Supporting Information

for the manuscript entitled

Analysis of the interaction of the surfactants oleic acid and oleylamine with iron oxide nanoparticles through molecular mechanics modelling.

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1. Models and simulation methods

Nanoparticle size

Since the nanoparticle with a diameter of 2.6 nm has the largest positive charge per surface area, this nanoparticle size was selected for the simulations since it would give the best adsorption response. Table S.1 shows some NP diameters with corresponding surface charges and figure S.1 shows such a 2.6 nm nanoparticle.

Nanoparticle Diameter (nm)	Charge/surface area (coulomb/nm^2)	Nanoparticle Diameter (nm)	Charge/surface area (coulomb/nm^2)
2.0	+0.63762031	6.6	+1.139953723
2.6	**+4.5203809**	7.0	+2.572465743
3.0	+0.530516925	7.6	+1.487945669
3.6	-0.810511969	8.0	+2.392299759
4	-0.397887694	8.6	-0.606837911
4.6	+1.714903482	9.0	+1.544393715
5.0	-0.229183312	9.6	-0.480090186
5.6	+1.705232973	10.0	+1.527888744
6.0	-0.477465233		

Table S.1. Nanoparticle charge/surface area for different NP diameters. The highlighted 2.6 nm diameter was the diameter used in this study.

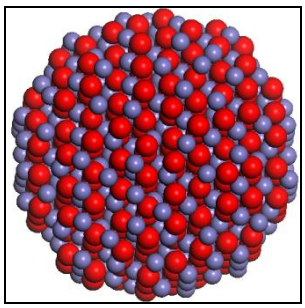


Figure S.1. Iron-oxide nanoparticle with diameter = 2.6 nm. Blue atoms are iron and red atoms are oxygen.

Simulation Experiment 1 and 2: COO^- and NH_3^+

Three different adsorption simulation experiments were performed. In the first experiment, only deprotonated oleic acid molecules were used with no oleylamine molecules present. In the second experiment deprotonated oleic acid molecules were used as shown in figure S.2. The amine groups of the oleylamine molecules were allowed to absorb these deprotonated H^+ atoms (figure S.2) thus forming NH_3^+. By using the 'adsorption locator' - module of the Materials Studio 6.0 (MS6.0) software package, different ratios of the number of oleic acid- to oleylamine – molecules were simultaneously adsorbed onto the nanoparticle surface. For the initial adsorption a universal forcefield was used and the charges were assigned using the QEq charge equilibration method. As a check, the same experiment was repeated using the charge consistent valence forcefield (cvff) with charges assigned by the forcefield. The same results were generated, however it was found that it was easier to visually inspect and find carboxyl-iron and amine-iron bonds by using the universal forcefield at this stage of the simulations. The summation method for the electrostatics and the Van der Waals interactions were both atom based and the quality of the calculation was set to 'fine'.

This experiment was repeated several times for the following oleic acid to oleylamine molecule ratios: 1:1, 1:2, 1:3, 1:4, 1:5, 2:1, 3:1, 4:1 and 5:1.

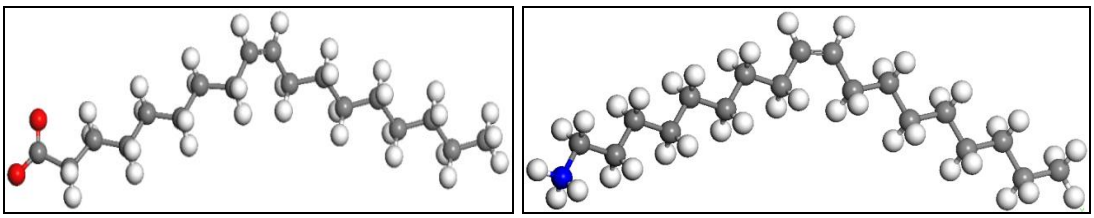


Figure S.2. (Left) A deprotonated oleic acid molecule with COO^- functional group. The red atoms are oxygen. (Right) oleylamine molecule with adsorbed H^+. The blue atom is nitrogen. Grey atoms are carbon and white atoms are hydrogens.

