

Nanoparticle metrology of silicates using time-resolved multiplexed dye fluorescence anisotropy

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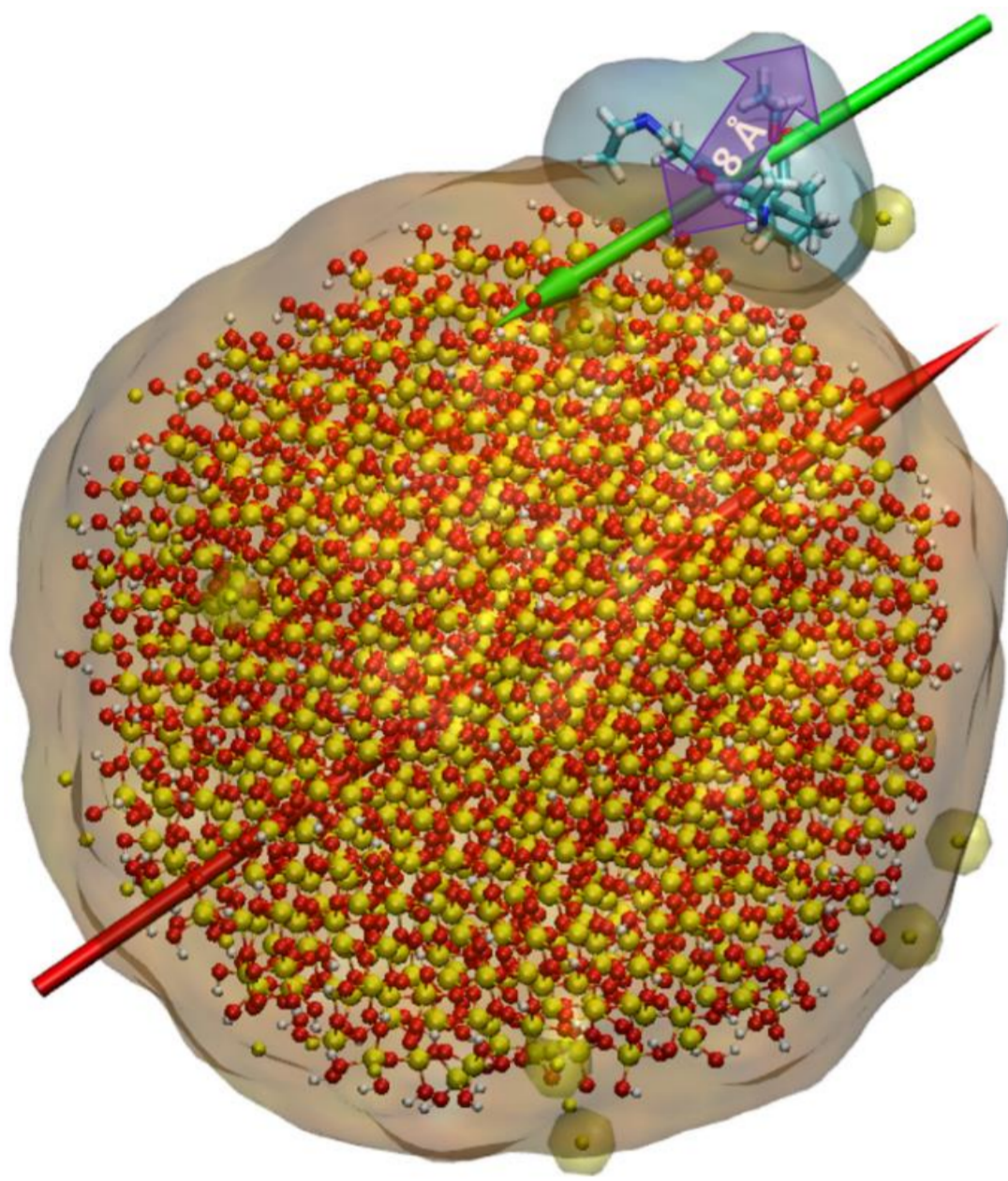
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Sodium silicates are versatile inorganic chemicals used in various bonding and coating applications as well as precursors to colloidal silica. Up to now, a gold standard used to qualitatively characterise them was NMR spectroscopy. In this work, we present a relatively simple method based on time-resolved multiplexed dye fluorescence anisotropy [1]. Rotational times of non-binding Rhodamine B and adsorbing Rhodamine 6G allow us to independently determine the medium microviscosity and the silicate particle radius, respectively. Furthermore, both dyes can be excited using a single excitation wavelength when both dyes are present in the sample [2]. The recovered size of $7.0 \pm 1.2 \text{ \AA}$ agrees with the recovered size using SAXS measurements. The dye's impact on the measured size is further assessed using molecular dynamics simulations [3].



