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Supporting information for manuscript

# Production of Concentrated Pickering Emulsions with Narrow Size Distributions using Stirred Cell Membrane Emulsification

Mohamed. S. Manga\* and David. W. York

School of Chemical and Process Engineering, Faculty of Engineering, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, United Kingdom.

## **Corresponding Author**

\*Email: <u>M.S.Manga@leeds.ac.uk</u>

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#### S1. Silica nanoparticle charging behavior: The influence of pH and electrolyte

concentrations on the silica nanoparticles dispersions is presented. The i.e.p. for the silica dispersions occurs between pH 2 - 3. As the pH increases the negative magnitude of the zeta potential value also increases. By increasing the NaCl electrolyte concentration the magnitude of the zeta potential at each pH decreases.



Figure S 1. Effect of pH and NaCl electrolyte concentration on the zeta potential of the silica nanoparticles in solution.

**S2. Aggregation behavior of the silica nanoparticles:** Although the primary particle size of the particles is 12 nm they aggregate when dispersed in water. At pH 6 and 0.1 M NaCl, the hydrodynamic diameter of these particle dispersions stirred at 1250 rpm is around  $185 \pm 10$  nm. These sizes remain consistent as a function of typical emulsification times as shown in Figure S2. The dispersions do undergo slow sedimentation taking several days to clear water if left standing still.



Figure S 2. Particle size distribution of the silica nanoparticle dispersions as a function of time prepared at pH 6, 0.1M NaCl and agitated at 1250 rpm.

**S3. Bulk emulsion studies:** Preliminary bulk emulsion studies using the silica nanoparticles and tricaprylin oil at pH 6 at different electrolyte concentrations. Increasing the concentration leads to improvements in emulsion stability.



Figure S 3. Preliminary emulsion studies investigating the bulk stabiliy of tricaprylin oil droplets in water (oil to water ratio = 50:50) stabilized by silica nanoparticles. The nanoparticles are dispersed at pH 6 in different electrolyte concentrations.

**S4. Impact on emulsion formation:** Assuming a diffusion limited adsorption process, simple calculations can be made to evaluate whether there are enough particles in the bulk to stabilise emulsions and whether they can reach the interface fast enough.

<u>Calculations</u> – Based on particles with a hydrodynamic diameter of 185 nm at a concentration of 4 wt% to stabilise an oil volume fraction of 10%.

| Volume of 1 particle                    | 3.3157 ×10 <sup>-21</sup> | m <sup>2</sup>    |
|---|---------------------------|-------------------|
| Density of silica                       | 60                        | kg/m <sup>3</sup> |
| Mass of 1 particle                      | 1.9894 ×10 <sup>-19</sup> | kg                |
| Total number of particles in continuous | 1 2006 × 10+16            |                   |
| phase                                   | 1.8090 ×10                |                   |
|   |                           |                   |
| Volume of oil droplet                   | 4.1635 ×10 <sup>-14</sup> | $m^2$             |
| Total no of droplets                    | 240181583                 |                   |
| Surface area of droplet                 | 5.8096 ×10 <sup>-09</sup> | $m^2$             |
| Area occupied by HCP packing            | 1.2811 ×10 <sup>-13</sup> | $m^2$             |
| Total no of particles to cover all      | 1 0002 10+13              |                   |
| droplets                                | 1.0892 ×10 <sup>-13</sup> |                   |
| For 1 droplet                           | 45347                     |                   |
|   |                           |                   |

Table S 1. Droplet coverage data at an oil volume fraction of 10%

Based on particles with a hydrodynamic diameter of 185 nm at a concentration of 4 wt% to stabilise an oil volume fraction of 50%.

| 3.32 ×10 <sup>-21</sup> | m <sup>2</sup>  |
|-------------------------|---|
| 60                      | kg/m <sup>3</sup>   |
| 1.99 ×10 <sup>-19</sup> | kg  |
| 1 01 ×10+16             |   |
| 1.01 ×10                |   |
|                         |   |
| 4.08 ×10 <sup>-13</sup> | $m^2$   |
| 1.23 ×10 <sup>+08</sup> |   |
| 2.66 ×10 <sup>-08</sup> | m <sup>2</sup>  |
| 1.28 ×10 <sup>-13</sup> | m <sup>2</sup>  |
| 2.55 ×10 <sup>+13</sup> |   |
| 207582                  |   |
|                         | $3.32 \times 10^{-21}$ $60$ $1.99 \times 10^{-19}$ $1.01 \times 10^{+16}$ $4.08 \times 10^{-13}$ $1.23 \times 10^{+08}$ $2.66 \times 10^{-08}$ $1.28 \times 10^{-13}$ $2.55 \times 10^{+13}$ $207582$ |

Table S 2. Droplet coverage data at an oil volume fraction of 50%

Based on particles with a hydrodynamic diameter of 185 nm at a concentration of 4 wt% to stabilise an oil volume fraction of 70%.

| Volume of 1 particle                        | 3.32 ×10 <sup>-21</sup> | m <sup>2</sup>    |
|---|-------------------------|-------------------|
| Density of silica                           | 60                      | kg/m <sup>3</sup> |
| Mass of 1 particle                          | 1.99 ×10 <sup>-19</sup> | kg                |
| Total number of particles in continuous     | 6 03 ×10 <sup>+15</sup> |                   |
| phase                                       | 0.05 ~10                |                   |
|   |                         |                   |
| Volume of oil droplet                       | 2.81 ×10 <sup>-12</sup> | $m^2$             |
| Total no of droplets                        | $2.49 	imes 10^{+07}$   |                   |
| Surface area of droplet                     | 9.62 ×10 <sup>-08</sup> | m <sup>2</sup>    |
| Area occupied by HCP packing                | 1.28 ×10 <sup>-13</sup> | m <sup>2</sup>    |
| Total no of particles to cover all droplets | 1.87 ×10 <sup>+13</sup> |                   |
| For 1 droplet                               | 751088                  |                   |
|   |                         |                   |

Table S 3. Droplet coverage data at an oil volume fraction of 70%

<u>Diffusion time of particles</u> – Based on particle size of 185 nm and Debye length in 0.1 M NaCl

Table S 4. Particle diffusion data during emulsification process

| Diffusion Coefficient | 2.35 ×10 <sup>-12</sup> | m <sup>2</sup> /s |
|-----------------------|-------------------------|-------------------|
| Debye Length          | 1 ×10 <sup>-09</sup>    | m                 |
| Diffusion Time        | 2.12 ×10 <sup>-07</sup> | S                 |