Simulation Experiment 3: COO^- and NH_2

In the third simulation experiment the same deprotonated oleic acid molecules were used. However, this time, the amine groups of oleylamine molecules were not allowed to adsorb the deprotonated H^+ atoms (figure S.3). Similar simulation conditions and settings as for experiment 1 were used. As with experiment 1, different oleic acid to oleylamine ratios were simulated.

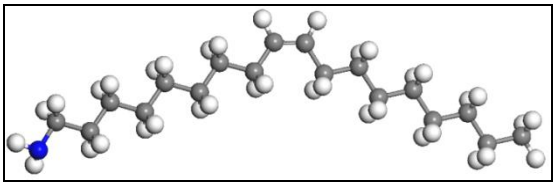


Figure S.3. Oleylamine molecule with NH_2 functional group. The blue atom is nitrogen. Grey atoms are carbon and white atoms are hydrogens.

Molecular Mechanics (MM): Geometry optimization

Molecular mechanics were used to determine the optimum geometries for each of the resulting oleic acid, oleylamine - nanoparticle systems. This was done by using the Discover – module of MS6.0. The charge consistent valence forcefield (cvff) was used with charges assigned by the forcefield. These settings were applied to both Van der Waals and Coulomb forces and the summation method was atom based. The minimization method was selected as 'smart', which uses combinations of the steepest descent, conjugate gradient and newton methods. For the conjugate gradient method, the Fletcher-Reeves algorithm was used and for the newton method the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm was used.

Molecular Dynamics simulations

After geometry optimization by MM, molecular dynamics simulations were performed on each of the aforementioned systems to arrive at the final, energy-optimized systems. A NVT

ensemble at room temperature was used with a time step of 1.0 femtoseconds and a dynamic time of 20.0 picoseconds. An Anderson-thermostat was used with a collision ratio of 1.0 and the number of simulation steps were 20 000.

Binding Energy

In order to calculate the binding energy between the surfactants (E_s) (oleic acid and oleylamine) and the nanoparticle (E_{np}) surface, it is well known that the total energy ($E_{totalsystem}$) is the sum of the total energy of each separate system plus the interaction energy between the nanoparticle and the surfactants. Thus the binding energy (E_b) is calculated according to the following equation:

$$E_b = (E_{totalsystem}) - E_{np} - E_s \quad (1)$$

The total energy of the surfactants is calculated according to the following procedure: after the optimum configuration of the nanoparticle-surfactants system was determined, the nanoparticle was removed from the system. Then a single point energy calculation was carried out, from which the total energy of the surfactant was determined. In order to calculate the total energy of the nanoparticle, the surfactants were removed and a single point energy calculation was carried out to get the total energy of the nanoparticle.

2. Materials and methods

Nanoparticle synthesis and pH-characterisation

Sterically stabilized colloidal dispersions of magnetite nanoparticles were prepared according to a well-known procedure previously described.[15,31] In this procedure magnetite nanoparticles are synthesized in 50 ml dibenzylether by reduction of iron(III) acetylacetonate (Fe(III)-acac) using 1,2-hexadecanediol. Prior to the reaction, a surfactant mixture of pure

oleic acid (cis-9-octadecenoic acid) and pure oleylamine (cis-1-amino-9-octadecene) is added. For each experiment a different ratio of oleic acid (OA) to oleylamine (OLA) was used: OA:OLA = 1:1; 1:2; 1:3, 1:4 and 1:5 as well as 2:1; 3:1; 4:1 and 5:1. The function of the hydrocarbons is to stabilize the nanoparticles that are formed as the reactant mixture is heated to reflux for 60 min at 180 °C under nitrogen. After cooling to room temperature, the particles are precipitated by adding ethanol (50 ml) and using a permanent magnet (0.1 T). After precipitation, the pH of the solution-mixture of supernatant and nanoparticles was measured with a Jenway Lasec 3510 pH meter in the organic solution containing the free hydrogens. Before every single pH measurement, the pH electrode was calibrated with the buffer-solution. After calibration the electrode was rinsed and submerged in the organic solution. Thereafter the supernatant was removed and the nanoparticles were finally dispersed in 20 mL dibenzylether.

