

Clouding observed for surface active, mPEG-grafted silica nanoparticles

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Supporting information

Functionalization procedure

The functionalization procedure was conducted according to previous work [1]. The mPEG silane was added to the silica suspensions at 70 °C during agitation using a syringe pump with a dosing rate of 0.8 (sample *i*) or 0.3 (sample *ii* and *iii*) $\mu\text{mol}/\text{m}^2\cdot\text{h}$, respectively. The synthesis was performed at pH 9-10, to promote hydrolysis and reduce particle aggregation [2, 3]. At the alkaline conditions the methoxy groups of the mPEG silane are hydrolyzed and the formed Si-OH groups can attach to the silica particle surface through condensation. The samples were purified either by using an ultrafiltration cell from Millipore with an applied N₂ pressure of 1.6 bar. The ultrafiltration membranes of regenerated cellulose (from Millipore) had a cut-off of 100 kDa, removing free unreacted silanes from the suspensions.

Determination of surface coverage

The silica suspensions (sample *i* and *ii*) were ultracentrifuged using an Optima XL-100K Ultracentrifuge from Beckman Coulter, equipped with a Type 90Ti rotor. The samples were spun at 50 000 rpm or ~214 000g for 2.5 h. A sediment (gel) of concentrated silica particles formed at the bottom of the centrifugation tubes. The supernatant, containing the free, unreacted mPEG silane, was carefully extracted using a pipette and analyzed for total carbon content using elemental analysis and methanol content using high performance liquid chromatography (HPLC). The results obtained from the HPLC and elemental analyses as well as the results from the calculations are seen in Table S 1. The surface coverage of sample *iii* was already known, determined through NMR diffusometry in previous work [1].

Table S 1: Results obtained from HPLC and elemental analysis used for determination of surface coverage. Also shown are mPEG silane properties and the results from the calculations performed to obtain the surface coverage.

mPEG silane properties	Molecular weight (when hydrolyzed)	636 g/mol
	Carbon fraction per mole	49 wt%
Sample <i>i</i>	Methanol content (in supernatant)*	1.9 wt%
	Total carbon, TC (in supernatant)**	80 g/L
	Total carbon from mPEG silane in supernatant (calculated by subtracting the carbon content from methanol)***	72.9 g/L
	Total amount of added carbon from mPEG silane	89.5 g/L
	Yield	18.5 %
	Added amount mPEG silane	4 $\mu\text{mol}/\text{m}^2 \text{SiO}_2$
	Surface coverage (bound mPEG silane)	0.74 $\mu\text{mol}/\text{m}^2 \text{SiO}_2$
Sample <i>ii</i>	Methanol content (in supernatant)*	0.2 wt%
	Total carbon, TC (in supernatant)**	29 g/L
	Total carbon from mPEG silane in supernatant (calculated by subtracting the carbon content from methanol)***	28.2 g/L
	Total amount of added carbon from mPEG silane	49.2 g/L
	Yield	42.6 %
	Added amount mPEG silane	2 $\mu\text{mol}/\text{m}^2 \text{SiO}_2$
	Surface coverage (bound mPEG silane)	0.85 $\mu\text{mol}/\text{m}^2 \text{SiO}_2$

* From HPLC

** From elemental analysis

*** This is the free, non-bound mPEG silane species

UV-Vis measurements

The absorbance at 700 nm was collected at increasing temperature, with an equilibration time of 10 minutes between every temperature change, using a UV-Vis spectrophotometer equipped with a heating block. The absorbance as a function of temperature is seen in Figure S 1, and corresponds to an increase in turbidity [1]. The initial turbidity is regained upon cooling and the cloud point temperature corresponds well to the one obtained from visual observation.

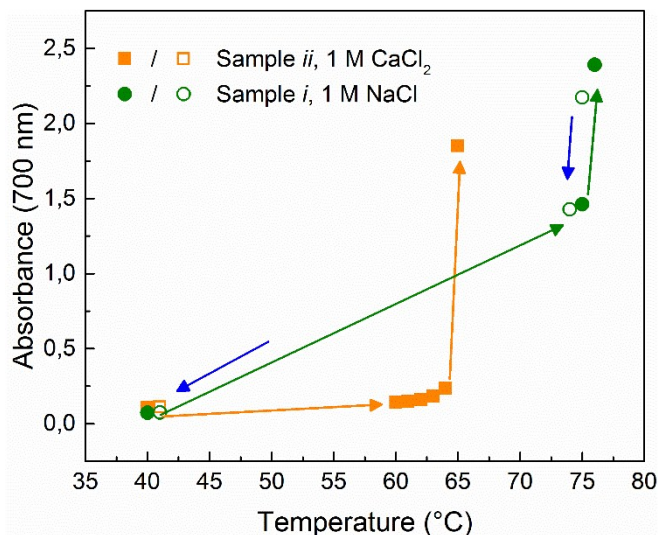


Figure S 1. Absorbance at 700 nm measured with UV/Vis spectroscopy, showing variations in turbidity as a function of temperature. The full symbols show the absorbance obtained while heating the suspensions, and the open symbols are the absorbance obtained while cooling, indicated by the blue arrows. The samples are surface functionalized with mPEG silane and were diluted to 2 wt% SiO₂.

