Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

NMR Proton Relaxation for Measuring the Relative Concentration of Nanoparticles in Liquids

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Materials and Methods

Materials

Two silica dispersions were purchased for this study: LUDOX® AS-40 and LUDOX® SM, which according to the Merck Life Science (Dorset, UK) supplier have nominal particle sizes of 22 nm and 7 nm, and concentrations of 40 wt% and 30 wt%. The full details reported by the supplier on the two samples are reported in Table S1.

Table S1 – Properties of samples as reported from the supplier

Sample name	Nominal particle size (nm)	Specific surface area (m^2/g)	Silica content $\%SiO_2$	Typical sodium content Wet Basis %Na
AS-40	20 - 24	129 - 155	40	0.07
SM	7	320 - 400	30	0.50

The initial concentration of the dispersions was verified gravimetrically by drying 3 sample aliquots from the sample stock solution by evaporation and was found to be within 10 % of the value reported by the manufacturer. The uncertainty on the starting concentration was therefore taken to be 10 % of the reported values.

Methods

Concentration calculations

Dispersions were diluted gravimetrically with ultrapure water to vary their silica content. Mass concentrations in the batch dispersions were taken as 0.30 ± 0.03 for SM and 0.40 ± 0.04 for AS-40 (c_i).

Samples were diluted gravimetrically by weighing the raw (as purchased) dispersion used, adding ultrapure water and recording the total weight of the final diluted dispersion. The particle weight was determined from their raw concentration and the weight of the raw dispersion as:

$$particle\ weight = c_i \cdot weight\ of\ raw\ dispersion \tag{S1}$$

The dispersant weight in the final dilution was determined as:

$$dispersant\ weight\ = total\ weight - particle\ weight \tag{S2}$$

The final mass fraction (c_f) after dilution were calculated as:

$$c_f = \frac{particle\ weight}{particle\ weight + dispersant\ weight} \tag{S3}$$

In a few cases, to achieve the lower concentrations used in this work, the dispersions were diluted in series by further diluting a previously diluted dispersion. However, in the majority of cases dispersions were diluted from the raw dispersions, to avoid error propagation in the dilution process.

Concentrations for UV-Vis were plotted as mass concentrations and calculated as:

$$mass\ concentration\ = \frac{particle\ weight}{particle\ volume + dispersant\ volume} \quad \text{(S4)}$$

In which the particle and dispersant volumes were calculated from the particle and dispersant weights assuming densities of 2.3 g/cm^3 and 1 g/cm^3 for silica and water respectively.

Concentrations for NMR proton relaxation measurements were calculated as volume ratios Ψ according to the formula shown below:

$$\Psi = \frac{particle\ volume}{dispersant\ volume} \quad \text{(S5)}$$

These were converted in a mass concentration c_{f} according to the formula:

$$mass\ concentration = \Psi \cdot \rho \cdot \frac{dispersant\ volume}{particle\ volume + dispersant\ volume} \quad \text{(S6)}$$

In which ρ is the density of the particles.

Finally, for Figure 4 all concentrations were converted into particle number concentration (kg^{-1}) assuming particles to be spherical and their diameters to be 7 nm and 22 nm for SM and AS-40 respectively.

The mass of one particle M_{p} was calculated modelling them as a perfect sphere with nominal diameter D:

$$M_p = \frac{\pi}{6} \cdot \rho \cdot D^3 \quad \text{(S7)}$$

Where ρ is the particle density, which was assumed to be 2.3 g/cm^3 for both silica particles.

Finally, the number concentration of nanoparticles N was calculated as:

$$N = \frac{c_f}{M_p} \quad \text{(S8)}$$

Uncertainties in the concentrations were calculated from multiple measurements of the mass of particles after drying of the stock dispersion, providing a 10 % uncertainty in the initial mass concentration. Negligible uncertainties were assumed in the densities, and an expanded uncertainty of ~0.8 mg at a 99 % confidence level (k=3) was used in all mass measurements unless specified. This was estimated for the balance used from repeatability, eccentricity, non-linearity and sensitivity uncertainty contributions. Uncertainties were propagated using standard error propagation formulae to all calculations.

Scanning Electron Microscopy (SEM)

Diluted silica dispersions were drop-cast on silicon wafers with a native oxide layer at the boiling point of the solvent (roughly 100 °C) for SEM analyses. Before the sample deposition, wafers were cleaned by sonicating them for 5 minutes in each solvent in the following order: acetone, water, isopropanol. Images were collected using a Zeiss (Oberkochen, Germany) Supra scanning electron microscope by measuring secondary electrons (In lens detector, 30 µm aperture, 5 kV accelerating voltage).

UV-Vis spectroscopy

Absorbance spectra were recorded on a Cary 60 UV-Vis Spectrophotometer from Agilent Technologies (California, US) between 250 nm and 800 nm for AS-40 and 245 nm and 600 nm for SM. Samples were measured in disposable plastic cuvettes from BRAND® UV (Wertheim, Germany). The spectrum of pure water was subtracted from the sample spectra to give the absorbance due to silica particles only. Absorbance values at selected wavelengths were then plotted against concentrations as calculated from gravimetric dilutions (see Materials section).

The measurement was performed in triplicate and the results averaged. The uncertainty in the absorbance values reported for selected wavelengths was calculated for a coverage factor k=3.

