Small Angle Neutron Scattering Study of Reversible Aggregation of Colloidal Particles In a Near Critical Binary Mixture

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Solvent

- Lutidine ($C_7H_9N$) and water

- Lower critical point at $\sim 33.6^\circ C$ and 29%wt lutidine

Solvent + Colloidal Particles

- Silica (SiO$_2$) nanoparticles
- Diameter ~ 30nm
- Exhibit reversible aggregation while approaching the coexistence curve from below

From Left to Right:
1. 25%wt lutidine/water and 3%vf Silica
2. 29%wt lutidine/water and 3%vf Silica
3. 33%wt lutidine/water and 3%vf Silica

Question?

• What is the nature of the interactions between these colloidal particles as the temperature of aggregation is approached?
Small Angle Neutron Scattering (SANS)

- Scattering vector: \( Q = \frac{4\pi}{\lambda} \sin \left( \frac{\theta}{2} \right) \)
- \( Q \approx \frac{1}{\text{Length scale probed}} \)

- Measured the scattering intensity:
  \[
  I(Q) = (\hat{\rho}_L - \hat{\rho}_w)^2 S_{\text{solvent}}(Q) + (\hat{\rho}_{\text{sol}} - \hat{\rho}_{\text{SiO}_2})^2 S_{\text{particle}}(Q)
  \]
- \( \hat{\rho} = \text{Scattering length density (a material property)} \)
Contrast Match Point

- Solvent’s scattering increases near the phase separation temperature
- Only want to see silica particle scattering
- Use D$_2$O in addition to H$_2$O to contrast match Lutidine
- $\hat{\rho}_L - \hat{\rho}_w = 0$
- Need ~73%wt H$_2$O in “water”
- Must also adjust %wt Lutidine to keep volume ratios the same
- Addition of D$_2$O will lower critical, phase separation, and aggregation temperatures
Experiment

• Prepared multiple contrast matched samples at silica volume fractions ranging from 0%-5% and at 25%wt, 29%wt and 33%wt lutidine

• Made SANS measurements at temperatures between 15⁰C and 33⁰C

• Made Dynamic Light Scattering (DLS) measurements on the same samples and at the same temperatures in order to construct a phase diagram and provide comparative data
Matched Solvent

- Insignificant scattering in matched sample
- Scattering in samples will be due to the silica particles only
Matched Solvent with $\text{SiO}_2$ Particles

- Upturn at low $Q$ as temperature increases
- After phase separation ($29^\circ\text{C}$), there is a large change in the scattering intensity
Phase Diagram

- Phase separation temperature decreases with increase in volume fraction.
- Phase separation temperature decreases more significantly at higher lutidine concentrations.
- DLS data correlates well with the SANS data.
Structure Factor

- Increase in strength of attractive interactions with increase in temperature towards $T_A$

\[ t = T_A - T \]
Conclusions

• Contrast matching works
• Clear change in SANS intensity data after the phase separation temperature has been reached
• The strength of the attractive interactions between particles increases as temperature increases towards phase separation
• These data help explain why the particles are aggregating
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Questions?