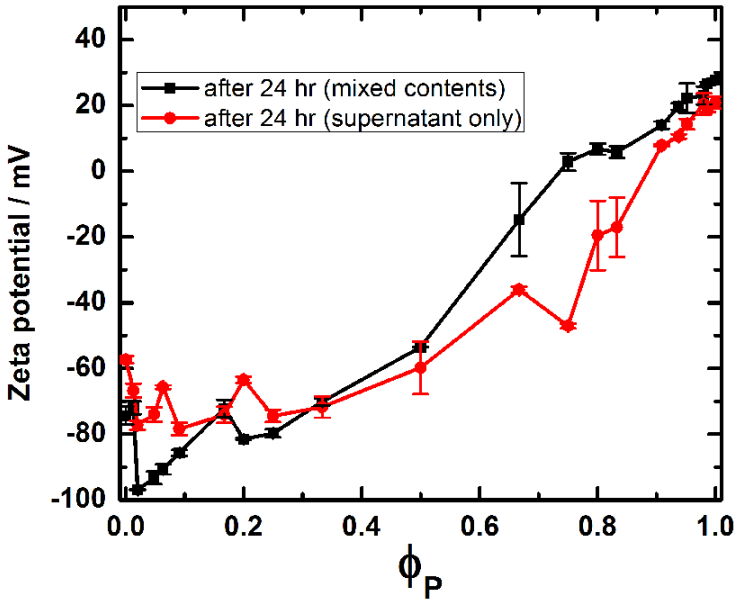

Figure S2. Zeta potential of mixtures of OCP shown in Figure S1 measured after 24 hr, both of the supernatant and the homogeneous dispersion.

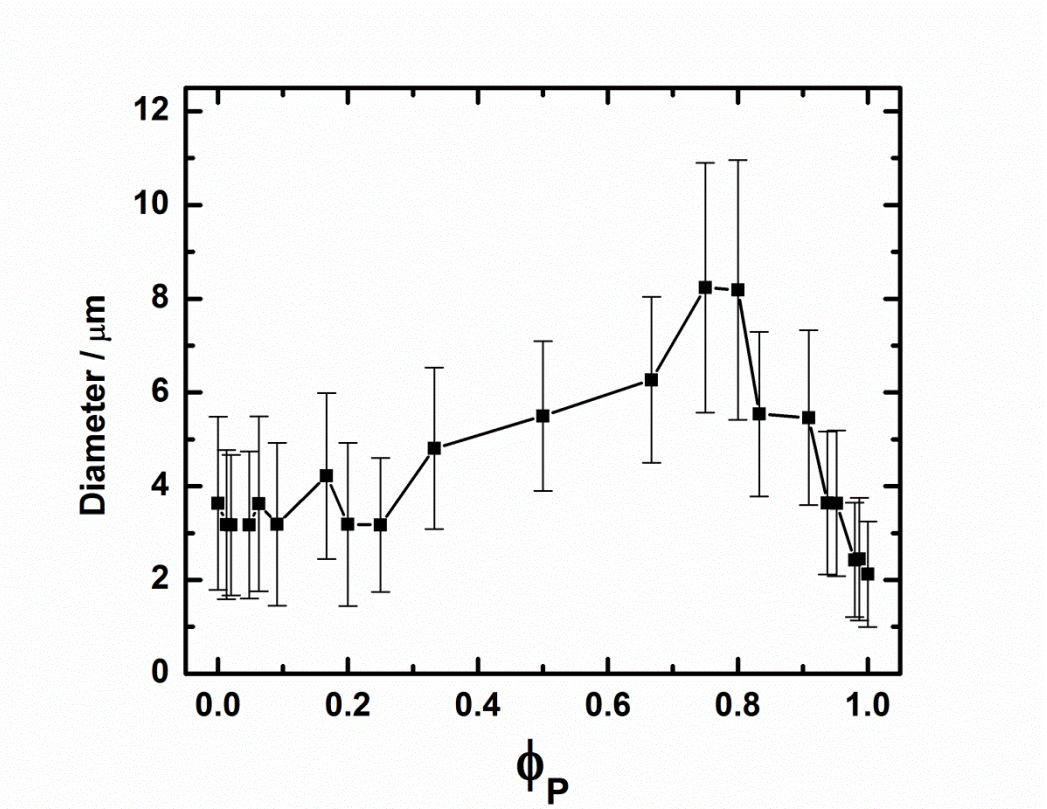

Figure S3. Size of the aggregates formed after 24 hr in vials shown in Figure S1. Since there was complete settling at intermediate compositions the contents of the vials had to be well mixed before measurement. It is possible that actual aggregate sizes will be larger than the measured values.