NMR proton relaxation

Silica dispersions were prepared as described in the “Materials” section and introduced into NMR tubes (100 MHz, 5 mm diameter) using long glass pipettes, immediately after vigorous mixing (~ 1 min vortex). Care was taken to fill the NMR tubes to the same height for each measurement (roughly 55 mm between the meniscus of the solution and the lower end of the tube). NMR tubes were then sealed with PTFE tube caps to prevent solvent evaporation. Spin-spin (T2) relaxation experiments were performed in an Acorn Area benchtop NMR from Xigo Nanotools (Orefield, PA, USA) operating at approximately 13 MHz. Prior to the start of the analysis, the resonance frequency was tuned with a standard test dispersion provided by Xigo Nanotools. The laboratory temperature was monitored in close proximity to the equipment and was observed to be relatively stable (21.0 ± 0.1 °C). “The instrument, however, generally operates at 3 °C above ambient temperature. The temperature of an NMR tube filled with water was measured with a thermocouple after 2 minutes inside the instrument (equivalent to the measurement time) and was found to be 24.5 °C ± 0.1 °C.” The relaxation time (T2) was measured with a Carr-Purcell-Meiboom-Gill (CPMG) method.

The T2 CPMG sequence employs a 90° pulse (6.78 μs) followed by a series of 180° pulses (13.56 μs). The time between the initial 90° and 180° pulse is termed τ, and 180° pulses are repeated every 2* τ. A τ of 0.5 ms has been employed for all measurements. An echo occurs following each 180° pulse until the signal decays. The average peak value of each echo is then plotted as a function of time. A scan is an application of this sequence of pulses. The number of echo cycles for each scan is calculated automatically from the software algorithm so that the total duration of the scan is 5 × T2. The first scan is a "dummy" and is not used in the calculation of T2, the subsequent measurement scans are averaged to calculate Mxy(t), which is fitted to a single exponential with an offset to calculate T2. A total of 4 scans were averaged in each experiment, as no significant effect on the resulting T2 values was observed as the number of scans was increased from 4 to a total of 15 scans. The recycle delay between each scan was set to 5 × T2. The measurement parameters were selected based on a chosen T2 value, which was first estimated by the user and then corrected based on the subsequent measurement result. Measurements were repeated until the initially chosen T2 values were within 20% of the measured values.

The measurement was performed in triplicate and the results averaged. The uncertainty in the relaxation rate was calculated for a coverage factor k=3.

Comparison of UV-Vis and NMR proton relaxation methods

To compare NMR proton relaxation and UV-Vis results we plotted them as a relative change in measurand between the sample and the dispersant (in this case water), normalised to the sample at 15 mg/mL according to equations S9 (for UV-Vis) and S10 (for NMR proton relaxation):

$$\frac{\Delta A}{\Delta A_{15}} = \frac{(A_x - A_{dispersant})}{(A_{15\,mg/ml} - A_{dispersant})} \quad \text{(S9)}$$

$$\frac{\Delta R_{av}}{\Delta R_{av15}} = \frac{(R_{av,\,x} - R_{av,\,dispersant})}{(R_{av,\,15\,mg/ml} - R_{av,dispersant})} \quad \text{(S10)}$$

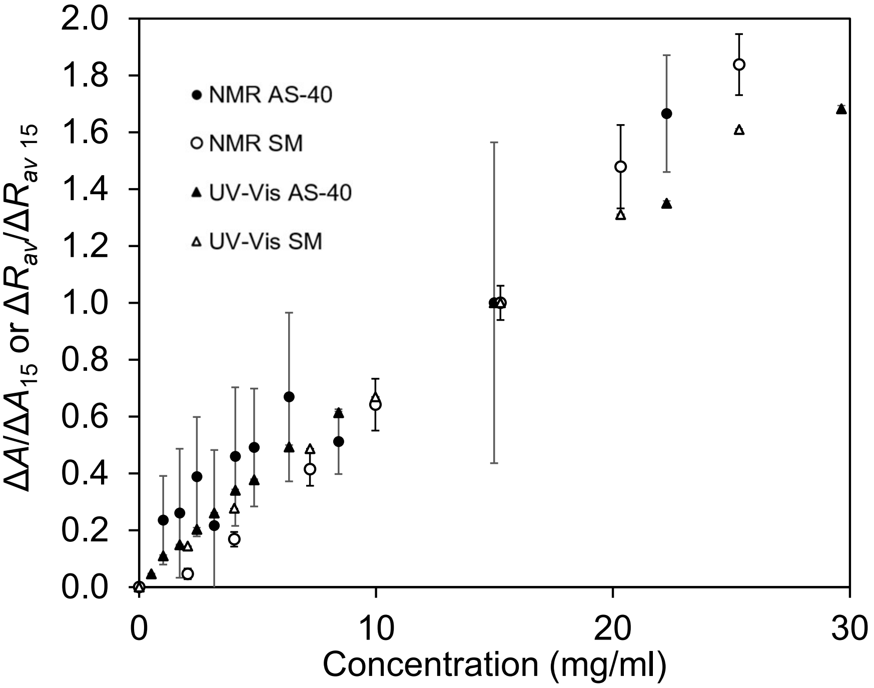

Figure S1: Lower concentration range showing NMR proton relaxation and UV-Vis results compared.