First conclusions of PCM viscosity measurements in the frame of Task 42-Annex 29-IEA

1st PCM Rheometry Workshop, FREIBURG, 7th March 2018

1 Introduction

Contributors, equipments and tested materials

Contributors and equipments

Institution	Instrument	Method	Geometries	T controller	T controlled-hood/ heated geometry	Min T (rot) [μN·m]	Min T (osc) [μN·m]
Fraunhofer ISE	MCR 502, Anton Paar	Controlled stress rheometer	Plate 60 mm	Peltier plate	Yes	0.001	0.0005
			Concentric cylinder	Peltier concentric cylinder	Yes		
University of Zaragoza-I3A	AR-G2, TA Instruments	Controlled stress rheometer	Plate 40 mm made of stainless steel	Peltier plate	No	0.01	0.003
University of Bayreuth	Imeter, Method 5 DiVA	Translational viscometer and rheometer	Concentric cylinder	Temperature chamber			

Materials

Product	Supplier	Tm(ºC)
Parafol 18-97 (Octadecane)	Sasol	28ºC
RT70 HC	Rubitherm	70ºC
Standard oil S3	Paragon Scientific	-

2 Methodology

Starting point → *Determining the rheological behavior of octadecane as phase change material*. Thermochimica Acta 548 (2012) pp. 81-87.

Procedure in rotational mode:

1. **Conditioning step**
   - Without shear rate during 5 minutes at 25ºC, to guarantee the set temperature
2. **Steady state flow**
   - In logarithm mode from 0,001 to 1000 s^{-1}, measuring 10 points per decade.
   - Conditions of steady flow: Tolerance lower than 5%, during three consecutive measurements. Maximum time if tolerance is not fulfilled=1 minute

10 seconds to measure the displacement by the optical encoder!!

Procedure in oscillatory mode:

1. **Conditioning step**

   Without shear rate during 5 minutes at 25ºC, to guarantee the set temperature

2. **Stress sweep step**

   In logarithm mode from 0,01 to 100 Pa at a frequency of 1 Hz at 25ºC, measuring 10 points per decade.

3. **Conditioning step**

   Without shear rate during 5 minutes at 25ºC, to guarantee the set temperature

4. **Frequency sweep step**

   In logarithm mode from 0,01 to 100 Hz at a stress within the linear viscoelastic region (determined by 2, a stress value when G’ is constant) at 25ºC, measuring 10 points per decade.

Procedure proposal

- A sample with a gap around 0.5 and 1 mm should be tested in the case of using a plate geometry.
- **Temperature ramp in rotational mode:**

  Conditioning step: Without shear rate during 20 minutes at 45ºC, to guarantee the set temperature.

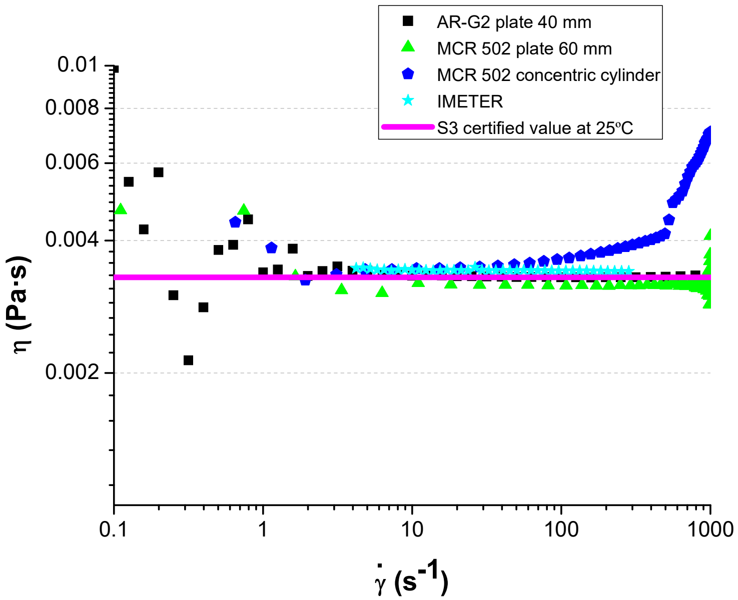
  Temperature ramp: At 100 s^{-1}(shear within the defined experimental window) from 45 to 25ºC at a cooling rate of 0.5 K/min.
- **Temperature ramp in oscillatory mode:**