A sodium silicate solution made by Millipore is used in the presented work. Three independent experiments were performed:

1. Diluting sodium silicate using dH_2O
2. The temperature of unmodified stock silicate was changed between 12 and 53 °C
3. Both dyes were added to the unmodified stock silicate solution. The sample was excited using 494 nm nanoLED.

The dyes were added to silicate solutions creating samples of 10 μM concentration.

Methods

Anisotropy decay function was generated:

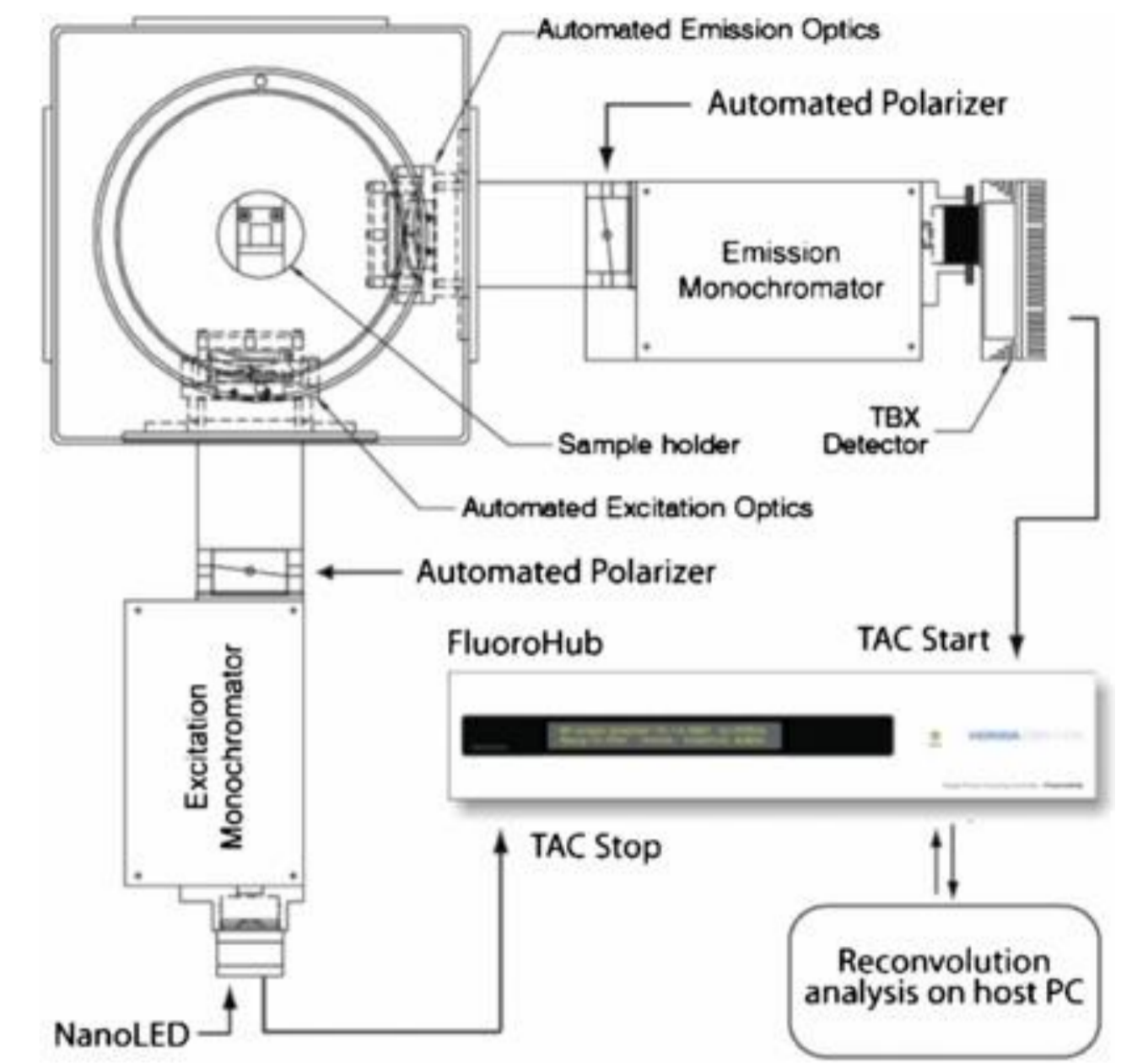
$$R(t) = \frac{I_V(t) - I_H(t)}{I_V(t) + 2I_H(t)}$$