Cloud points of purified samples and of mPEG silane

Table S 2. DLS particle sizes of sample *ii*, purified through ultrafiltration, after being heated above their cloud points, at pH 9. The sample without added salt was heated to 110 °C, but did not cloud.

CaCl ₂ concentration (M)	$d_{p,vol}$ after heating (nm)
Without added salt	33.4 ± 0.5
0.1	43.0 ± 1.6
0.3	44.9 ± 0.9
0.5	63.1 ± 2.4
1	84.2 ± 2.0
1.5	140 ± 66

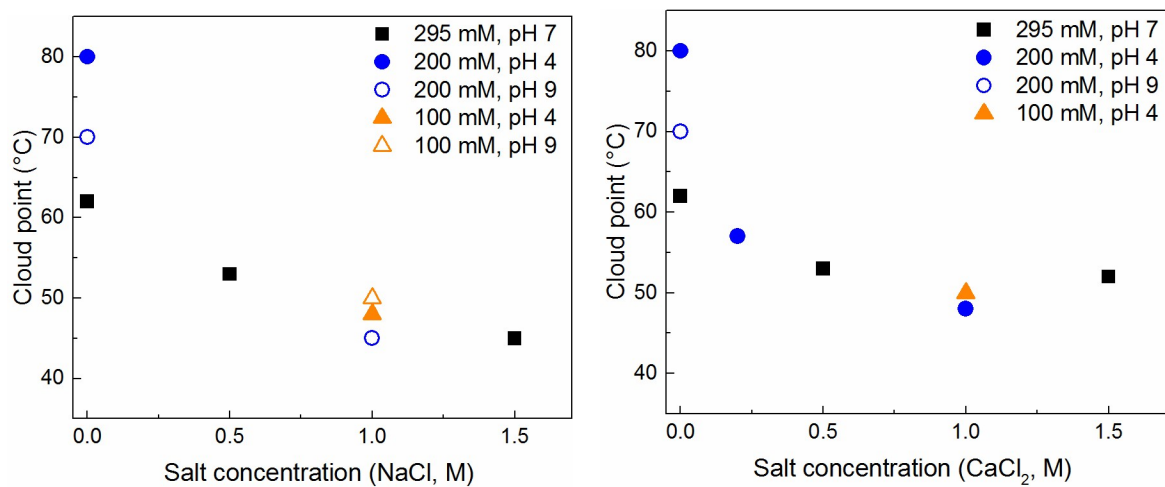


Figure S 2. Observed cloud points of mPEG silane in solution without particles, as a function of salt concentrations, at varying mPEG silane concentrations and pH conditions. The samples containing more than 0.5 M CaCl₂ remain cloudy after heat treatment, indicating an aggregation process. Since visual inspection was used for cloud point determination, an error of ± 2 °C should be accounted for.

Repeated experiments, potentiometric titrations

Figure S 3 shows the repeated potentiometric titrations and that the experimental error seems to be small.