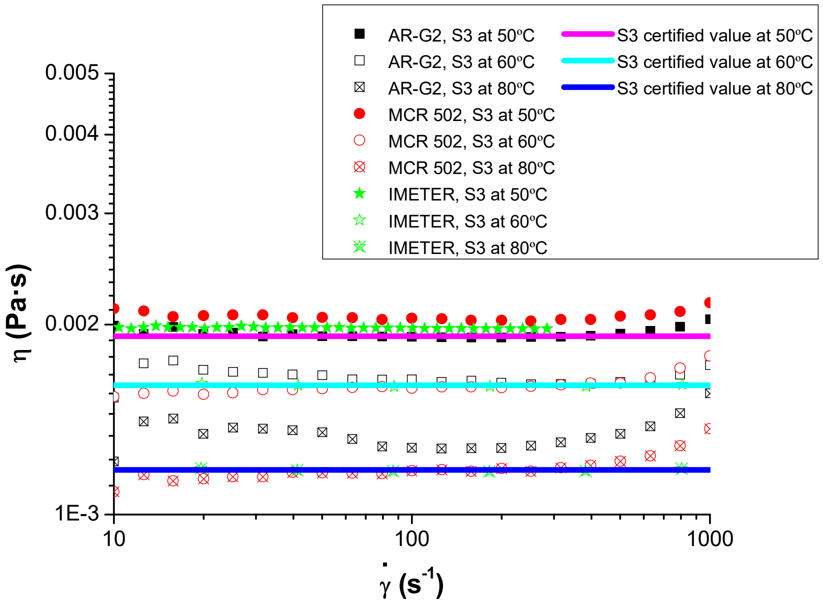
  Conditioning step: Without shear rate during 20 minutes at 45ºC, to guarantee the set temperature.

  Temperature ramp: At 1 Hz (frequency within the defined experimental window) and with a stress of 1 Pa from 45 to 25ºC at a cooling rate of 0.5 K/min.

3 Results

Standard oil S3-Rotational mode

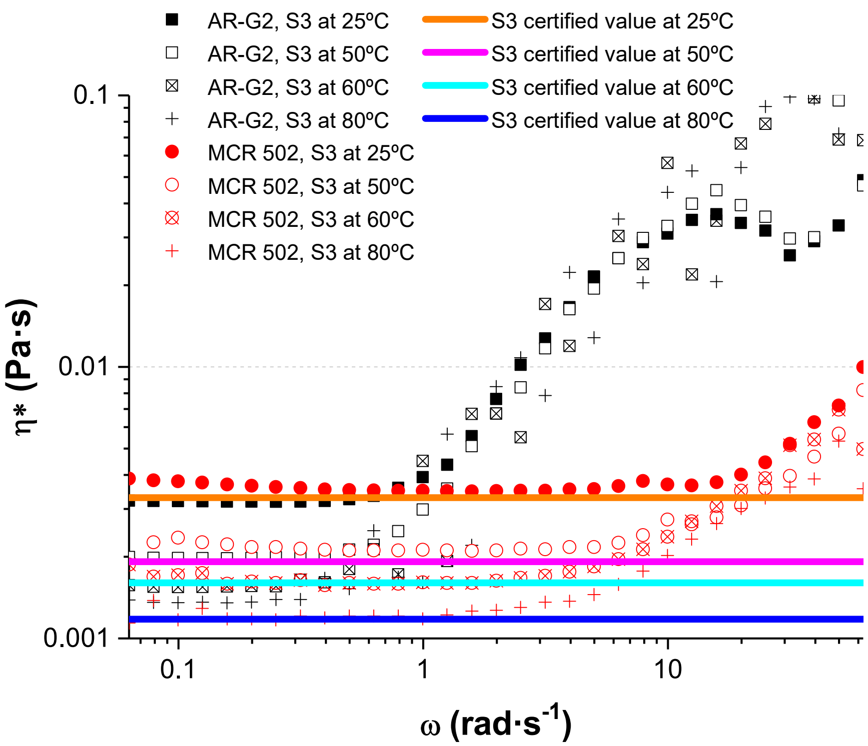




	Shear rate range (s^{-1})	Average deviation (%)	Relative standard uncertainty (%)
	25ºC		
AR-G2	2-1000	1.00	0.26
MCR 502	1.65-982	-3.77	0.34
IMETER	4.22-283.10	2.03	0.08
	50ºC		
AR-G2	6.31-1000	1.20	0.39
MCR 502	12.60-794	7.18	0.24
IMETER	7.13-284.18	1.33	0.06
	60ºC		
AR-G2	10-1000	3.12	0.66
MCR 502	5.01-794	-0.92	0.50
IMETER	2.10-808.70	0.85	0.54
	80ºC		
AR-G2	79.43-251.20	8.05	0.17
MCR 502	5.01-794	-1.10	0.75
IMETER	2.10-803.6	1.43	0.87