Using the rotational time of non-binding RB the microviscosity was calculated using:

$$\eta = \frac{3kT\phi_r}{4\pi R_p^3}$$

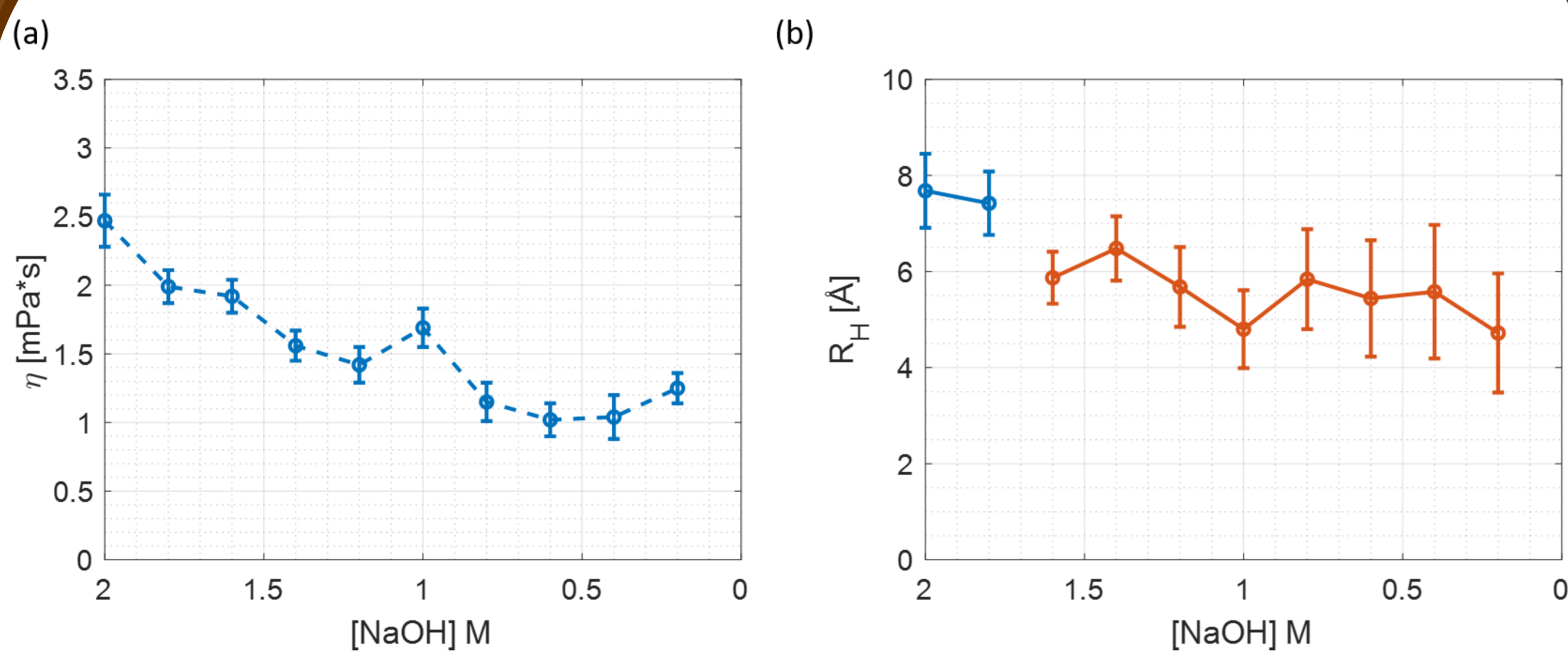
Using the rotational time of binding R6G the R_H was calculated using:

$$R_p = \sqrt[3]{\frac{3kT\phi_r}{4\pi\eta}}$$



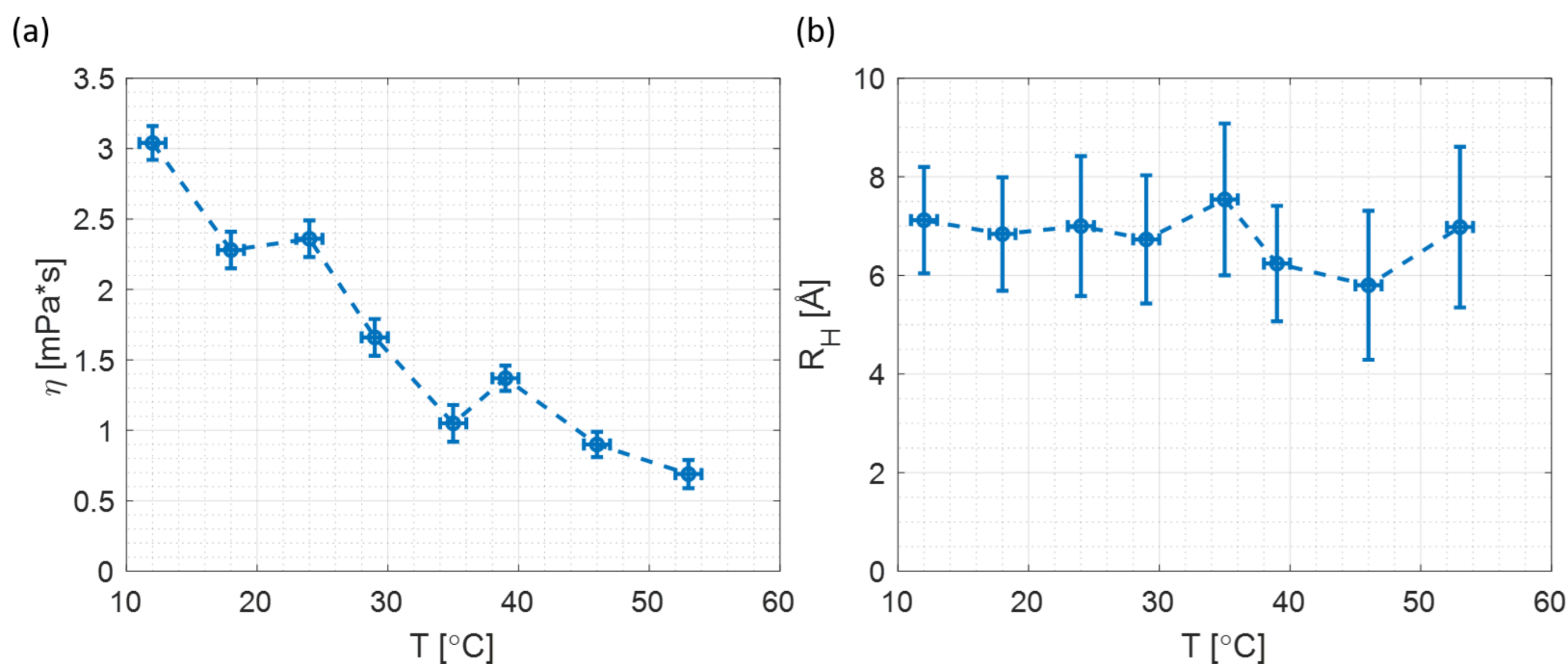
Results

Dilution of stock silicate

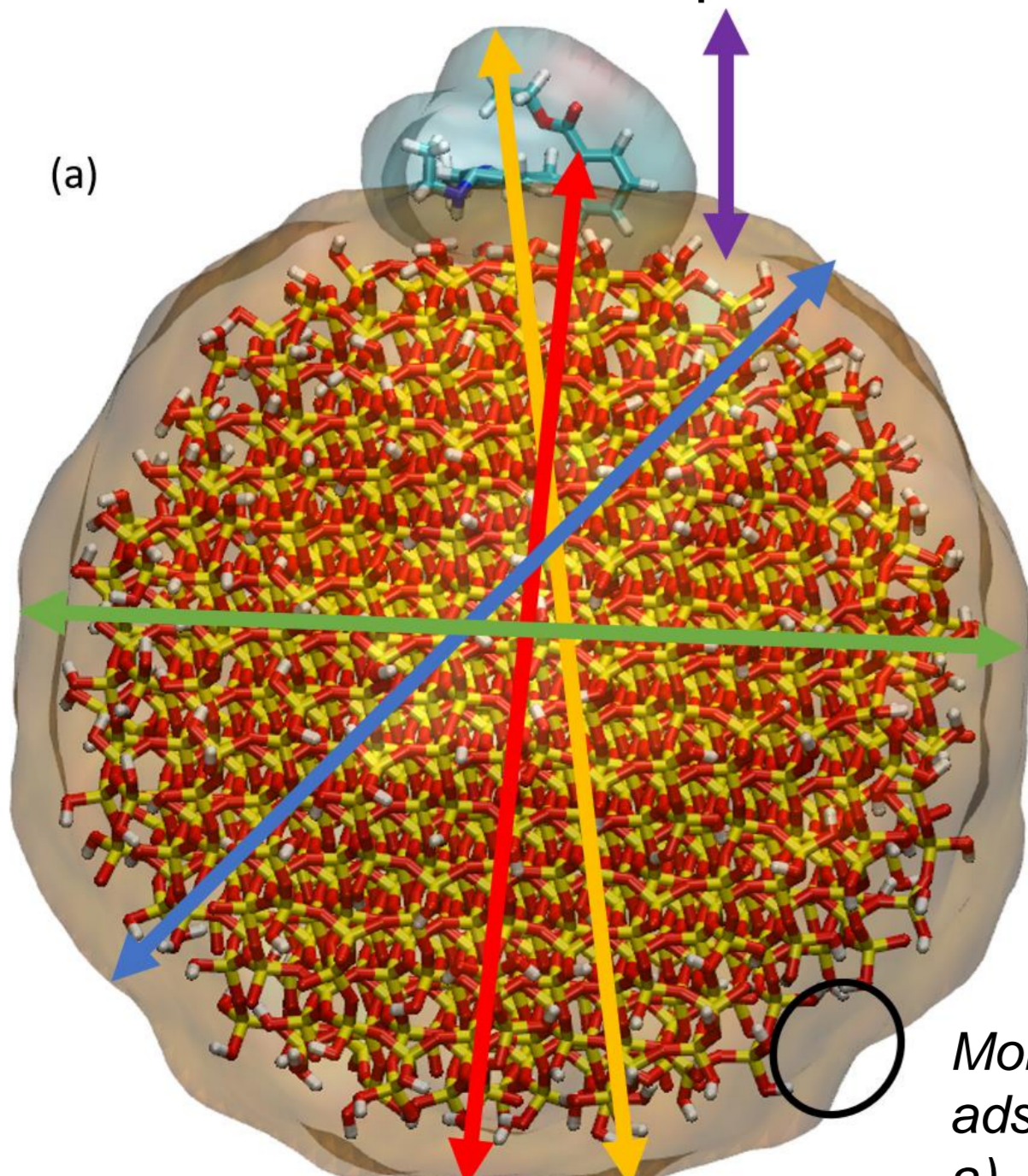


The measured sizes are significantly smaller when compared with the undiluted and 1.8M samples. Due to the dilution, the amount of silicate particles in the sample decreases. As the dye concentration is maintained at the value of 10 μM the anisotropy decay might be dominated by the free dye.

