Supplementary Materials

Pickering emulsions stabilized by charged nanoparticles

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1. Characterization of Ludox[®] AS40

Ludox[®] AS40 is a concentrated (40 wt%) aqueous suspension of non-aggregated precipitated silica nanoparticles supplied in basic medium at pH 9.1. The *z*-average hydrodynamic diameter of Ludox[®] AS40 particles measured by dynamic light scattering was 30 nm; the polydispersity index given by the cumulants method was *PdI* = 0.3. Electron microscopy (SEM and TEM) pictures of Ludox[®] AS40 showed a nice collection of non-aggregated spherical particles (Fig. S.1). Although the aqueous suspensions have been dried for performing their observations by SEM and TEM, the pictures did not show aggregated particles; this definitely showed that the silica particles were non-aggregated in the aqueous suspension. The mean diameter of silica particles as inferred from the image analysis of 30 particles on the TEM pictures was 25 ± 4 nm, significantly smaller than that measured by DLS. Indeed, TEM gives the gives the actual diameter of the particles whereas DLS gives the hydrodynamic diameter, that is, the diameter of the object that undergoes Brownian motion, including all surface species and bound water. Since Ludox[®] AS40 particles are negatively charged and the medium has a low ionic strength under the dilution conditions of DLS, the difference between diameters of DLS and TEM might correspond to twice the thickness of the electrical double layer (twice the Debye length).



Fig. S.1 TEM image (A) and SEM image (B) of non-aggregated Ludox® AS40 silica nanoparticles.

Aqueous suspensions of Ludox® AS40 are stable in basic and in acidic media. The negative surface charge of silica particles at pH's above the isoelectric point ensures a high colloidal stability in aqueous suspensions of low ionic strength because of electrostatic repulsions preventing coagulation. Ludox® AS40 keeps its colloidal stability as the isoelectric point is approached; it has been suggested that such stability that appears surprising based on electrostatic considerations, came from non-DLVO forces due to the presence of a layer of waterswollen gel that provided a supplementary steric repulsions between the silica particles.¹ The negative surface charge of silica particles was revealed by electrophoresis measurements of the zeta potential ζ as a function of pH (Fig. S.2). The ζ potential was indeed negative for pH values above the isoelectric point at pH between 1 and 2. ζ potential measurements have been performed on suspensions diluted to 5% in water without addition of background electrolyte, which were the same as in the Pickering emulsions prepared without addition of salt. Fig. S.2 also reports the ζ potentials of emulsion droplets and residual silica particles present in the aqueous phase of the emulsions. Notice that the ζ potential of emulsion droplets was calculated from the Henry's law using the Smoluchowski approximation where $f(\kappa \alpha) = 3/2$ valid for $\kappa \alpha >> 1$ because the radii of emulsion droplets were quite large with respect to the Debye length. As expected, ζ potentials were strongly negative and the isoelectric point was the same as for aqueous suspension of Ludox[®] AS40. The negative ζ potential of the oil droplets indicated adsorption of silica particles. The ζ potential of residual silica particles as a function of pH was the same as for the original suspension of Ludox[®] AS40, showing that the surface of silica particles did not change upon contacting oil during the emulsification process.



Fig. S.2 ζ potential as a function of pH for Ludox[®] AS40 silica particles at 5 wt% concentration (blue diamonds) and for the components of the o/w emulsion (5 wt% silica and 50 vol% DIPA): oil droplets (green triangles) and free silica particles present in the aqueous phase separated by centrifugation (red squares).

Aggregation of Ludox[®] AS40 did not take place under the experimental conditions of the present study. Indeed it might be expected that aggregation of silica particles occur as the isoelectric point is approached. The technical literature provided by the Ludox[®] manufacturer² is not clear to that respect however, since the stability assessment was based on the time required for detecting the onset of gelation. Aggregation can occur with no gelation taking place. The silica particles aggregation has been assessed in the present experimental conditions through measurements of the hydrodynamic diameters of silica particles or their aggregates by means of dynamic light scattering (Fig. S.3). Aggregation of silica particles could hardly be detected unless the silica concentration was high. Thus, no significant silica aggregation was observed within 20 days for silica concentrations lower than 10 wt%. Aggregation of silica under the present conditions. The non-adsorbed silica particles present in the aqueous phase of the emulsion were not aggregated as shown by DLS measurements in the aqueous phase after its separation by centrifugation: the size of silica particles was the same as in the original Ludox[®] AS40 sol in the whole investigated pH range from 1 to 9 (Fig. S.4).



Fig. S.3 Aggregation of silica as a function of time at pH 3 for different concentrations of Ludox® AS40 silica as monitored by dynamic light scattering.



