# New Insights into Microstructure, Rheology & Molecular Level Structural Changes During Self-Assembly & Gelation in Complex Fluids Through Combined DLS-Optical Microrheology-Raman Spectroscopy

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**Summary:** Soft matter / complex fluid systems are ubiquitous across a range of industrial and consumer sectors with common examples being inks, paints, drilling fluids, cosmetics, personal care products and foodstuffs. In many instances, the final product format of these complex fluids are gels or soft solids and the processing and product functionality attributes of such materials are often dependent on their rheological response and viscosity. The rheology evolution in such complex fluid systems as a function of formulation parameters (e.g. pH, ionic strength) is intimately connected to corresponding changes in the micro- and mesostructure and intermolecular and intramolecular associations and interactions. Most insights developed into understanding the self-assembly and rheology evolution process in such systems has primarily focused on elucidating the associated micro- and mesostructural changes through various scattering (light, x-ray, neutron) and imaging techniques (cryo-TEM, SEM, AFM). Furthermore detailed insights into the associated chemical conformational/structural changes and various non-covalent interactions (e.g. H-bonds, hydrophobic interactions) leading to the self-assembly process have been very limited. An understanding of the changes in the molecular level structural changes as self-assembly and gelation progresses will provide new mechanistic insights that will allow better optimization and control over performance controlling formulation design rules in industrial complex fluids. In this talk, we provide new structural/interaction insights into the self-assembly and gelation mechanism of complex fluids through combination of a number of well-established analytical techniques namely dynamic light scattering (DLS), Raman spectroscopy and optical microrheology. The talk will illustrate the utility of the combination of mesoscale structure-property elucidation techniques such as DLS/microrheology with the high resolution chemical structure/conformation elucidation techniques such as Raman spectroscopy in generating novel mechanistic insights that will allow the performance engineering of complex fluids and soft matter systems. This will be exemplified through studies into the self-assembly/gelation mechanisms in three very different complex fluids-mixed anionic/zwitterionic surfactant wormlike micelles, polyvinyl alcohol and a thermo-reversible, gel-forming agarose biopolymer.

## Introduction: Technique

A combined DLS-Raman technique (Helix, Malvern Instruments Ltd) has been used to obtain DLS (nanoscale particle size) and Raman (structural information) data sequentially on a single sample. Microrheological measurements (viscosity and viscoelasticity) were performed with the same instrument. The Helix system uses a proprietary non-invasive backscatter (NIBS) detector with dynamic (DLS), static (SLS) and electrophoretic (ELS) light scattering to measure the hydrodynamic radius of particles from 0.15 nm to 5 µm. Raman spectra are collected using 785 nm excitation (~280 mW) from 150 to 1925 $cm^{-1}$ at 4 $cm^{-1}$ resolution. To perform the microrheological measurements, 900 nm polystyrene particles were added to obtain a final


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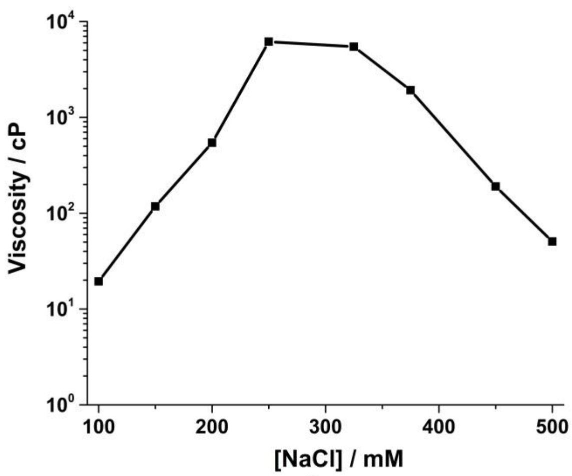
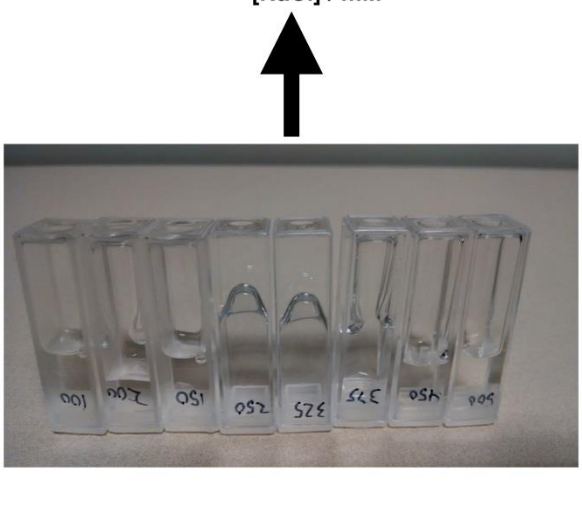
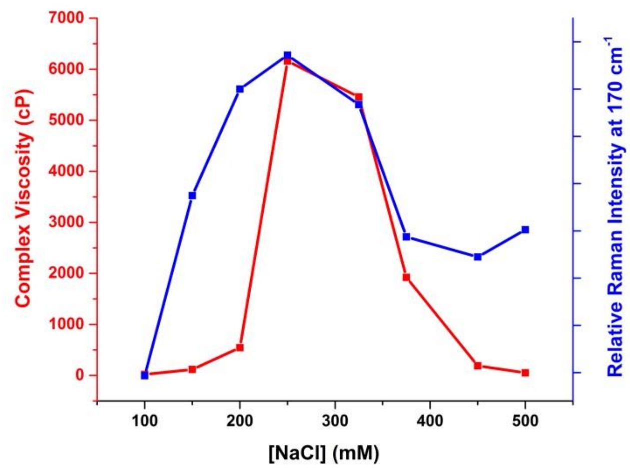
concentration of 0.1% w/w in the complex fluid systems.

