AN014e

Non-standard geomtries for rheological characterization of complex fluids

A. Franck, TA Instruments Germany

Keywords: systemic rheology, rheo-reactor, emulsions, product formulation, emulsions, bitumen, Couette analogy

SCOPE

Traditional rotational rheometry has been dealing with ideal flow conditions (viscometric flows) using plate-plate, cone-plate or concentric cylinder geometries to characterize complex materials, preferably in the linear viscoelastic region.

Complex fluids, however are often difficult to measure under these conditions. Sedimentation during testing or slippage at the sample-tool interface have a significant effect on the results and reduce the operation range of the instruments.

Furthermore do viscoelastic flows by no means represent the real flow situation in batch or continuous reactors and processing machines during mixing and/or incorporation of additives, etc. For example, in order to simulate and to understand the gelatinization of starch, a mixing element is used as the standard geometry to avoid settling of the non soluble starch particles since the early days of rheological testing.

Many complex fluids can be tested using the rheometer as an instrumented batch reactor with different types of mixing elements to measure under real flow conditions (systemic rheology => the rheology of the system including material and environment) while even conducting complementary measurements, for example conductivity measurements.

Since the flow is complex and the material behaves usually non-linear, the calculation of a true or representative deformation or deformation rate for the mixing element is an issue. Based on a Couette analogy, average deformation and stress coefficients can be determined which relate the motor rotation speed to the material deformation rate and the measured torque to the stress.

COUETTE ANALOGY

The COUETTE analogy assumes the mixing device in a mixing chamber to be a virtual cylindrical bob in a cylindrical chamber as shown in figure 1. The analogy consists in determining for the mixing element an equivalent inner cylinder with a radius R_i and the height of the impeller, which generates the same torque M at the same rotational speed N. The outer cylinder of the rheo-reactor has the same radius then the outer cylinder of the equivalent concentric cylinder system.

Since the equivalent inner radius varies only slightly with the power law index n [(1)], a calibration procedure could be developed for the mixing element using a Newtonian or a well characterized power law fluid.

Once R_i has been obtained, shear rate and shear stress can be calculated as a function of the radius r. Ait-Kadi et al. have shown, that at a given radius $r^*=(R_i+R_e)/x^*$, where $x^*=2$ for small gaps ($R_i/R_e>0.9$) the shear rate is essentially independent of the nature of the fluid i.e. independent of the local power law index.

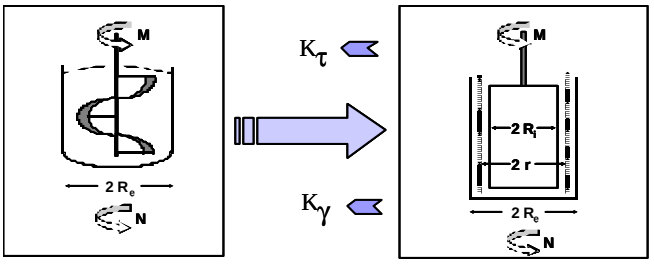

Figure 1: Couette analogy

For large gaps x* becomes greater than 2.

Figure 2 shows the viscosity as a function of shear rate for the silicone oil AW1000, measured with a standard Couette and a single helical ribbon. The geometry constants derived using the Couette analogy calibration are: 2.73 Pa/gcm for the stress constant; 2.46 1/rad for the strain constant.

To prove the validity of the Couette analogy, flow curve and dynamic spectrum have been compared for a complex fluid (salad dressing) obtained with different types of non-standard flow geometries and the double wall Couette (Figure 3). Excellent agreement has been obtained for the flow curve. Note also, that depending on the geometry used, different ranges of shear rates were accessible when applying the same range of rotation speeds.

Excellent agreement, also slightly more scatter has been obtained for the same salad dressing in oscillation for G' and G'' as a function of frequency (Figure 4).