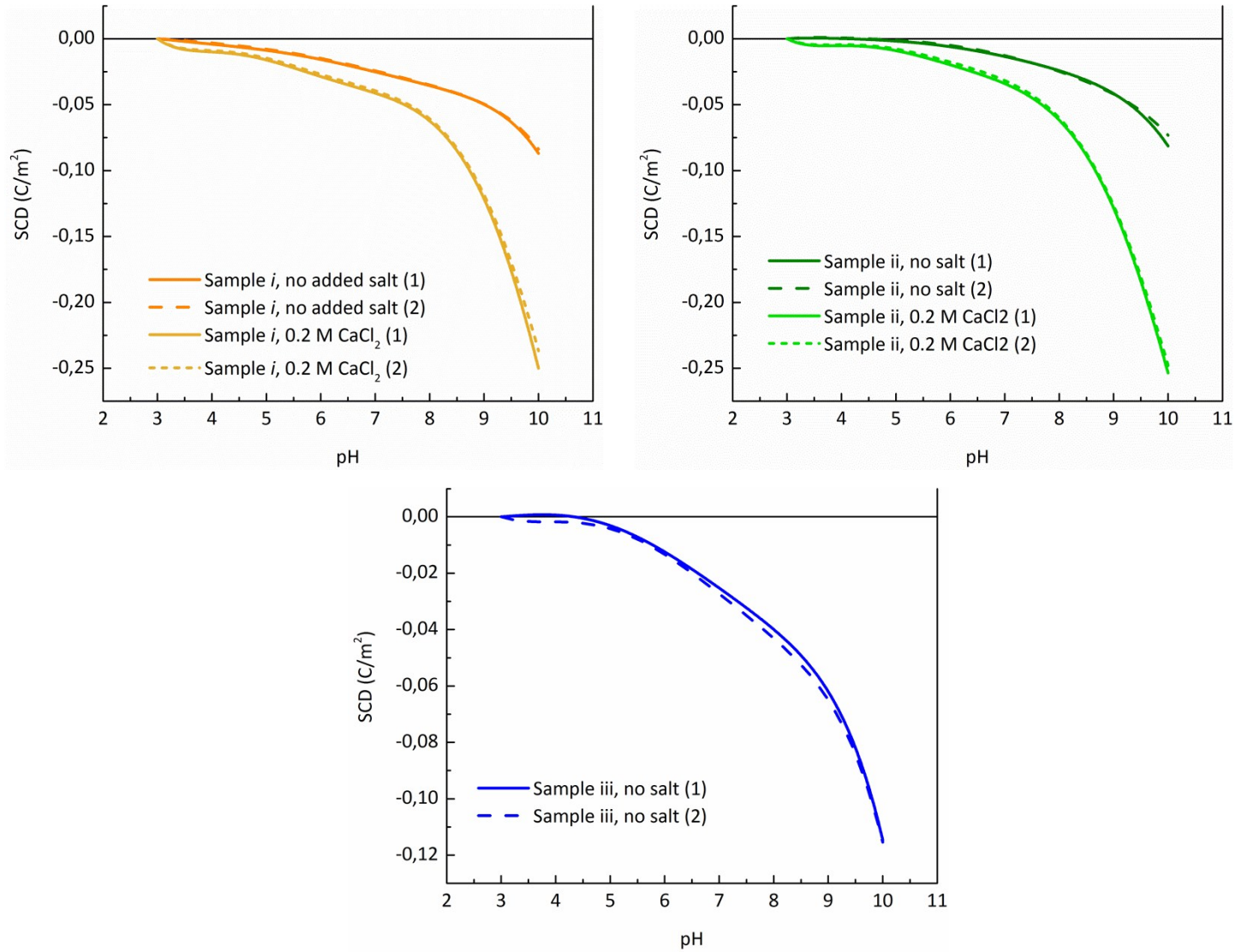


Figure S 3. SCDs obtained from repeated potentiometric titration measurements.

Additional NMR results

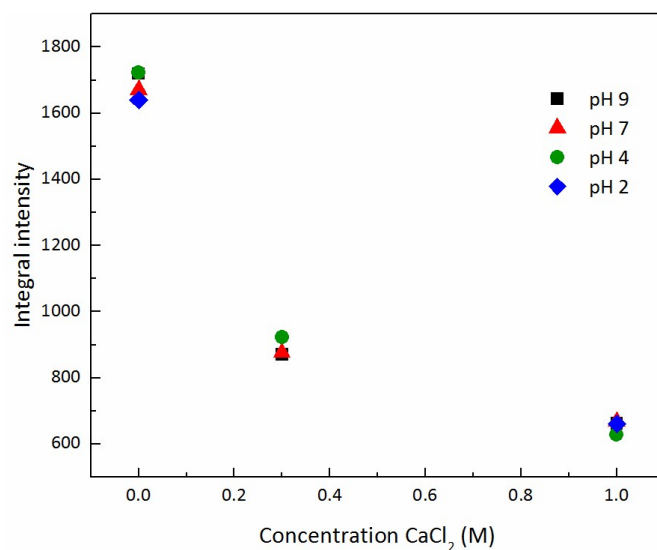


Figure S 4. The integral intensities, obtained from ¹H NMR measurements, of the peak arising from the poly(oxy ethylene) units of the mPEG silane of sample *ii* as a function of CaCl₂ concentration, at varying pH conditions. The spectra were recorded on a Varian 400.

References

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2. Osterholtz, F.D. and E.R. Pohl, *Kinetics of the hydrolysis and condensation of organofunctional alkoxysilanes: a review* Journal of Adhesion Science and Technology, 1992. **6**(1): p. 127-149.
3. Iler, R.K., *The Chemistry of Silica*. 1979, New York: Wiley.