Temperature controlled measurements

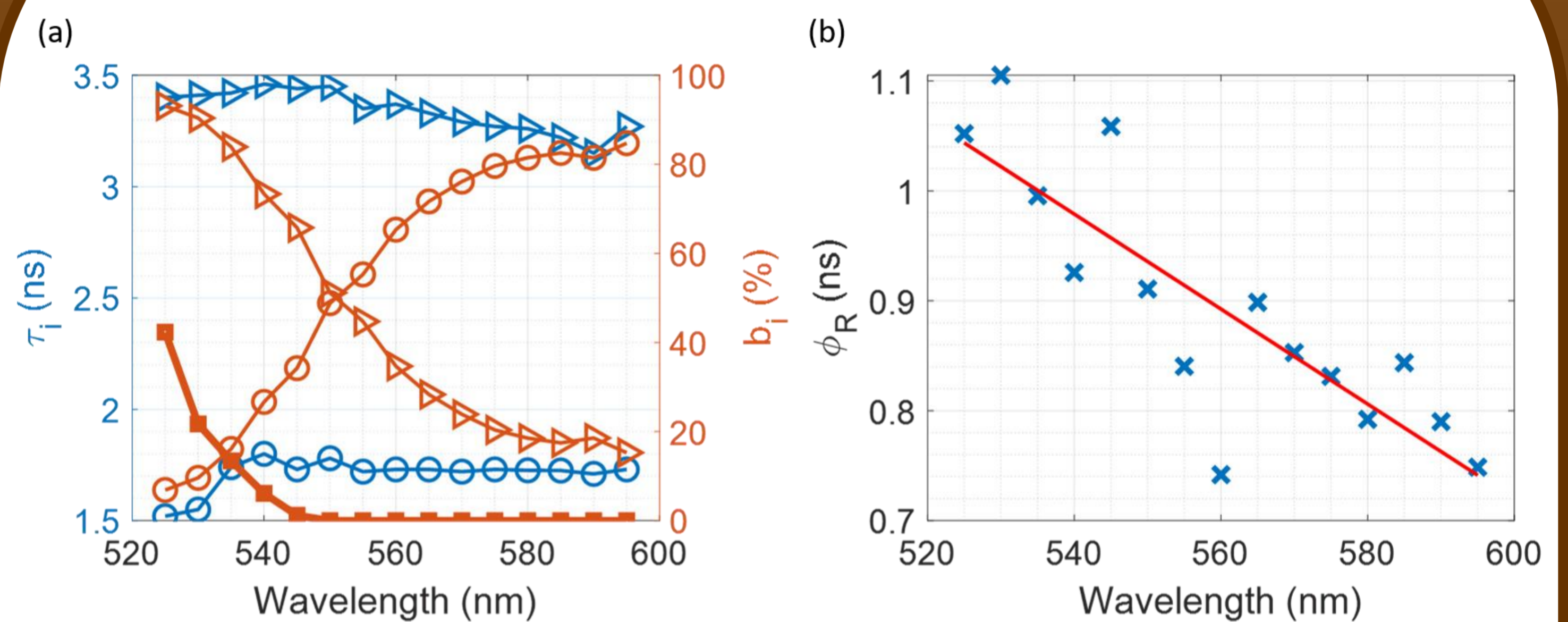


The detected particle size remains constant at a wide range of temperatures. Additionally, the measured particle size at various temperatures matches the results obtained for 2M and 1.8M samples in the dilution experiment.