3. Results

Standard oil S3-Oscillatory mode

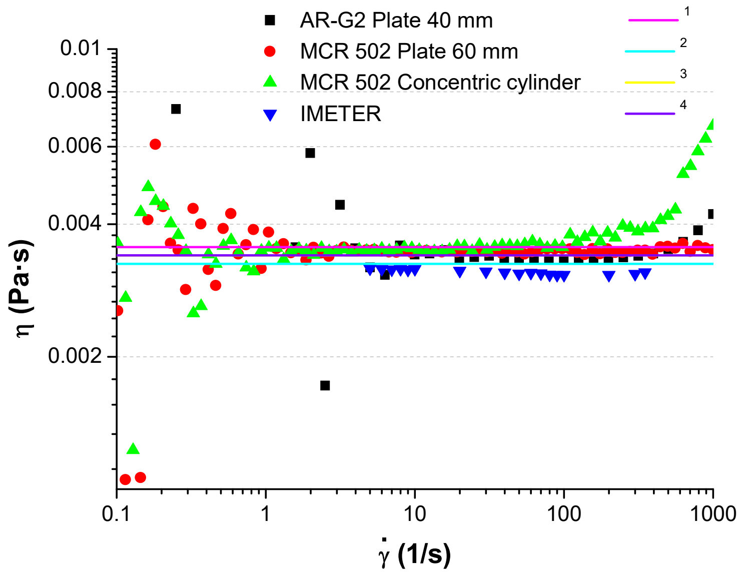


	Shear rate range (s^{-1})	Average deviation (%)	Relative standard uncertainty (%)
	25ºC		
AR-G2	0.06-0.79	-1.59	1.04
MCR 502	0.25-4.99	6.73	0.28
	50ºC		
AR-G2	0.06-0.40	3.86	0.42
MCR 502	1.58*	9.54	-
	60ºC		
AR-G2	0.06-0.40	-1.80	0.76
MCR 502	0.08-3.15	2.02	0.75
	80ºC		
AR-G2	Deviation higher than 10%		
MCR 502	0.10-1.99	2.60	0.84

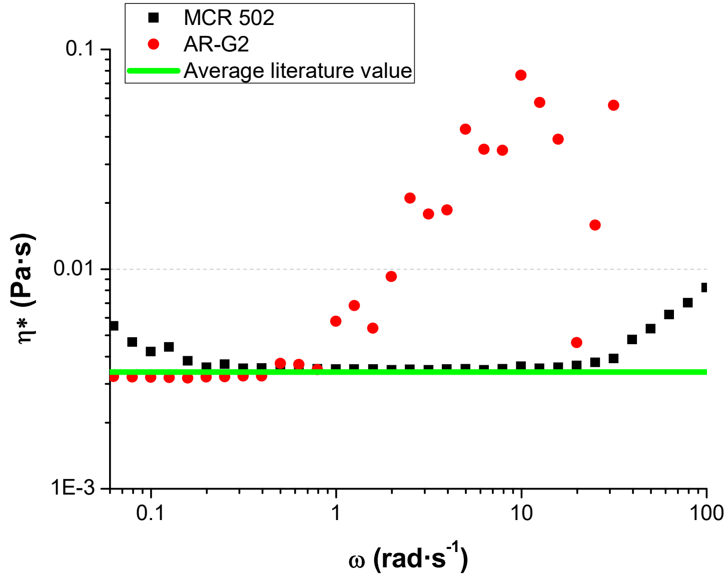
- An experimental window with limits must be established to avoid unappropiate results at low shear rates because the low torque and at high shear rates due to instrument and sample inertia.
- All the instruments obtain precise and accurate results within those shear rate ranges with the exception of the AR-G2 at 80ºC,due to temperature gradients inside the sample, since the geometry used was not an upper heated plate for Peltier plate

