Sodium Silicate Particle Size Measurements using Time - Resolved Fluorescence Anisotropy

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Abstract

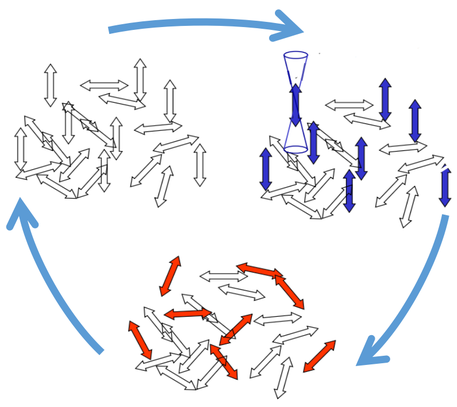
We present a development of the method for determining the particle sizes in sodium silicate liquors at high pH by using the measurement of time-resolved fluorescence anisotropy. Rather than the previous approach of using a single dye label, we demonstrate the use and advantages of using two fluorescent labels. Rotational times of the non-binding rhodamine B and electrostatically binding rhodamine 6G are used to independently determine the medium microviscosity and the silicate particle radius, respectively. The anisotropy measurements were performed on the range of samples prepared by diluting the stock solution of silicate to the concentrations ranging between 0.2M and 2M of NaOH and on the stock solution at different temperatures. The recovered average particle size has an upper limit of 7.0±1.2Å.

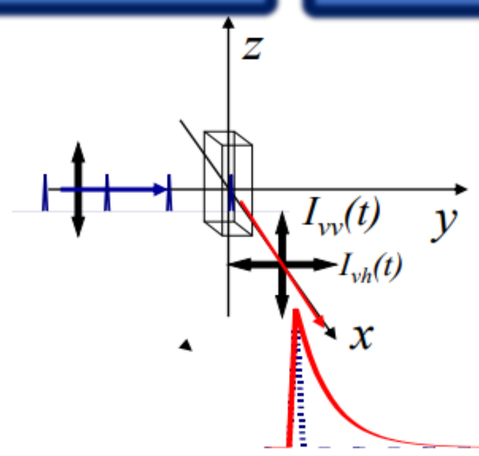
Introduction

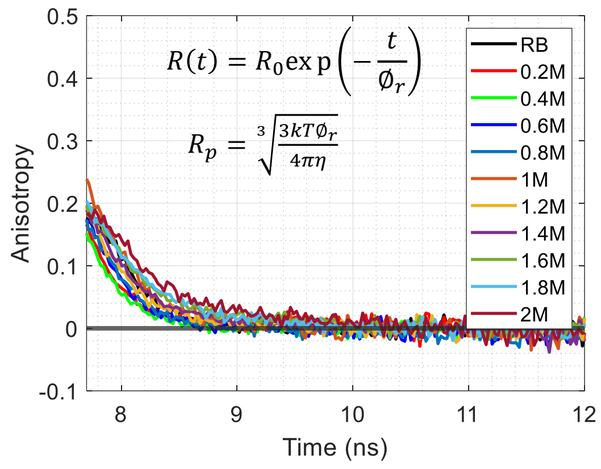
What are Sodium Silicates?

- Versatile inorganic chemicals produced by combining silica sand and sodium carbonate under high temperature
- When in aqueous solution are often used in coating and bonding applications and are precursors to colloidal silica
- Exhibit a range of attractive characteristics such as being odourless, non-toxic, have high strength and rigidity, resistant to high temperatures and are low-cost.

- Most important characteristic of silicates is the relationship between the ratio of silica to soda concentrations and the size of species.
- Traditionally, the sizes of the nanoparticles are determined using methods such as DLS, SAXS, SANS or TEM, however each of them are far from ideal and have significant drawbacks.
- We present an approach that utilizes the relationship between the silica particle size and the rate of the probe's rotational diffusion when bound to the silica particle.