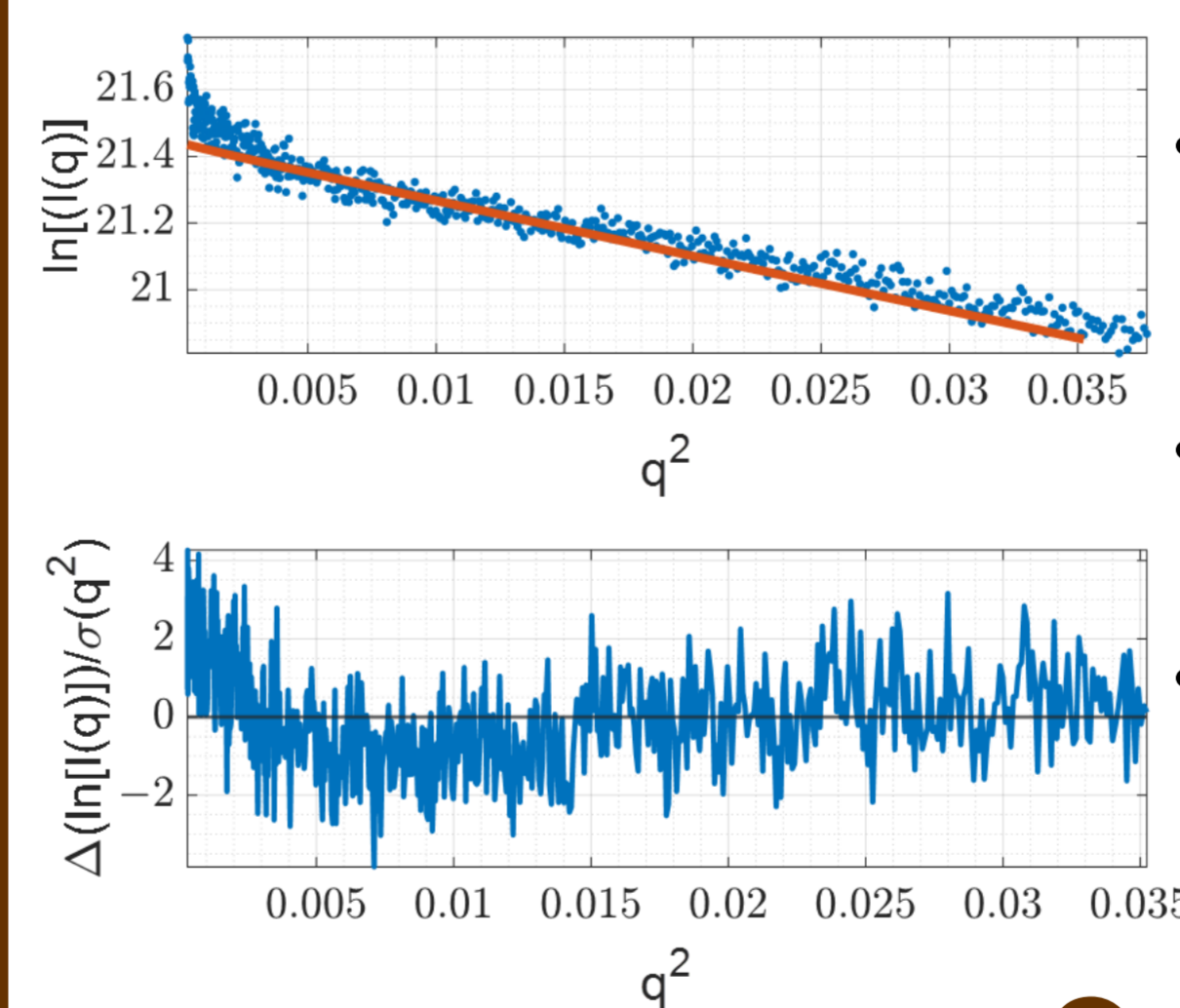
Molecular Dynamic simulations [2,3] of R6G adsorbed on the silica nanoparticle surface.
a) direction of size measurement;
b) measured size as a function of simulation time

Multiplexed time-resolved measurements



- The results are split into three groups: (1) R6G dominated at shorter λ_{em} , (2) RB dominated at longer λ_{em} , (3) mixture of both in between, resulting from a significant overlap between dye absorption and emission spectra
- Using the average values from groups (1) and (2) we recovered a size of $R_H = (7.1 \pm 0.9) \text{ \AA}$, matching that of the previous two experiments and SAXS

SAXS to cross-validate our results



- Five 30 min images collected, summed and corrected for the background scattering from the instrument, Kapton dots and residual atmosphere
- A characteristic downturn in the residuals plot is caused by the polydispersity in the silicate species present in the sample
- Obtained value for the R_g was $6.50 \pm 0.08 \text{ \AA}$ with R^2 equal to 0.95

Conclusions:

- ✓ The measured size of silicate-R6G complex matches between different experimental approaches.
- ✓ The R_g/R_H ratio suggests that particles are slightly elongated and matches results found in the literature [4].
- ✓ Disagreement between MD and experimental results further supports 2nd point.
- ✓ Provided the pH and dye are compatible, i.e. the dye is stable at highly alkaline pH and maintains a sufficiently long lifetime in that environment, the methods described here allow efficient determination of average silicate oligomer particle sizes.

References

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- [4] Hu, G., S. Jin, and K. Liu, Structure-Directing Effect on Silica Nanoparticle Growth in Sodium Silicate Solutions through Small-Angle X-ray Scattering. *The Journal of Physical Chemistry C*, 2023.

Acknowledgements:

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