Octadecane at 35ºC

Rotational mode



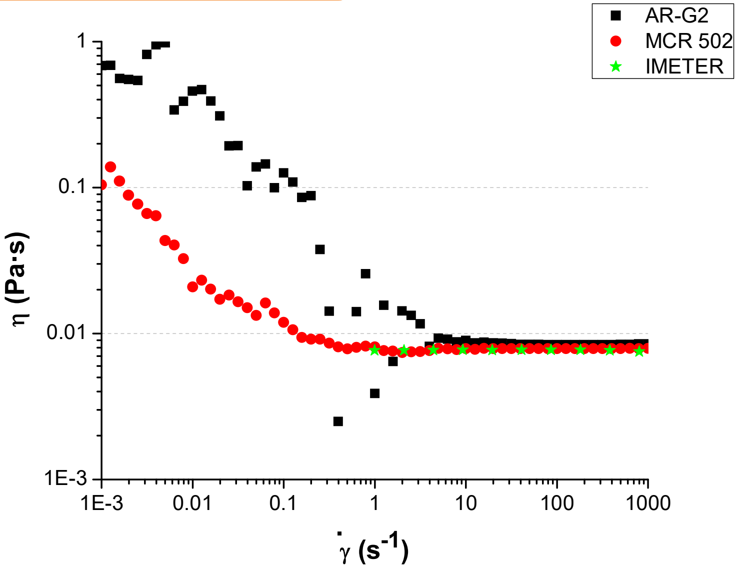
Oscillatory mode



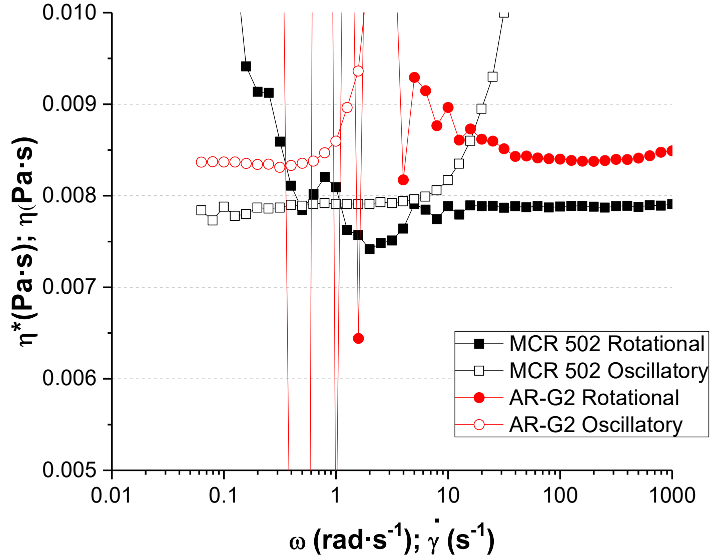
	Rotational			Oscillatory		
	Average viscosity value (mPa·s)	Average deviation (%)	Relative standard uncertainty (%)	Average viscosity value (mPa·s)	Average deviation (%)	Relative standard uncertainty (%)
AR-G2	3.444	1.29	1.36	3.222	-5.23	0.24
MCR 502	3.486	2.53	0.22	3.500	2,94	-
IMETER	3.112	-8.47	0.32	-		-