Transmission electron microscopy (TEM)

A JEOL JEM-2100F field emission transmission electron microscope (TEM) was used to image the iron-oxide nanoparticles. The microscope was operated at 200 kV. The samples were imaged in the high-angle annular dark field imaging mode (HAADF), which provides Z-contrast imaging, where the brightness depends on the thickness and approximately the square of the atomic number. The instrument is equipped with a bright field (BF) and high angle annular dark field (HAADF) detector. The JEM-2100F uses a high-brightness schottky field emission electron gun producing a probe size of less than 0.5 nm and ultra-high point-to-point TEM resolution of 0.19 nm. ImageJ was used to statistically analyse the size distribution of each TEM micrograph.

Fourier Transform Infrared (spectroscopy) (FTIR)

FTIR spectra were measured with a diamond ATR attached to a Fourier Transform (FT)-Raman 5700 Nicolet® spectrometer from Thermo Electron Corporation: 128 scans were collected per analysis at a resolution of 8.

3. Acid-Base Complex Formation (ABC-pairs)

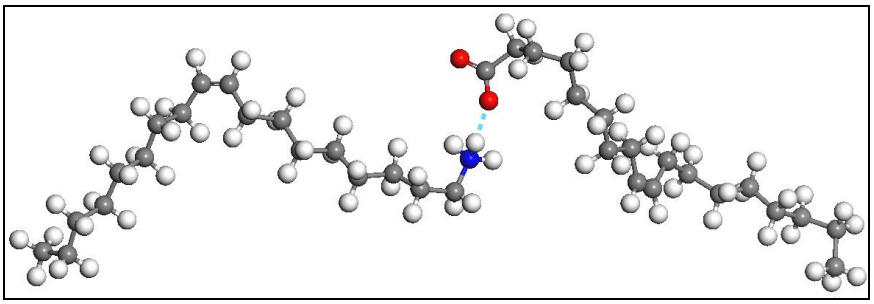


Figure S.4. Acid-base complex formation between an oleic acid and olaylamine molecule in Regime I. The blue dotted line shows the hydrogen bond between the deprotonated, H^+, and oxygen molecule.