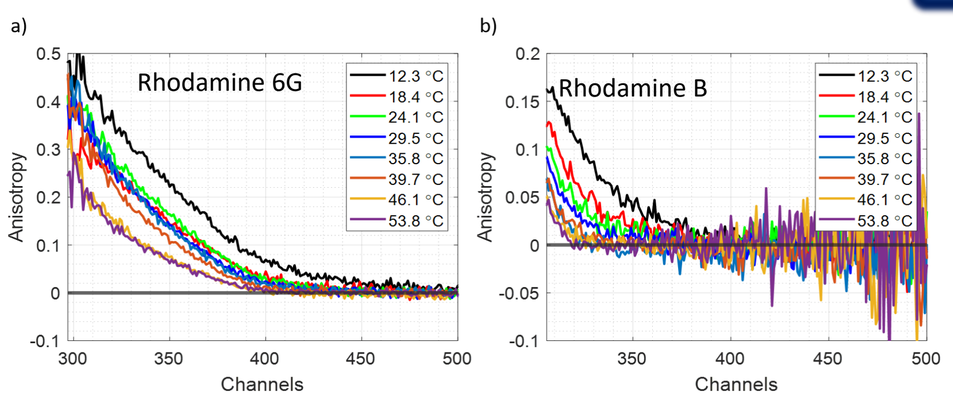
Methods

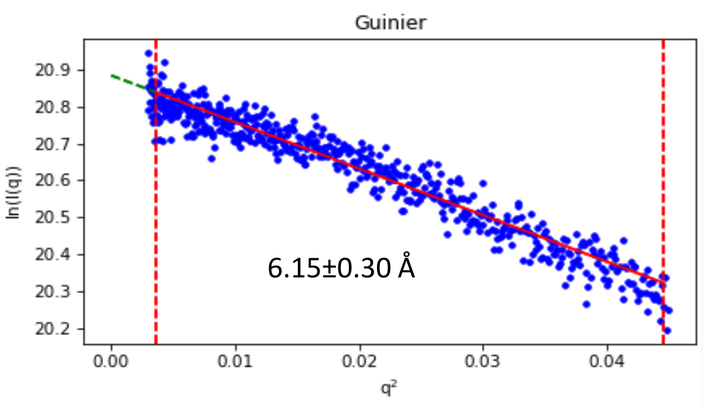
Rhodamine 6G, which binds electrostatically to silica nanoparticles is added directly to the sample

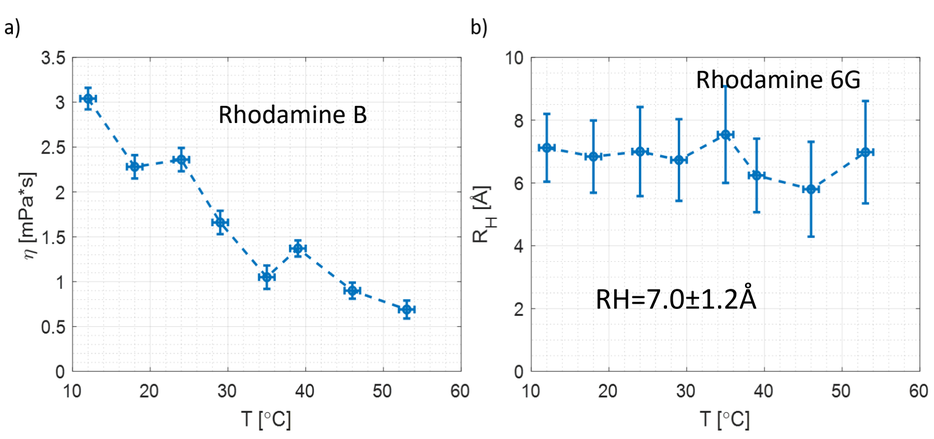
Another sample is prepared in the same way but using Rhodamine B, which does not bind and allows to determine microviscosity precisely in time.

Time resolved anisotropy measurements are performed, with SAXS used as a cross-reference

Results







- Recovered size using SAXS measurements: 6.15±0.30 Å (R^2=0.94), which agrees with the results published in [4].
- Determined upper size limit is RH=7.0±1.2Å, which agrees with the SAXS measurements performed
- Changing temperature is better way to manipulate microviscosity when compared with dilution as the sample composition remains unchanged, however we are dealing with more noise due to short R6G lifetime at high temperatures. This could be improved by using an excitation source with higher repetition rate.

Conclusions and Future Work

- Provided that the dye and pH are compatible, this simple method can be used to determine particle sizes successfully, at a much more cost effective way when compared with traditionally used techniques.
- Next step is to analyse performed Molecular Dynamics (MD) simulations to understand how the dye adsorbs to the particle surface to make a size correction for the dye.

[1] Yip, P., J. Karolin, and D.J. Birch, Fluorescence anisotropy metrology of electrostatically and covalently labelled silica nanoparticles. Measurement Science and Technology, 2012. 23(8): p. 084003.
[2] Birch, D.J. and P. Yip, Nanometrology, in Fluorescence Spectroscopy and Microscopy. 2014, Springer. p. 279-302.
[3] Geddes, C.D., J. Karolin, and D.J. Birch, Fluorescence Anisotropy in Sol-Gels: Microviscosities or Growing Silica Nanoparticles Offering a New Approach to Sol-Gel Structure Elucidation? Journal of Fluorescence, 2002. 12(2): p. 135-137.
[4] Nordström, Jonas, et al. "Silica/alkali ratio dependence of the microscopic structure of sodium silicate solutions." Journal of colloid and interface science 397 (2013): 9-17.