RT70 at 80ºC

Rotational mode



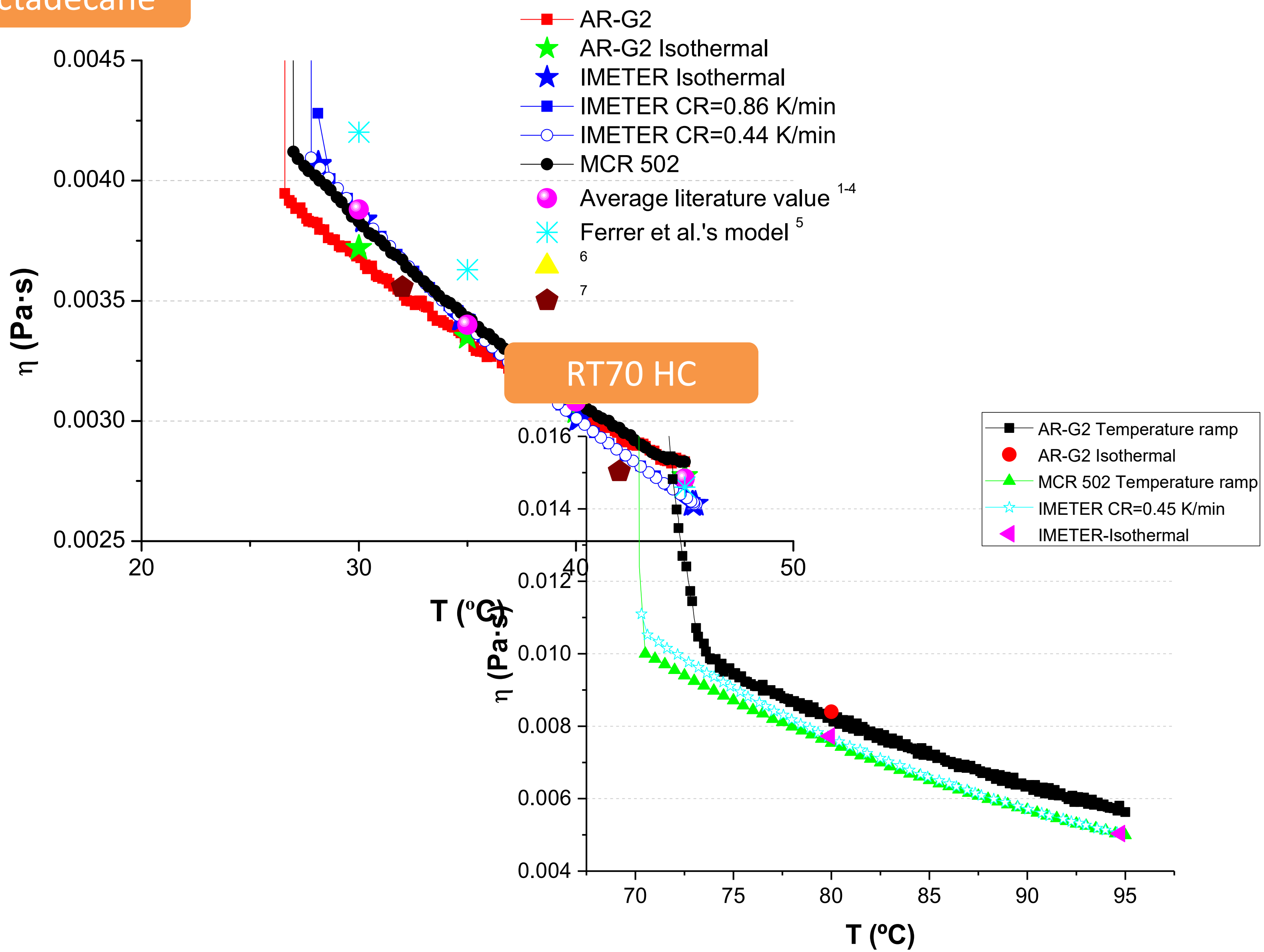
Oscillatory mode



	Rotational		Oscillatory	
	Average viscosity value (mPa·s)	Relative standard uncertainty (%)	Average viscosity value	Relative standard uncertainty (%)
AR-G2	8.388	0.05	8.350	0.09
MCR 502	7.873	0.10	7.880	0.14
IMETER	7.682	0.28	-	-

Viscosity based on the temperature

Octadecane



4 Conclusions

Conclusions

- Good agreement between the viscosities measured with the different rheometer types and between the certified values for standard oil S3 and octadecane.
- Requirement of temperature-controlled geometry or a temperature-controlled hood at elevated temperatures.
- The procedures in both rotational and in oscillatory mode turn out to be appropriate to accurately measure viscosity.
- Experimental window with limitations at high shear rates or frequencies due to instrument and sample inertia, as well as a limitation at low shear rates due to the torque limit.
- Average deviations when measuring S3:

  -Below 7.18 % in rotational mode for the two controlled stress rheometers

  -Below 3.86% in oscillatory mode for the AR-G2 rheometer

  -Below 6.73% in oscillatory mode for the MCR 502 rheometer

  -Below 2.03% for the translational rheometer IMETER

5 Next steps

Measurement of high temperature PCM

- First material proposed to be measured → KNO_3 (molten salt considered as high temperature standard)
- Change of the temperature controller: Peltier plate → Oven
- Main characteristics of the sample and problems encountered:

  1) Low viscous fluid

     -Low viscous torque

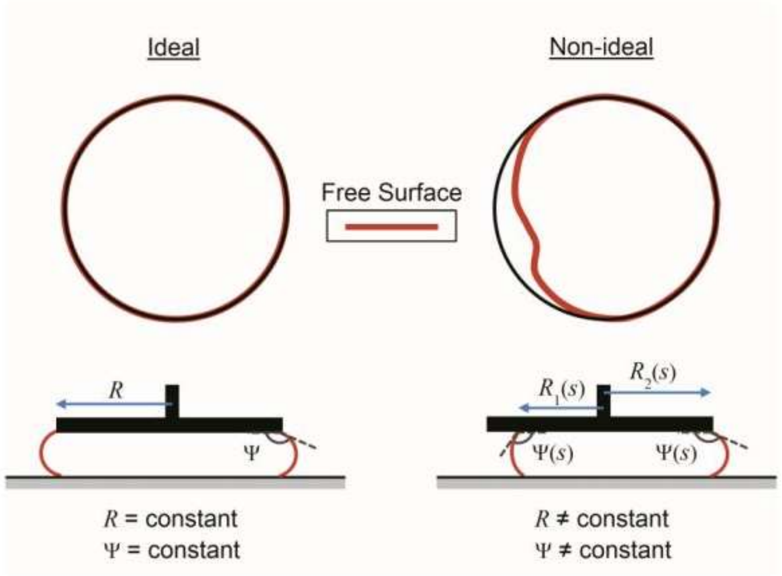
     -Secondary flows

     -Outward migration

  2) High surface tension

Surface tension

- Surface tension results in a torque that should not occur in an ideal, rotationally-symmetric geometry.
- It appears as a constant torque independent of rate → newtonian liquids as shear thinning
- This surface tension torque is sensitive to wetting conditions and contact line asymmetries and cannot be corrected in experimental measurements.



When must be this phenomenon considered? → When low viscous and high surface fluids are being measured

Substance	Surface tension (mJ·m^{-2})	Viscosity (mPa·s)
Water	73 (20ºC)	1.0016 (20ºC)
n-dodecane[9]	22 (50ºC)	
n-octacosane[9]	22 (125ºC)	
KNO3[10]	106 (395ºC)	2.1263[11] (394ºC)

High shear rate rheometry

How can we face to this problem ? → Measuring at high shear rates

$$\dot{\gamma} = \frac{U}{H}$$

1) Increase the velocity → loss of viscometric flow

2) Reduce the gap → non-paralelism between the plates

At very high shear rates, there are also factors that influce on the rheometric measurements:

- Inertial effects → secondary flows
  Secondary flows increases the measured torque.

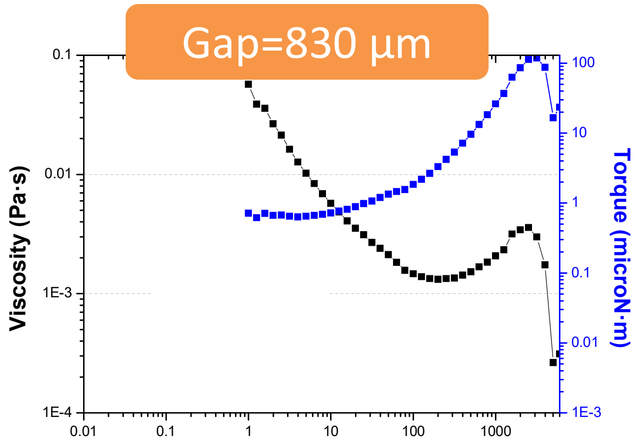
$$\frac{T}{T_0} = 1 + \frac{3}{4900} \cdot Re^2$$

- Radial migration effect → when centrifugal stresses overcome surface tension stresses and the confined fluid is partially ejected → drop in measured torque → drop in measured viscosity