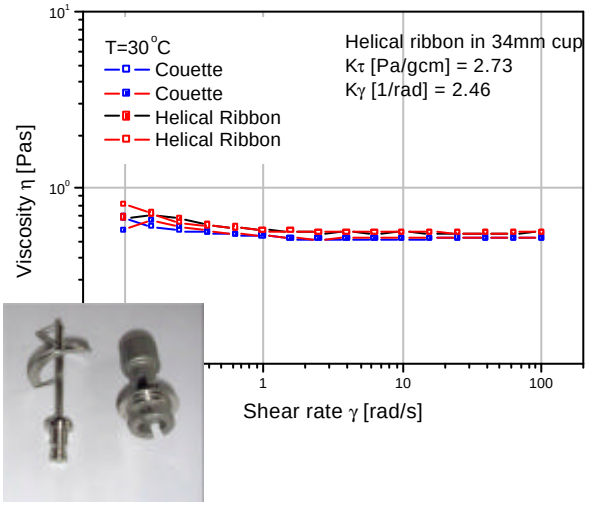

Figure 2: Rheological measurements on the silicone oil AW1000 using the Couette and the Helical ribbon mixing element

A concentrated suspension of glass beads measured in oscillation as a function of frequency in a standard Couette and with the helical ribbon is shown in figure 5. Whereas with the helical ribbon smooth data could be obtained, artifacts and noisy data were obtained using the Couette. This is a result of particle bridging in the gap of the standard Couette. The helical ribbon does not show this effect, since due to enough clearance particle bridging can be avoided.

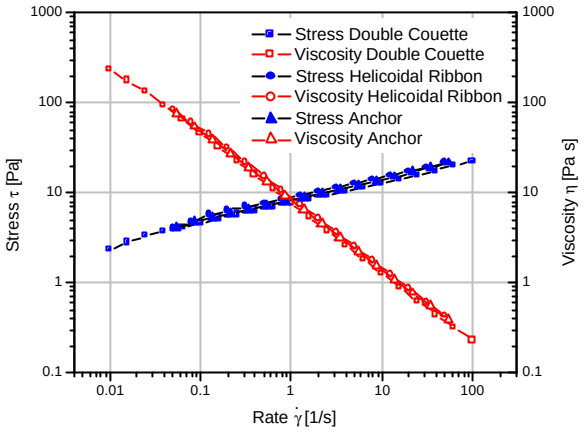

Figure 3: Flow curve for salad dressing measured with different flow geometries

WHY USE THE RHEO-REACTOR WITH NON STANDARD TEST GEOMETRIES?

Standard rheometers like the ARES or the AR can operate with non-standard geometries and allow the input of the previously determined strain and stress constants. Following a list of main features and advantages of non-standard flow geometries:

- Non-standard geometries with the right calibration provide an "absolute" viscosity and modulus as expected from tests with standard parallel plate or cone plate geometries

- Measurement of difficult rheological material systems are easy to perform. Sedimentation during testing can be avoided. Systems with large particles can be measured as a continuum (no particle jamming), etc.

- Mixing of complex fluids (with or without additional mixer) allows the measurement under

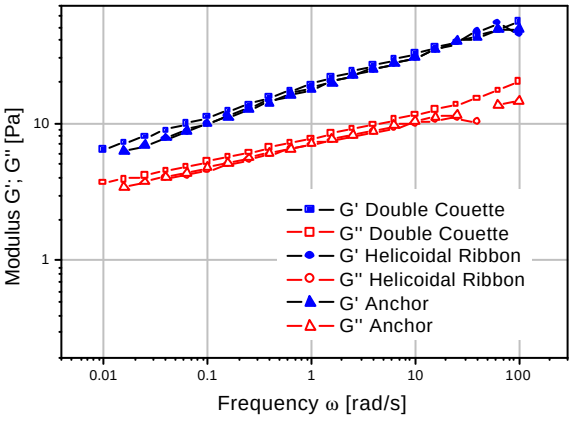

Figure 4: Dynamic moduli for salad dressing measured with different flow geometries

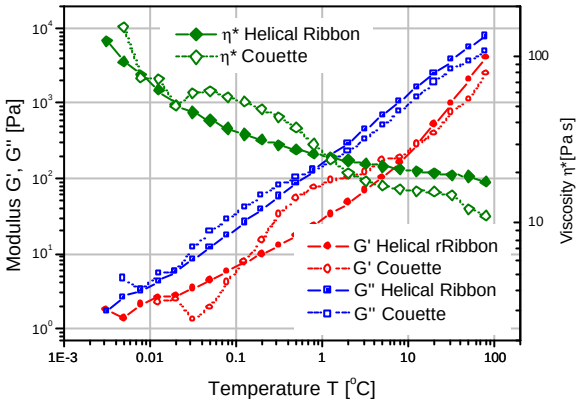

Figure 5: Viscoelastic resaponse for a higly concentrated suspension of glass beads, measured with the standard Couette and the helical ribbon

"process-like" conditions. Mixing time and power consumption during the incorporation of solid or liquids can be studied

- Chemical or physical changes over time after mixing two or more components, incorporation of additives in batch or semi-batch operation, etc. can be monitored. After the formulation, the product can be rheologically characterized (performance testing) without the need to transfer the sample.