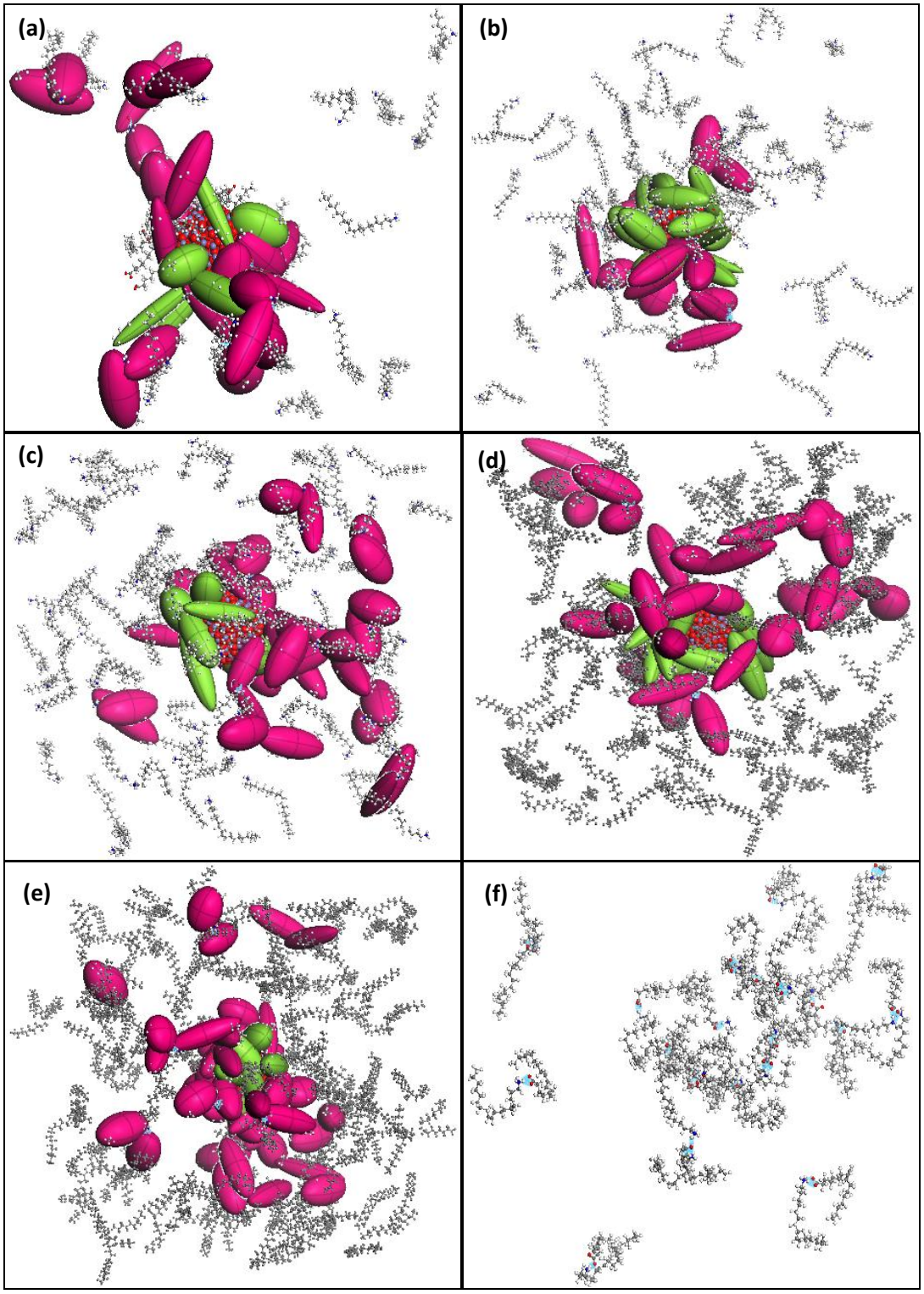
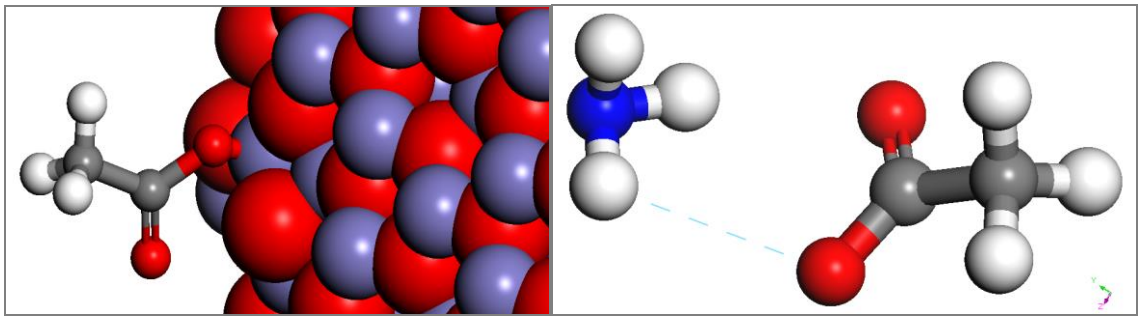


Figure S.5. Complete system geometries for OA:OLA (a)1:1; (b)1:2; (c)1:3; (d)1:4 and (e)1:5. (f) A representative sample of only the ABC pairs for the sample OA:OLA = 1:5.