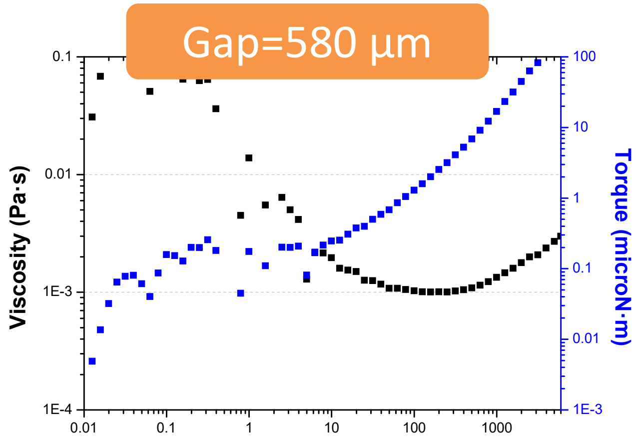
$$\dot{\gamma}_c = \sqrt{\frac{20 \cdot \sigma}{3 \cdot \rho \cdot H}}$$

- Viscous heating

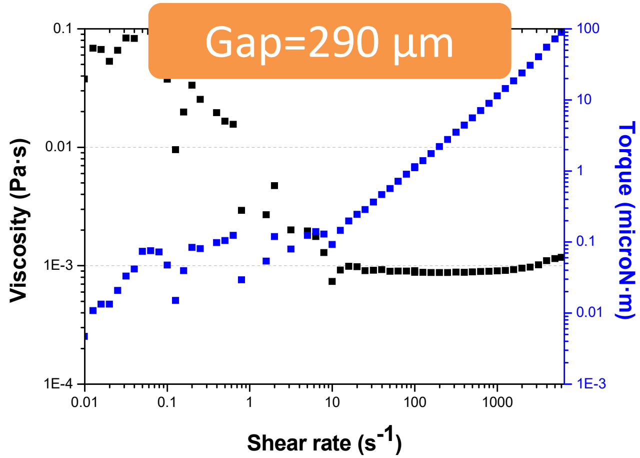
Tests with water with plate geometry



- Constant torque around 0.7 µN·m
- Secondary flows from approx. 100 s^{-1}
- Outward migration from approx. 2000 s^{-1}
- A newtonian plateau is not observed



- Constant torque around 0.2 µN·m
- Outward migration is avoided
- Secondary flows from approx. 500 s^{-1}
- Average viscosity=1.030 mPa·s
  Shear rate range [50-400 s^{-1}]
  Deviation=15%

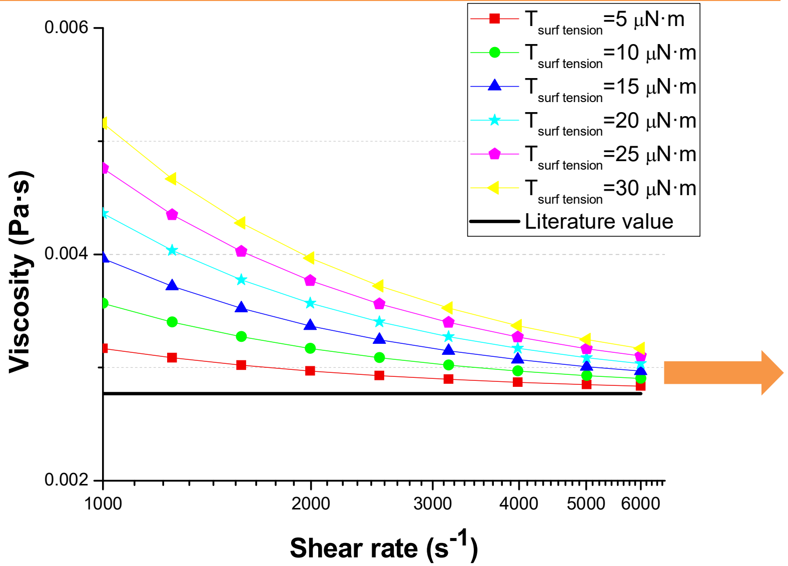


- Constant torque around 0.12 µN·m
- Secondary flows is hardly observed
- Wider newtonian plateau observed
- Average viscosity=0.891 mPa·s
  Shear rate range [25-1000 s^{-1}]
  Deviation=0%

Tests with KNO_3 with plate geometry

- Samples of KNO3 with different gaps have been tested. Gap range [309-890 µm]
- Constant torque independent of the shear rate within the range [9-26 µN·m], which depends on how well the sample has been loaded (in terms of rotational simmetry), as consequence of the surface tension.
- We should pay the attention to the measurements with low gaps to avoid secondary flows and outward migration and with low constant torque due to surface tension.