- A Rheo-reactor with rotating cup and stationary mixing element can be easily complemented with other in-situ probes for simultaneous measurements like conductivity, optical, etc. during the formulation or the characterization phase.

APPLICATION EXAMPLES

Formulation of bitumen

A typical example to show the usefulness of the Rheo-reactor is the formulation of bitumen [2]. Bitumen is loaded into the cup and heated to temperature as shown in figure 6. The change of viscosity was monitored using the helical ribbon mixer under steady rotation. After temperature equilibrium has been reached, a polymer was added to modify the bitumen (Figure 7). The viscosity raised sharply followed by a slow drop over time as a result of dispersion of the polymer in the bitumen. After approximately one hour the sulfur was added and the compound started to crosslink. The effect of incorporating other compounds during the formulation process i.e. dispersing and cross linking in this case, can be easily monitored and represented with an absolute value of the viscosity.

The formulation process completed, the final material performance was tested in oscillation. The complex modulus G* was recorded as a function of temperature in the Rheo-reactor using the same helical ribbon mixer to measure the torque. From the data obtained the rut criterion according to SHARP could be easily determined (Figure 8).

The formulation and the performance test of the material have been completed in one single step - thus eliminating the need to transfer of the sample. Maximum information in a minimum of time can be obtained with this approach.

Starch pasting

The pasting curve of starch has been measured for a long time with a mixing element in formulation of new products, or as a QC tool in production. Starch dispersions require continuous mixing during the initial part of the pasting to prevent sedimentation of the starch granules. During the pasting process, the temperature

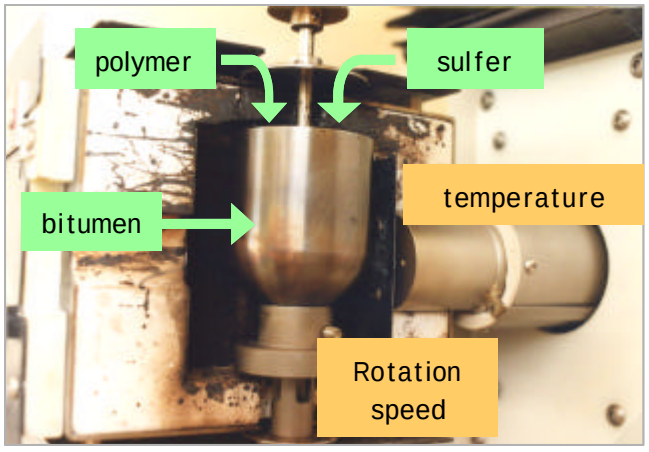

Figure 6: Rheo-reactor for bitumen formulation mounted on the ARES rheometer

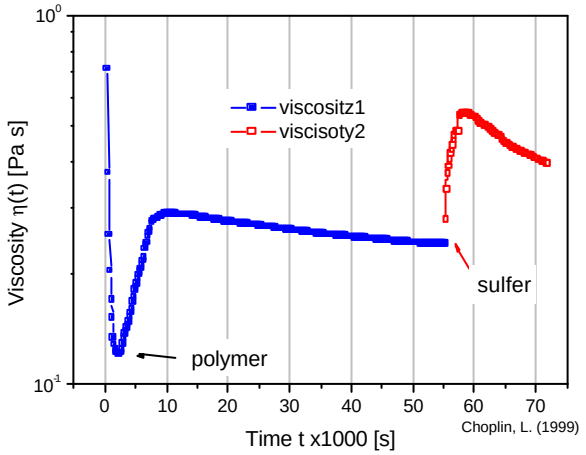

Figure 7: Viscosity during the formulation of bitumen (Data L.Choplin, 1999)

is increased and above a critical temperature the starch granules undergo a irreversible process, the gelatinization (Figure 9). During this process, the starch granules absorb water and swell to many times the original size.