4. Desorption of ligands

The binding energy of a carboxyl group bound to the NP surface was compared to the binding energy of the carboxyl group bound (via a hydrogen bond) to an amine group (adsorption-, molecular mechanics-, dynamics- and binding energy- calculations were done as described before). Figure S.6 shows the resulting configurations. It was found that the binding energy for the carboxyl bound to the NP surface was much larger (-22.781109 kcal/mole) compared to the carboxyl group bound to the amine group (-4.209456 kcal/mole). Thus under 1:1 conditions, the OA molecule prefers to bind to the NP surface. However, by increasing the number of OLA molecules, the electrostatic force towards OLA and away from the NP surface (for the OA molecules) also increased. Figure S.7 shows how some OA molecules desorb from the NP surface to form ABC-pairs with OLA molecules. The yellow molecules in figure S.7 (b) are OLA molecules. Figure S.7 (c) is the same capped nanoparticle of figure S.7 (a) after the introduction of more OLA molecules. It is clearly observed how some OA molecules desorb from the NP surface to form ABC-pairs.



Binding energy = -22.781109 kcal/mole; Binding energy = -4.209456 kcal/mole

Figure S.6. (Left) Carboxyl group adsorbed to NP surface. The resulting binding energy is -22.781109 kcal/mole. (Right) Carboxyl group binding to amine group. The resulting binding energy is -4.209456 kcal/mole.

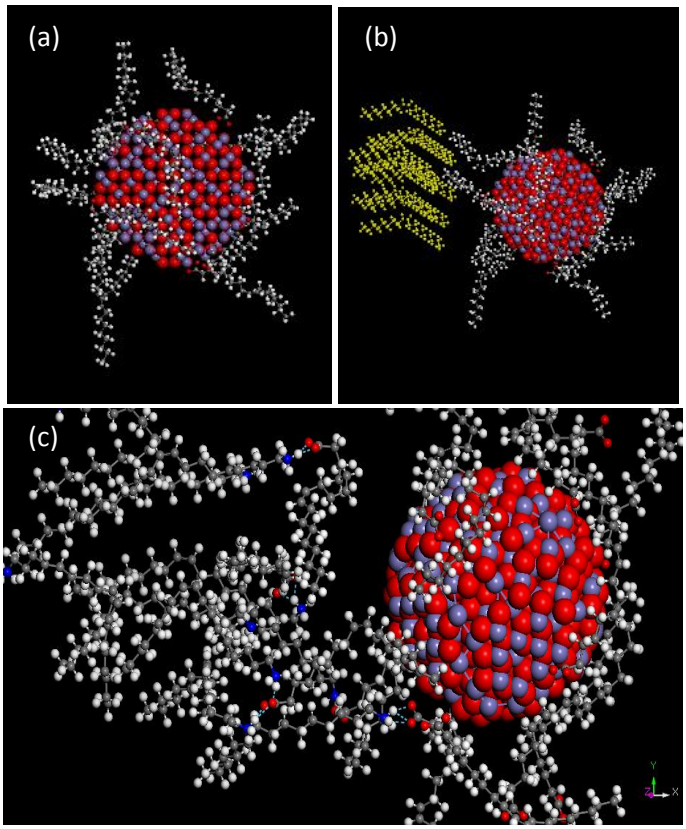


Figure S.7. (a) Iron oxide nanoparticle stabilized with OA molecules. (b) By adding OLA molecules (yellow) the steric force towards the OLA and away from the NP surface is increased leading to (c) some OA molecules desorbing from the NP surface to form ABC pairs.

5. Additional Information: A

To do TEM microscopy *during* NP synthesis we would have to remove some of the material, and allow it to cool down to room temperature, deposit it onto a TEM grid and insert it in the vacuum. However during this entire process both the local environment as well as the temperature of the material would have changed, effectively changing the very structure of the observed material since this structure is a function of the local temperature and reaction environment.