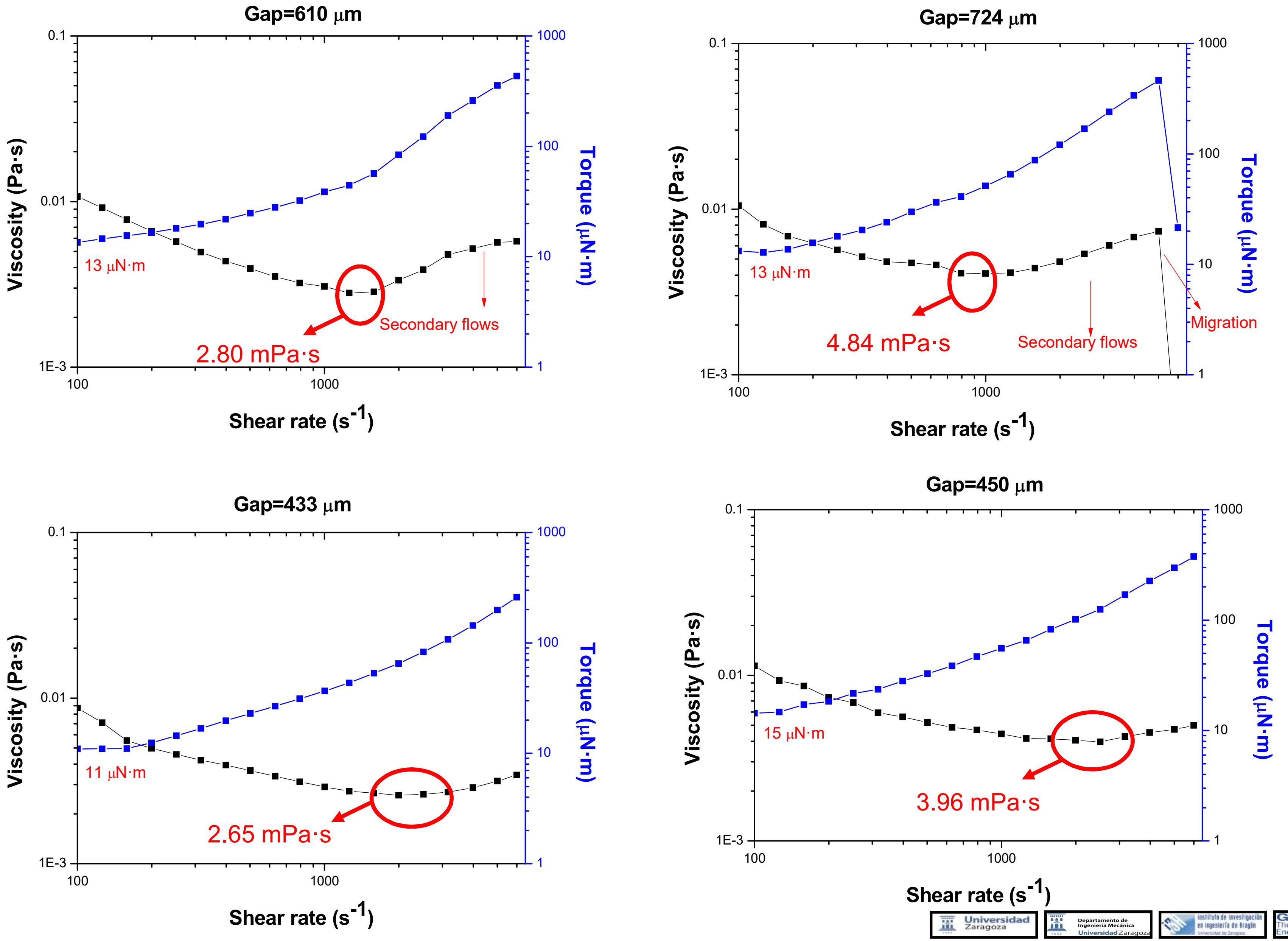
Theoretical calculation of the influence of the torque due to surface tension on the KNO3 viscosity



Surface tension torque should be lower than 15 µN·m for deviations lower than 10%

Tests with KNO_3 with plate geometry

η_{KNO3} =2.77 mPa·s



Thank you!

Any question?