Fig. S.4 Hydrodynamic diameter of the silica particles present in the bottom liquid layer of the creamed emulsion as a function of pH. Composition of emulsions: 5 wt% Ludox® AS40 silica in water and 50 vol% oil.

2. Emulsification of diisopropyl adipate

Pickering emulsions were prepared at pH 9 and the pH was shifted down to lower values in order to increase the stability. Fig. S.5 shows the behavior after 14 days storage for various oil contents. Emulsions at pH 9 (Fig. S.5a) were unstable since a large amount of oil was released as a top layer of pure oil after 14 days. Emulsification failed for samples containing 70% and 80% oil, so that full separation of oil and water was observed after 14 days; the aqueous phase at the bottom was slightly turbid because of the few oil droplets that have been emulsified. Emulsification was successful for samples containing less than 60% oil, which meant that the full oil content was dispersed as droplets. But the emulsions were not stable as revealed by the release of pure oil upon storage revealing droplets coalescence. After 14 days, a top clear layer of pure oil has been released and the emulsion has undergone creaming, so that an intermediate layer of creamed emulsion was observed. The clear bottom layer is the aqueous phase of the creamed o/w emulsion. The amounts of released oil and creamed emulsion obviously increased with respect to the total oil content. After the pH has been shifted down, the same kind of behavior was observed for unstable emulsions at pH 7 (Fig. S.5b). Below the later pH, emulsions were stable as revealed by the absence of a top layer of pure oil. Emulsions underwent creaming however, the volume of the creamed layer increased with respect to the oil content (Fig. S.5c and d). For all pH, the behavior did not depend on the oil content; the stability was the same for dilute and concentrated emulsions.



Fig. S.5 Pictures of o/w Pickering emulsions stabilized by 5 wt% Ludox® AS40 silica in water at various pH and containing increasing volume fractions of DIPA from the left to the right: 20, 30, 40, 50, 60, 70, 80 vol%. (a) pH 9, (b) pH 7, (c) pH 6, (d) pH 5, (e) pH 3. Pictures were taken after 14 days storage.

3. Calculations of the ionic strength and Debye length for various silica concentrations and pH

Electrostatic repulsions strongly depend on the concentration of ionic species (ionic strength) that form an electrical double layer around the particles. The range of electrostatic interactions taking place through water corresponds to the thickness of the electrical double layer given by the Debye length κ^{-1} that depends on ionic strength as

$$\kappa^2 = \frac{e^2 N_{Av} \, 10^3}{\varepsilon_0 \, \varepsilon_w \, kT} \sum_{ions} C_i \, z_i^2 \tag{S.1}$$

where *e* is the elementary charge, N_{Av} is the Avogadro number, 10^3 is the conversion factor from the mol L⁻¹ units of concentration into mol·m⁻³, ε_0 is the dielectric constant of vacuum, ε_w is the dielectric permittivity of water, *k* is the Boltzmann constant, *T* is the temperature, *C*_i and *z*_i are the concentrations (mol·L⁻¹) and valences of the ionic species in water.

The concentrations of ionic species were calculated as follows. The Ludox[®] AS40 sol at 40 wt% silica contains from 0.1 to 0.2 % ammonia according to manufacturer's information,³ which corresponds to 0.05-0.1 mol·L⁻¹ ammonia. A concentration of ammonia of 0.1 mol·L⁻¹ was taken in the following, so that the overall

concentration of ammonia was $C_{ammonia} = 0.1 \frac{\phi_{SiO_2}}{0.40} (mol \cdot L^{-1})$ after dilution of silica from its concentration in

the Ludox[®] AS40 slurry to φ_{SiO_2} . Since the Ludox[®] AS40 silica sol was stabilized by ammonia, ionic species were ammonium cations NH₄⁺, hydroxide OH⁻ and hydronium H⁺ ions. Ammonia is a weak base that is not converted into ammonium hydroxide in water. The fraction of protonated ammonia is controlled by the acid-base equilibrium that depends on the pH.

$$NH_4^+ \leftrightarrows NH_3 + H^+ \qquad K_A = \frac{[NH_3][H^+]}{[NH_4^+]}$$
 (S.2)

Accordingly, the concentration of ammonia that was under its protonated form NH_4^+ was calculated from the pH and $pK_A = -\log(K_A) = 9.244$ ⁴ as

$$[NH_4^{+}] = \frac{C_{ammonia}}{1+10^{-(pK_A^{-}pH)}}$$
(S.3)