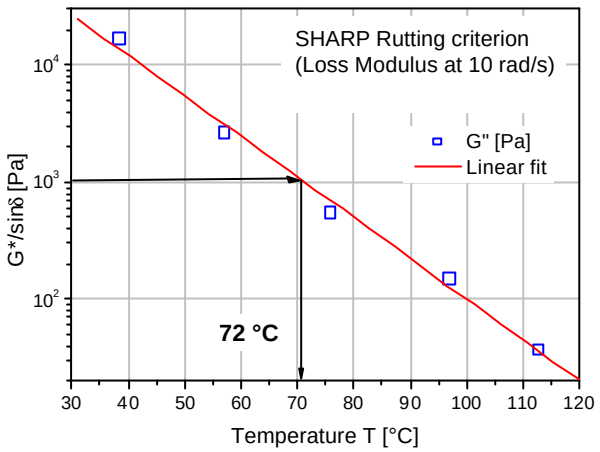

Figure 8: Performance testing in situe using the helical ribbon according to the SHARP rutting test (Data L. Choplin 1999)

Finally the granules rupture and the amylose and amylpectin leach into the solution. As the starch mixture is subsequently cooled, re-associations between the starch molecules occur, which usually results in the formation of a gel and the viscosity increases.

During the initial phase of the pasting process, a continuous mixing is required to keep the starch granules in suspension. After swelling, the starch granules occupy most of the space and mixing is not necessary anymore. At this stage the test mode can be switched to oscillatory shear and the complex viscosity and the dynamic moduli monitored as a function of time. While the starch suspension is fluid, the complex and steady viscosity are in full agreement, - as soon as the starch molecules starts to form a gel, the complex viscosity deviates from the transient viscosity. At that point, the G' is increasing faster then the G'' and becomes dominant at the end of the test.

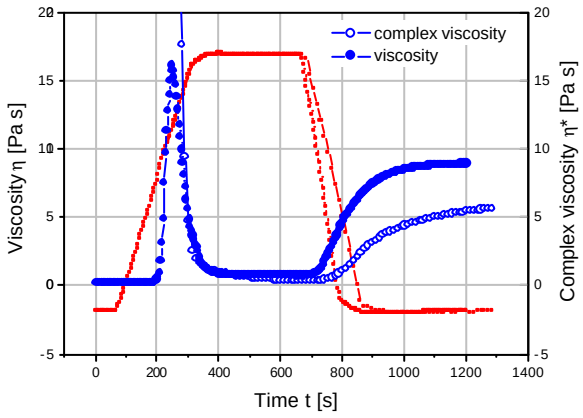

Figure 9: The transient and complex viscosity during starch pasting using the AR2000 starch cell

Formulation of a cosmetic cream.

The objective of studying the emulsification of a cosmetic cream is to evaluate the influence of the mechanical history during the formulation on the performance of the end product. The Reo-reactor is equipped with the helical ribbon and a high speed mixer (Figure 11). The mixer provides a local high speed mixing zone to break down the droplets. The helical ribbon is a macro-mixing device and provides good concentration and temperature homogeneity throughout the reactor vessel. The shaft of the macro-mixer transmits the torque necessary to monitor the viscosity evolution during the emulsification process. Note also, that this set-up is very simple on an ARES rheometer since the cup is rotating and not the macro-mixing element.

The evolution of the temperature and the torque is

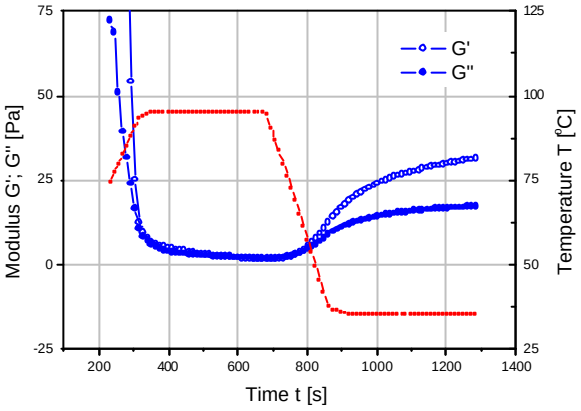

Figure 10: G' and G" trace during starch pasting

monitored during the formulation of a simple cosmetic lotion. In this case an anchor instead of the helical ribbon is used, which provides better macro-mixing due to the proximity to the vessel walls[3]. The ingredients are added in different steps as shown in figure 12. After the addition of the preservative, the viscosity increased significantly. The cooling rate, the speed of the high speed mixer, and the dwell time at constant temperature (85°C) have a significant influence on the final viscosity of the product at the end of the emulsification process.

Two formulation protocols were used to formulate the cream.

