

Supporting Information:

The Nature of Alcohol Co-Adsorption Sites and their Effects on Surfactant Aggregate Structure on Silica Investigated by ^2H and ^{13}C NMR

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The sample pH of 9 used in this study was chosen to ensure a high TTAB adsorption density. It was found that the adsorption of TTAB on Aerosil OX50 silica increased with increasing pH values, where a maximum was reached around pH 9 (Figure S1). This is similar to what is reported in previous literature for TTAB.^{1, 2} The maximum TTAB adsorption density at pH 9 of $5.5 \mu\text{mol}/\text{m}^2$ is equal to that previously found for TTAB adsorbed on silica at pH 9.7,² while the adsorption density of $1.7 \mu\text{mol}/\text{m}^2$ at pH 5 is significantly lower than the adsorption density of $4 \mu\text{mol}/\text{m}^2$ previously reported at this pH.¹ The low adsorption at lower pH values compared to previous literature may be due to differences in silanol density, which for Aerosil OX50 is relatively low ($2.0 \text{ OH}/\text{nm}^2$ when dry and $3.3 \text{ OH}/\text{nm}^2$ when hydrated, see Materials and Methods) compared to other silica materials, and consequently results in a lower charge density on the surface. This demonstrates the necessity of relatively high pH values in order to obtain maximum adsorption on fumed silica particles, such as Aerosil OX50. At even higher pH values the adsorption decreases, which is shown in Figure S1.

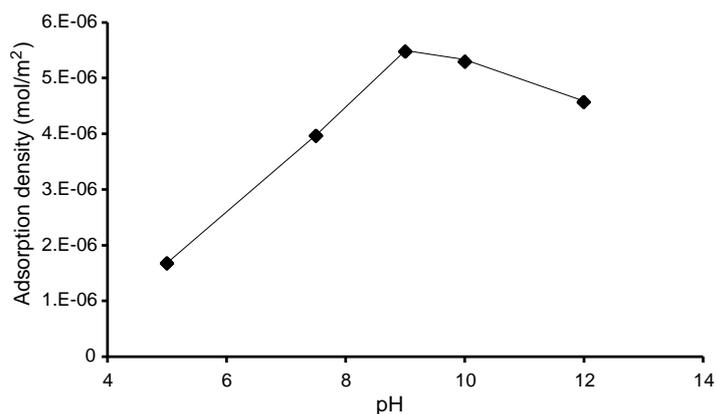


Figure S1. TTAB adsorption densities on Aerosil OX50 fumed silica versus pH. The pH was adjusted by adding small amounts of a 1.0 or 0.1 M NaOH solution. A high TTAB equilibrium concentration of 0.05 M was used to ensure that the adsorption plateau was reached in all the samples of varying pH. The samples were equilibrated for 24 hours.

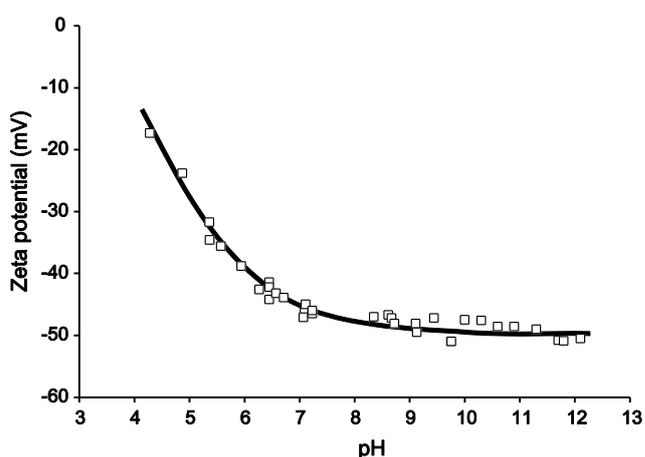


Figure S2. Zeta potential versus pH for the Aerosil OX50 silica particles used in this study. Each point is an average of three measurements with eleven individual runs in each measurement. 0.1 wt % silica dispersed in pure water was titrated automatically with a 0.25 M NaOH and a 0.25 M HCl solution.