3.1. Debye length at pH 9. At pH 9, the ionic species were ammonium cations coming from ammonia, free hydroxide ions that set pH 9 and hydronium ions of negligible concentration. The concentration of ammonium cations depended on the dilution factor of silica. The ionic strength depended on the mass fraction of silica $\phi_{SiO_{2,2}c}$

$$\sum C_{i} z_{i}^{2} = [NH_{4}^{+}] + [OH^{-}] + [H^{+}] = 0.1 \frac{\phi_{SiO_{2}}}{0.40} \frac{1}{1 + 10^{-(pK_{A}^{-}pH)}} + 10^{-(14-pH)} + 10^{-pH} (mol \cdot L^{-1})$$
(S.4)

The Debye length was $\kappa^1 = 3.4$ nm for $\phi_{SiO_2} = 10$ wt%, and $\kappa^1 = 23$ nm for $\phi_{SiO_2} = 0.2$ wt%. The Debye length was quite long when the concentration of silica was low. The Debye length of a suspension diluted to 5 wt% was then $\kappa^1 \approx 5$ nm and the radius of the silica particles was a = 15 nm, so that the condition of validity of the Smoluchowski approximation ($\kappa a >> 1$) was hardly fulfilled. The Henry factor $f(\kappa a)$ varies between 1 at very low electrolyte concentration ($\kappa a << 1$) to 3/2 at high ionic strength ($\kappa a >> 1$), which is a weak variation. The value $f(\kappa a) = 1.09$ was calculated for $\kappa a = 3$ using the equation given by Ohshima.⁵

3.2. Debye length at pH 3. Upon addition of hydrochloric acid so as to reach pH 3, ammonia and ammonium hydroxide were converted into ammonium chloride. Supplementary ionic species H^+ and Cl^- were present for setting pH 3. The total concentration of chloride ions was $[Cl^-] = [NH_4^+] + [H^+]$ because the concentration of OH⁻ was vanishingly small at pH 3:

$$\sum C_{i} z_{i}^{2}$$

$$= \left[NH_{4}^{+} \right] + \left[Cl^{-} \right] + \left[OH^{-} \right] + \left[H^{+} \right] = 2 \times 0.1 \frac{\phi_{SiO_{2}}}{0.40} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(14 - pH)} + 2 \times 10^{-1} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(14 - pH)} + 2 \times 10^{-1} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(14 - pH)} + 2 \times 10^{-1} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(14 - pH)} + 2 \times 10^{-1} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(14 - pH)} + 2 \times 10^{-1} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(14 - pH)} + 2 \times 10^{-1} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(14 - pH)} + 2 \times 10^{-1} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(14 - pH)} + 2 \times 10^{-1} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(14 - pH)} + 2 \times 10^{-1} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(14 - pH)} + 10^{-(14 - pH)} + 2 \times 10^{-1} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(14 - pH)} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(14 - pH)} + 10^{-(14 - pH)} + 10^{-(14 - pH)} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(14 - pH)} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(14 - pH)} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(14 - pH)} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(14 - pH)} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(14 - pH)} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(14 - pH)} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(pK_{A} - pH)} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(pK_{A} - pH)} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(pK_{A} - pH)} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(pK_{A} - pH)} \frac{1}{1 + 10^{-(pK_{A} - pH)}} \frac{1}{1 + 10^{-(pK_{A} - pH)}} + 10^{-(pK_{A} - pH)} \frac{1}{1 + 10^{-(pK_{A} - pH)}} \frac{1}{1 + 10^$$

The ionic strength at pH 3 was much larger than at pH 9. Accordingly, the electrical double layer was very thin for high silica concentrations but reached significantly large values of the same magnitude as the particle size (*a*

= 15 nm) for the most diluted suspensions of silica. As example, $\kappa^1 = 2 \text{ nm}$ for $\phi_{SiO_2} = 10 \text{ wt\%}$, and $\kappa^1 = 8 \text{ nm}$ for $\phi_{SiO_2} = 0.2 \text{ wt\%}$.

The Debye lengths calculated as a function of the silica concentration at pH 9 and pH 3 are shown in Fig S.6.



References

- 1 G. Vigil, Z. Xu, S. Steinberg, J. Israelachvili, J. Colloid Interface Sci. 1994, 165, 367-385.
- 2 Ludox[®] Technical Literature. Product Description, available at: nathan.instras.com/documentDB/paper-190.pdf.
- 3 W.R. Grace & Co.-Conn, Ludox[®] colloidal silica, Grace Davison technical information, 2008, available at https://grace.com/general-industrial/en-us/Documents/ludox_binders%20refractory_E_08_081110.pdf.
- 4 R.G. Bates and G.D. Pinching, J. Res. Nat. Bur. Stand. 1949, **42**, 419-430.
- 5 H. Ohshima, J. Colloid Interface Sci. 1994, 168, 269-271.