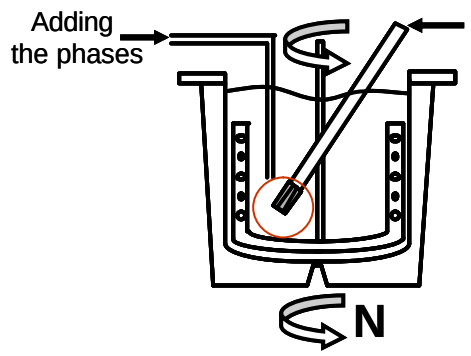

Figure 11: Setup for the formulation of a cosmetic cream

In protocol one, the high speed mixer was on all the time, in protocol two, the high speed mixer was switched off after adding the perfume.

For both protocols, the dynamic response at the end of the formulation was identical, which means the mixing after incorporation of the perfume has no influence on the consistency and stability of the lotion (Figure 13).

Tests for both protocols were repeated, but instead of characterizing the emulsion right at the end of the formulation, the emulsion was left to rest in the reactor for 1 hour and then followed by a 30 min macro-mixing (anchor at 60 rpm) to simulate pumping. The dynamic frequency response was different in this scenario and G' and G'' slightly lower for protocol two. For protocol one (high speed mixing all the time during formulation), the G' and G'' did decrease significantly demonstrating, that the high speed mixing at the end of the formulation significantly reduces the stability of the emulsion against pumping.

Any eventual recovery, or other evolution can be quantified with this methodology without any artifact due to sampling, rheometer loading, etc.

Monitoring the phase inversion of an emulsion

The stirred rheo-reactor can, when equipped with additional testing probes become an extremely powerful tool to investigate changes during the formulation process.

In the following example the inversion of an emulsion is monitored while the system is under constant agitation. Whether an emulsion is present as an oil-water (O/W) or water-oil (W/O) is dependent of the free energy to transfer a surfactant molecule from the oil to the water phase. This is described by the Hydrophilic Lipophilic Difference (HLD). HDL measures the relative affinity of the surfactant for the aqueous and the oleic phase. At HLD = 0, the surfactant affinities are matched and a minimum interfacial tension is reached.

In this example the phase inversion [4] is introduced by changing the temperature. The experimental setup consists of the Rheo-reactor with the anchor as the mixing and rheological sensor element, a high speed mixer and a conductivity probe (Figure 14).

The emulsification of a 50/50% water oil system is carried out directly in the rheometer at constant rotational speed of the impeller (effective shear rate of 100 s^{-1} and a temperature of 50 °C). Then the temperature was decreased to 10 °C at a cooling rate of 0.05 °C/s under constant agitation of 100 s^{-1}. Good concentration and temperature homogeneity was assured by the macro-mixing of the impeller. The

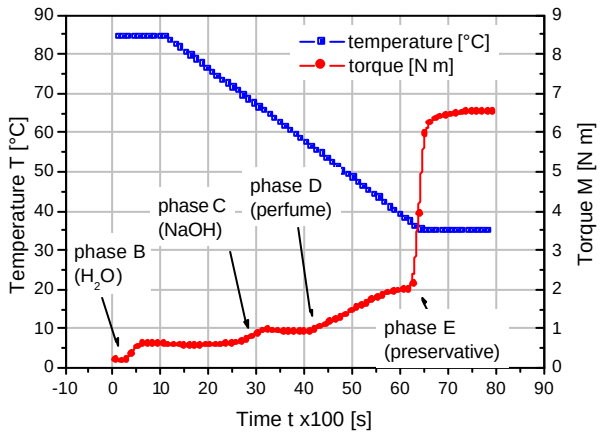

Figure 12: Formulation process for a cosmetic cream monitored with an anchor mixing element (Data L. Choplin)

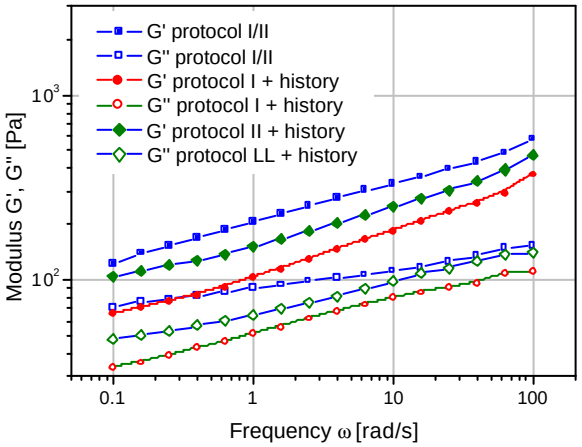

Figure 13: Characterization of the cream in situe in oscillation using the ancer mixing element Data L. Choplin)