Similarly: to do Zeta-potential measurements *in situ*, both the temperature as well as the electrostatic potential will be affected. On top of that, in the presence of an electric current, the magnetic component of the current will activate the superparamagnetic nanoparticles,

causing them to interact magnetically and therefore agglomerate. As an example, Figure S.8 shows the zeta-potential measurements for OA:OLA = 1:1 coated magnetite. A Malvern Zetasizer instrument was used where the NPs were dispersed in hexane with a dielectric constant of 1.88. A zeta dip cell at RT was used and 100 zeta runs were run, repeated 3 times. For these measurements the zeta potentials were 32 ± 60 mV (at Peak 1), -107 ± 35.3 mV (at Peak 2) and 0.00 (at Peak 3). Thus no clear conclusion on the zeta potential value can be made since the presence of the electric current, and its associated magnetic field, activates the magnetic properties of the NPs and causes them to agglomerate. This does not mean that these particles do not have a zeta potential. They surely do. However, to *measure* this potential without disturbing the local environment and cause the NPs to interact magnetically, is a huge challenge.

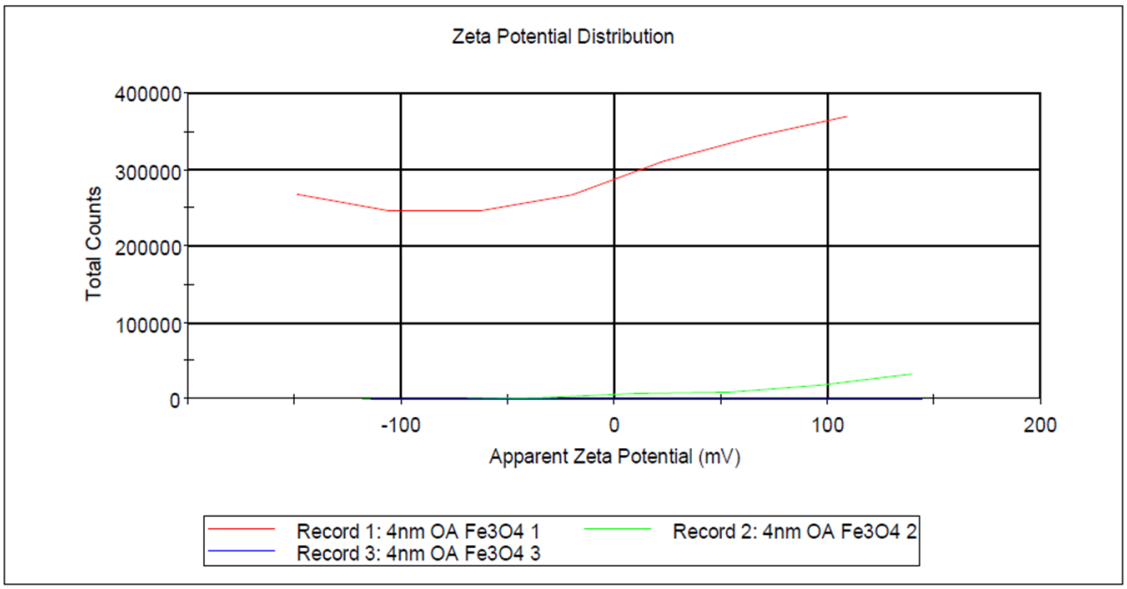


Figure S.8. Zeta potential measurements of an OA:OLA = 1:1 coated magnetic NP. No zeta potential value can be concluded as the electric current's associated magnetic field activate the superparamagnetic NPs and allow them to interact magnetically and agglomerate.

6. Additional Information: B

It is important to emphasize that the ASC will not *really* become electrically neutral or zero when all the Fe atoms are capped, since the presence of uncapped O atoms on the NP surface

will actually result in the average NP surface charge becoming negative. However, since negative surfaces will not attract nor bind to OA, to simplify this discussion, we will treat a NP surface with only uncapped O atoms as “electrically neutral”.