**Results:** DLS, Raman Spectroscopy and DLS-based optical microrheology were carried out on three different self-assembling systems-wormlike micelle forming SLES/CAPB (investigated as function of NaCl addition), polyvinyl alcohol (PVA) (investigated as function of extent of hydrolysis) and agarose (investigated as function of temperature). Microrheology data (complex viscosity, elastic modulus G') was obtained and the results were compared with low frequency Raman data and DLS data (size) to derive new insights into the link between rheology-microstructure-molecular structural changes as these systems undergo self-assembly. Some of the comparative data (highlights) on the worm-like micelles, agarose and PVA are shown below:

**System: SLES/CAPB wormlike micelles**





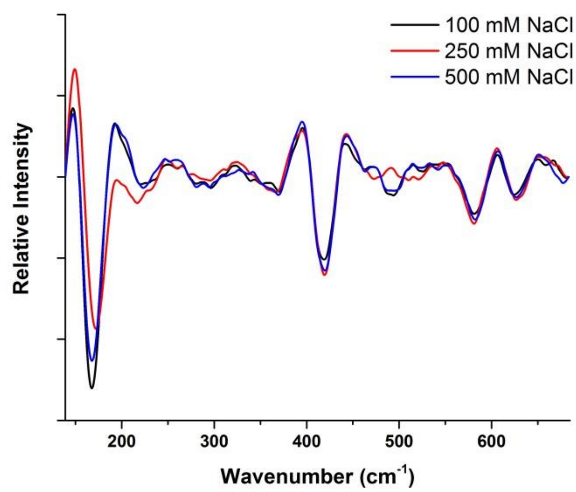




***Figure:*** *SLES/CAPB: Viscosity enhancement and then decrease with NaCl addition. Interesting correlation with low frequency Raman marker. Raman low frequency intensity marker behavior may be sensitive to microstructural differences (e.g. branching) at high and low concentrations of NaCl due to differences in water structuring.*

## System: Agarose

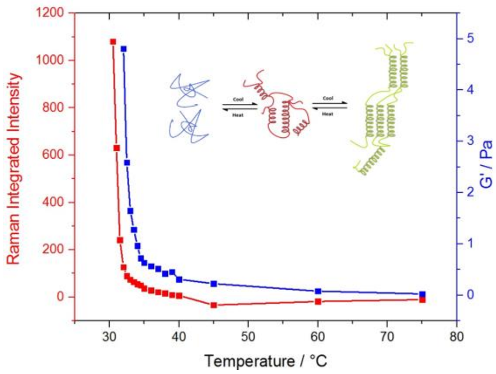
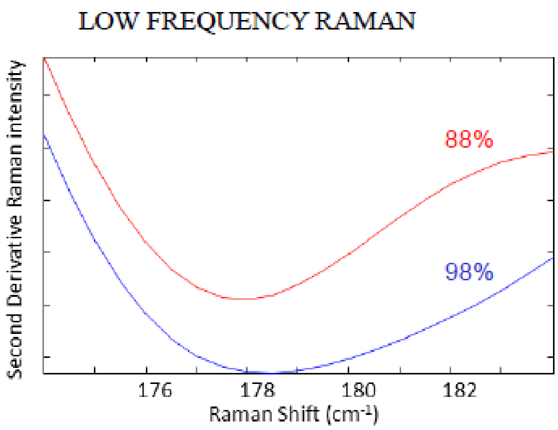
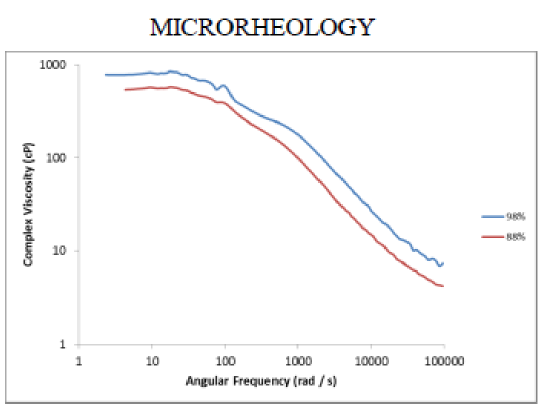



***Figure:*** *Agarose: Enhancement of both G' and low frequency Raman marker with decreasing temperature. Low frequency Raman exhibits good correlation with elastic modulus G' for agarose gelation. A two-step process is seen in both G' and low frequency Raman data. The low frequency Raman data seems to be a good indicator of molecular nature of gelation/self-assembly in range of complex fluid systems*

## System:Polyvinyl Alcohol:




| Hyrdolysis | Viscosity (cP) | Intensity |
|---|---|---|
| 88% | 542.7 | -4.18 |
| 98% | 947.2 | -4.50 |

**Figure:** *PVA viscosity enhancement with extent of hydrolysis correlates well with low frequency Raman intensity.*

## Conclusions:

The connectivity between rheology and molecular level structural changes is a new unexplored area that has been opened up by combined- DLS-DLS optical microrheology-Raman Spectroscopy and should help to develop new insights that will allow the optimization of performance enhancing formulation design rules for industrial complex fluids.

## References: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