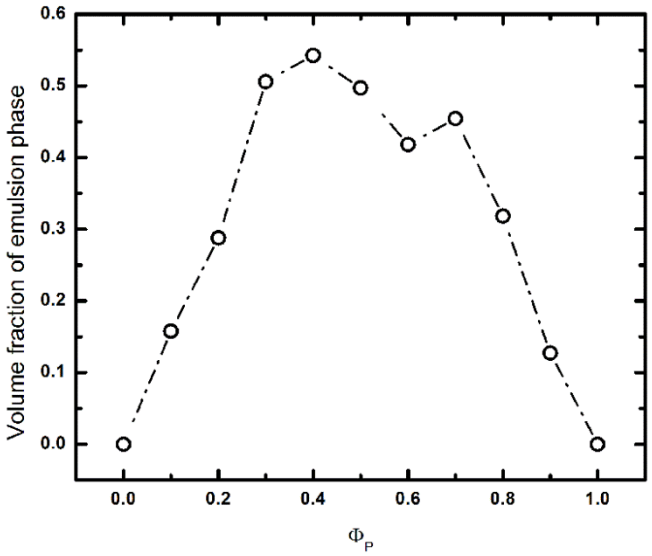

Figure S4. Variation of the volume fraction of stable emulsion (relative to total volume) versus ϕ_p in vials shown in Figure 3 of main text measured 1 hr after preparation.

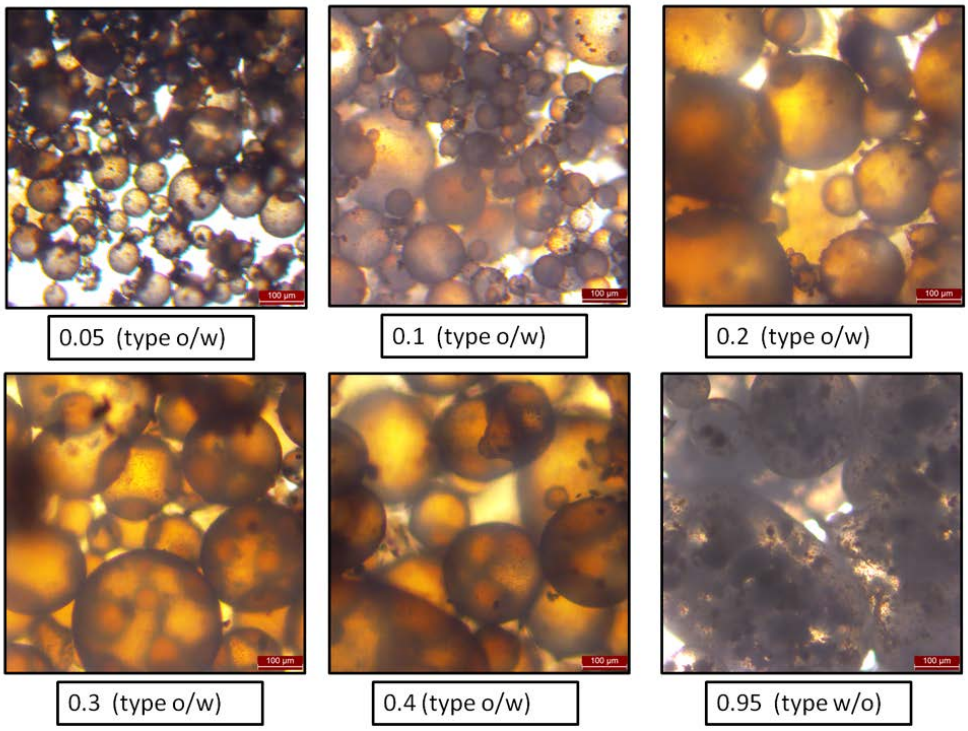

Figure S5. Representative optical microscopy images of emulsion droplets formed in vials shown in Figure 4 of main text. The numbers refer to fraction of oil phase ϕ_o. An increase in droplet size was observed towards phase inversion. The average drop diameter ranged from 105 μm at ϕ_o = 0.05 to 350 μm at ϕ_o = 0.4. Scale bar = 100 μm.