viscosity was calculated from the restoring torque of the impeller and the conductivity measured using the conductivity probe. At 50 °C, the emulsion is a water in oil emulsion and consequently the conductivity zero (Figure 15). With decreasing temperature the viscosity is increasing. A maximum in the viscosity occurs around 31 °C. The HLD is approaching zero, which means the interfacial tension is decreasing, which favors the breaking up of the droplets and the reduction of the droplet size. However the stability of the emulsion decreases as well as the likelihood for the droplets to coalesce increases. The maximum of the viscosity can be attributed to a minimum in the droplet size. Below 31 °C, the conductivity increases to a value of 0.8 mS/cm which is an indication of a morphological change in

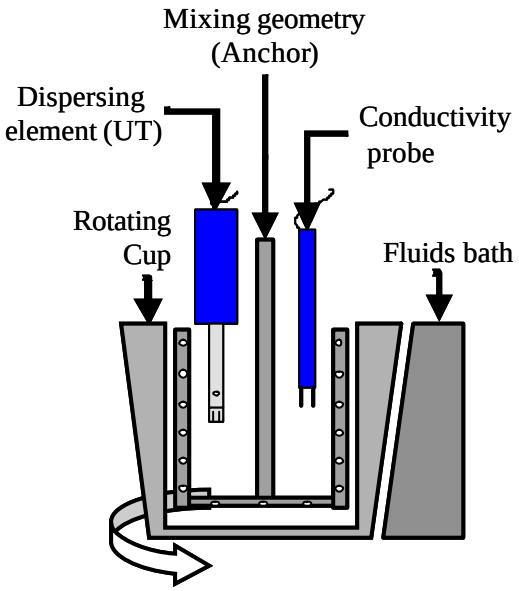

Figure 14: Test setup for monitoring the inversion of an emulsion

the system. This is explained by the presence of a bi-continuous conductive micro-emulsion, the continuous phase still being the oil. The decrease of the viscosity at the same time supports this explanation. From 27 to 23 °C, the conductivity undergoes a significant increase of the viscosity. The continuous phase in this temperature range is neither the oil nor the water, the external phase being a kind of micro-emulsion, which explains the increase of the viscosity and the conductivity. From 23 to 20 °C, the conductivity continues to increase slightly; meanwhile the viscosity goes though a maximum and decreases sharply. This means, that the system progressively transforms into a simple fine oil in a water (O/W) emulsion. Below 20 °C, the conductivity is constant, the viscosity slowly decreases, which can be attributed to the slow increase of the droplet size of the O/W emulsion.

CONCLUSION

Non-standart geometries can be used after adequate calibration based on the Couette analogy to characterize complex fluid systems in transient and oscillatory testing regimes.

The rheometer can be used as a rheo-reactor to monitor the rheology while simulating the formulation process. Without changing the test geometry, the new formulation can be easily characterized using existing rheological techniques.

The simultaneous in-situ monitoring of both conductivity and viscosity of the temperature induced transitional inversion of a simple W/O emulsion is a good example how the instrumented rheo-reactor can be used to analyze the complex structure changes in materials formulation. The instrumented rheo-reactor is ideal to study how the morphology can be influenced by the formulation conditions

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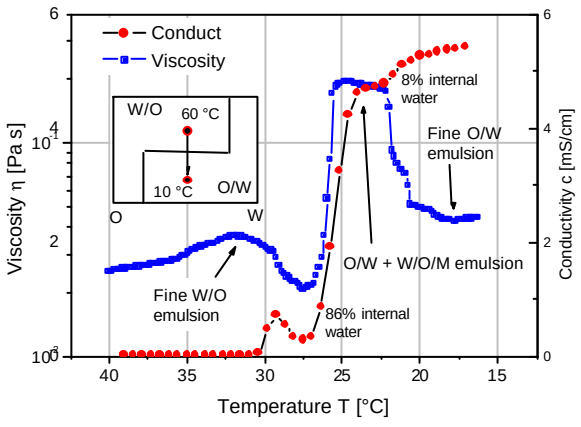

Figure 15: Viscosity and Conductivity trace during the inversion of an emulsion. Surfactant: Tween85 4.5% p/v$_{total}$); NACL 1% (p/V$_{water}$); Alcohol 2%(v/v$_{total}$). Ramp rate 0.05 °C/min (Data L. Choplin)