When exposing silica to high pH there is a risk of silica dissolution and this is likely the reason for the reduced adsorption at pH 10-12. The producer reports that the turbidity of an 1.0 wt % Aerosil 200 (similar particles, about 10 nm in diameter) dispersion starts to decrease above pH 10 after equilibration for 24 hours.³ At pH 12 the turbidity is more than halved. In order to be certain that the silica would be stable at a pH value of 9, Scanning Electron Microscopy (SEM) pictures were recorded of two silica samples that had been equilibrated at

pH 9.5 and pH 10.5 for 48 hours, as well as a picture of untreated silica for comparison. As an additional test, Dynamic Light Scattering (DLS) was used to measure the hydrodynamic diameter of the silica after the equilibrium period for the samples equilibrated at pH 9.5 and 10.5, as well as a sample equilibrated at pH 7. Both the SEM and DLS results show that there is no detectable dissolution of the silica, even after equilibration at pH 10.5 for 48 hours. Therefore, the results presented in this study, where an equilibration pH of 9 was used, should not be affected by silica dissolution.

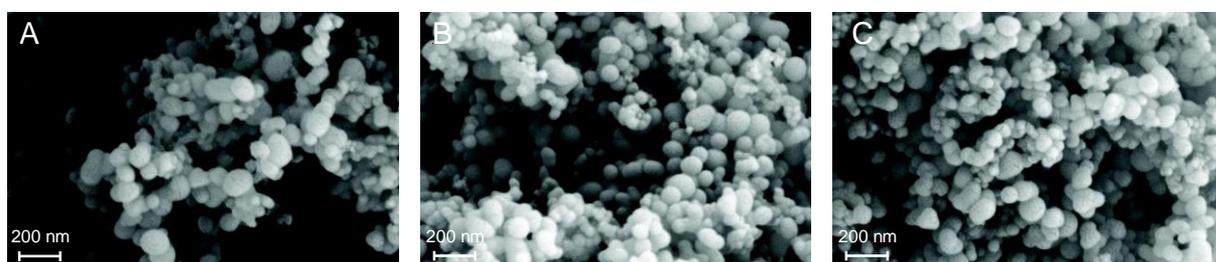


Figure S3. SEM pictures of Aerosil OX50 fumed silica equilibrated for 48 hours in solution of pH (B) 9.5 and (C) 10.5. Picture (A) shows an SEM picture of untreated silica.

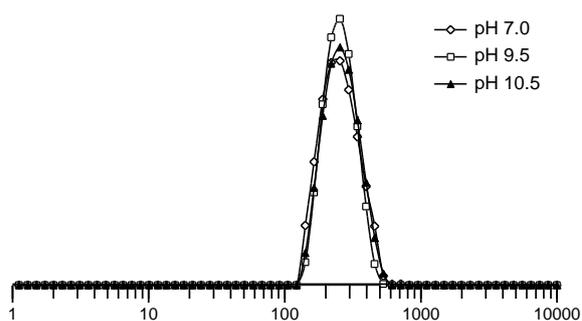


Figure S4. DLS results for Aerosil OX50 fumed silica equilibrated for 48 hours at pH 7, 9.5 and 10.5. The measurements are performed in a 10 mM NaCl suspension at 295 K. The high hydrodynamic diameter compared to the average diameter of 40 nm found by Transmission Electron Microscopy³ is likely caused by a certain degree of agglomeration.

REFERENCES

1. P. Wängnerud and G. Olofsson, *Journal of Colloid and Interface Science*, 1992, **153**, 392-398.
2. P. Waengnerud and B. Joensson, *Langmuir*, 1994, **10**, 3268-3278.
3. H. F. G. Michael, *Schriftenreihe Pigmente: Grundlagen und Anwendungen von AEROSIL*, Degussa AG, 1993.