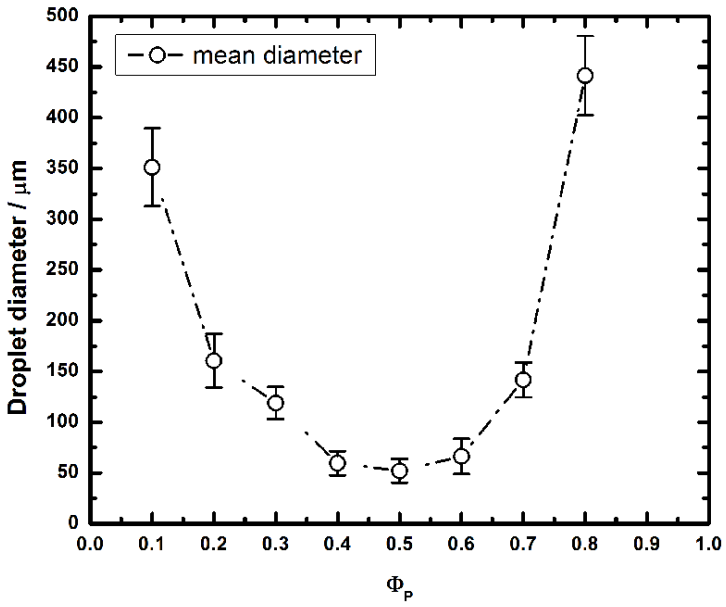

Figure S6. Variation of average droplet diameter of o/w emulsions (ϕ_o = 0.05) formed in vials shown in Figures 7 and 8 of main text *versus* ϕ_p. Error bars represent standard deviation.

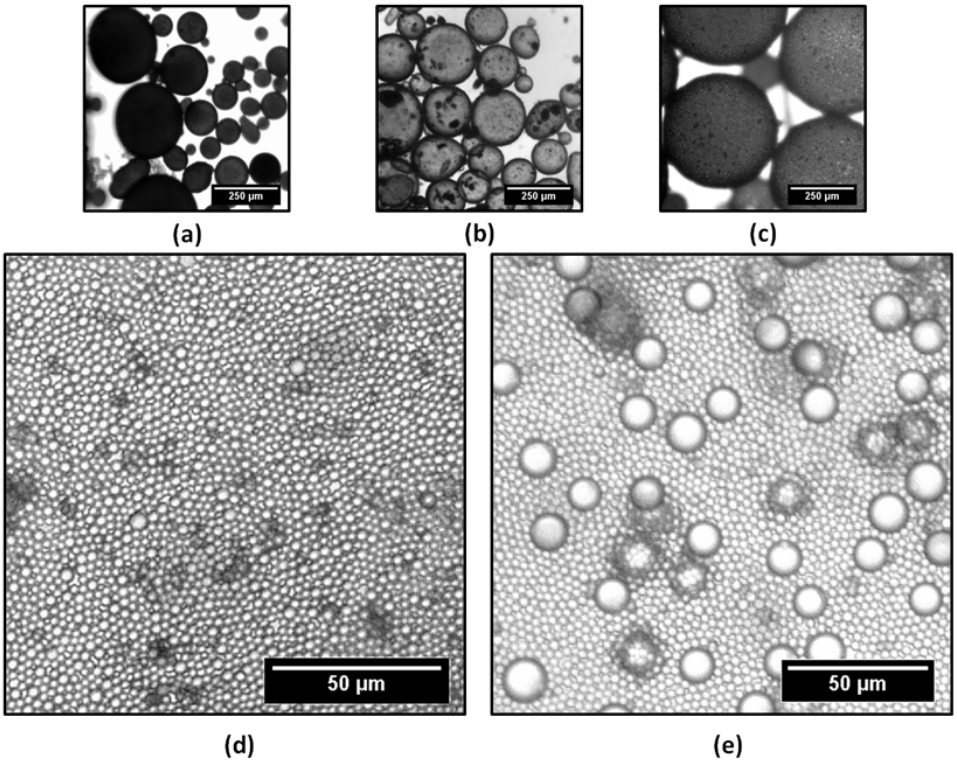

Figure S7. Emulsification of aqueous dispersions of OCP of polystyrene latex of different sizes. All emulsions are w/o (ϕ_o = 0.9). (a) Mixture of 2.2 µm (+)/3.0 µm (-) particles, (b) mixture of 0.5 µm (+)/0.5 µm (-) particles, (c) mixture of 2.2 µm (+)/9.0 µm (-) particles. Close up of the surfaces of a water drop in oil are shown in (d) corresponding to system in (a), and in (e) corresponding to system in (c) respectively. Ratio of positive:negative particles used are (a) 1:1, (b) 1:2 and (c) 17:1 respectively.

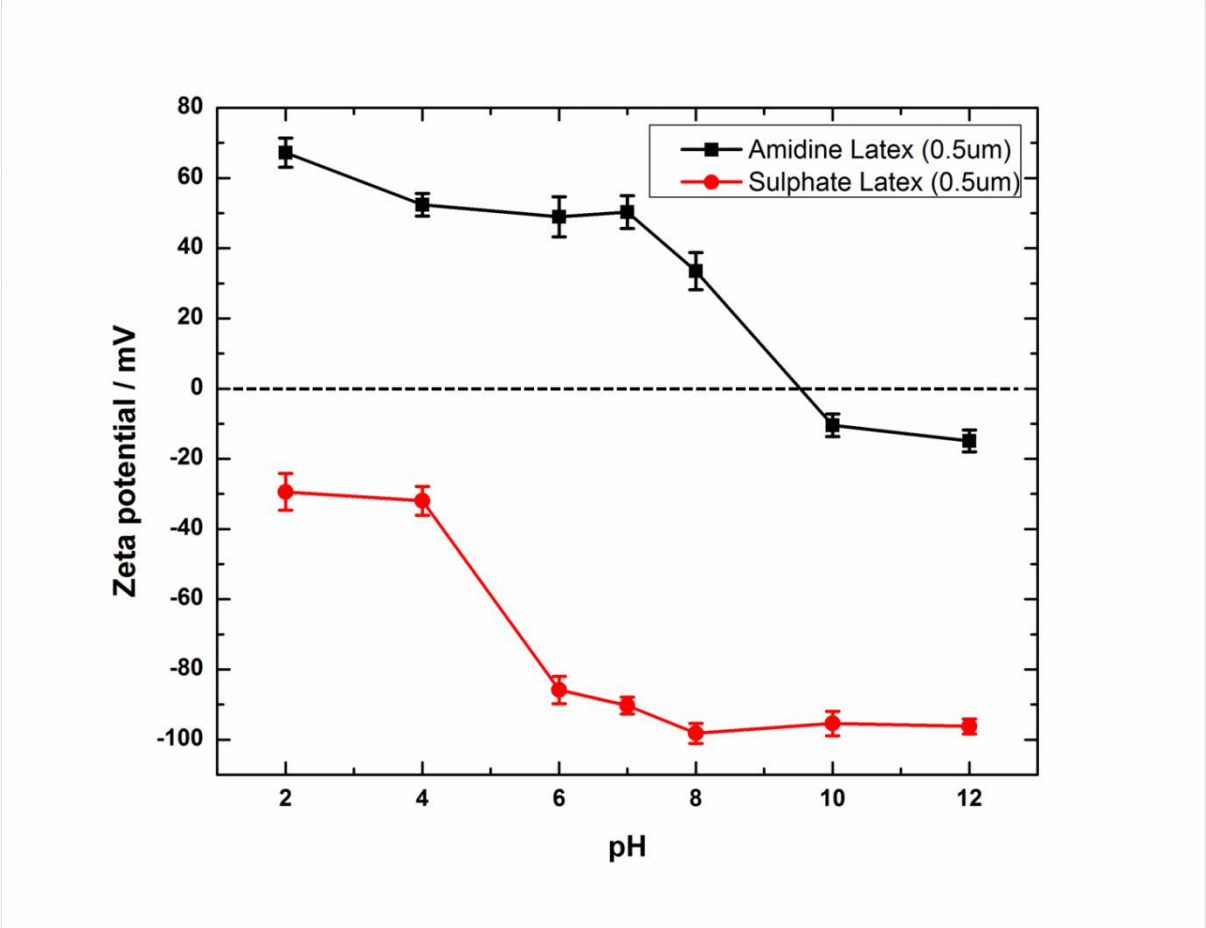

Figure S8. Zeta-potential of pure amidine (0.5 µm) and sulphate (0.5 µm) polystyrene particles at different pH. Sulphate-coated particles remained stable over the whole pH range. Amidine-coated particles were stable over the pH range of 2 to 8 but aggregated at pH 10 and 12.