VISCOSITY REFERENCE LIQUIDS FOR INDUSTRIAL APPLICATIONS

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Introduction

- **Industry need new industrial viscosity standards with various viscosities, at high pressures and high temperature**
  - oil exploration industries - viscosity of petroleum fluids at the oil reservoir temperatures and pressures
  - other industrial activities dealing with high viscosity fluids
- **Industrial viscosity standards**
  - used for calibration and tests of industrial viscometers for use in-well or on-line at the adequate working conditions
- **Fluids have a viscosity range which varies over several orders of magnitude**
  - need to use a number of "industrial reference materials" to cover a large range of practical conditions
    - calibrate or verify the calibration of the instruments

Introduction

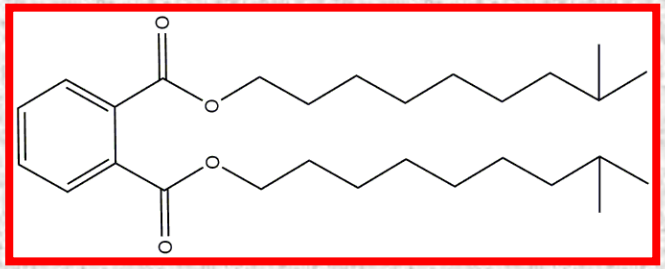
- **Certified reference fluids**
  - have viscosities traceable to standards from national metrological laboratories
    - capillaries calibrated by a step-up procedure, from the water primary reference
    - Time consuming procedure
    - can be expensive particularly for very viscous liquids
  - mixtures of oils, whose composition has only a general description
  - their viscosity must be determined for each batch and its utilization should take place within strictly defined time limits.
- **These facts point to the convenience to establish secondary reference fluids for industrial use.**
- **There are no commercial certified reference fluids with certified viscosity data <u>at pressures above atmospheric pressure</u>**

Viscosity Reference Liquids

Goals and International Projects for Viscosity Reference Liquids	
IUPAC project (No. 2002-005-1-100) ***Started: 2003; Ended 2009*** Thermodynamics of ionic liquids, ionic liquid mixtures, and the development of standardized systems U= ±(2 - 5)%	**IATP project; Started 2008;** ***Still Running*** High-temperature, high-pressure viscosity standards. J.M.N.A. Fareleira – Coord., F.J.P Caetano (PT), W. A. Wakeham, J.P.M. Trusler (UK), A.P. Froba, A. Leipertz, B. Rathke (DE), K. Harris (Aus), A.R.H. Goodwin, A. Laesecke (USA), J. Fernandez (ES), K. Schmidt (CA), Chr. Boned (FR)
IATP project; Started 2008; Round Robin project on ionic liquids viscosity and thermal conductivity measurements. C.A. Nieto de Castro, J.M.N.A. Fareleira (PT); A. Leipertz , A. Froeba, U. Hammerschmidt, B. Rathke (DE); J. Fernandez (ES), R. Perkins (USA), and K. Harris (Au).	Proposed to IATP in 2010 20 mPa.s, 241 MPa, 533 K (deepwater – Gulf of Mexico) 1000 mPa.s , 10 MPa, 473 K (surface – Canada) U= ±5% acceptable; U= ±2% desirable
IUPAC project (No. 2012-051-1-100) *Started in 2013; Still Running* **20 mPa.s, 200 MPa, 473 K** U= ±5%	High Viscosity High Pressure High Temperature

Industrial viscosity standard

- **DIDP (plasticizer) was proposed (Caetano et al. 2008), by IATP (International Association for Transport Properties), as an industrial reference fluid for moderately high viscosity;**
  - no other pure fluid has been proposed to be a reference fluid for such high viscosity



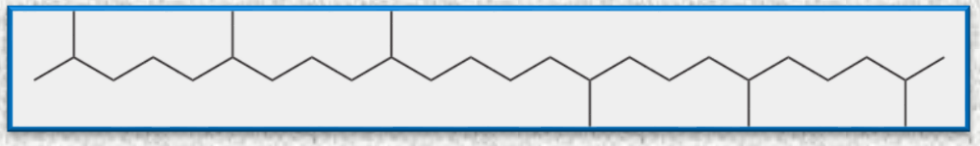
Liquid	η(293 K, 0.1 MPa) (mPa.s)	T range (K)	p range (MPa)	η range (mPa.s)	*U* (%)	Min Purity (%)	year
DIDP[3]	123.0	288-308	0.1	49.3-179.8	0.3-2	99.8	2008

- **Disadvantages:**
  - mixture of isomers;
  - production stoped.
- **DIDP - not considered as a possibility for viscosity industrial standard**

Industrial viscosity standard

- **Replacement for DIDP - Several liquids, have been suggested as possible candidates to be viscosity reference fluids at moderately high viscosity**
  - Phthalates, sebacates, benzoates, squalane, perfluoropolyethers and ionic liquids

- **Squalane was proposed (Mylona et al. 2014), IUPAC (Project No. 2012-051-1-100), as an industrial reference fluid for moderately high viscosity;**



Liquid	η(293 K, 0.1MPa) (mPa s)	T range (K)	p range (MPa)	η range (mPa s)	U (%)	Min Purity (%)	year
Squalane[4,5]	36.1	273-373	0.1-200	0.85-954	1-5	99	2013, 2014

- Extended for pressures up to 350 MPa (DIDP and DEHP used as calibrant in some points)

- **Disadvantage:**
  - viscosity to low for the high viscosity goals

Industrial viscosity standard

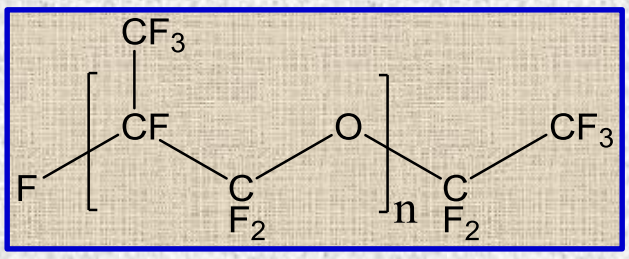
- **Di(2-ethylhexyl) phthalate (DEHP) - possible substitute of DIDP**
  - included by the European Chemical Agency in a list of possible high concern substances regarding their toxicity
  - 57.9 mPa.s, 298 K, @0.1 Mpa

- **Use of Ionic Liquids as reference fluids is very appealing**
  - vast ion combinations which can be used to select the appropriate characteristics
  - very difficult to achieve very accurate and even reproduce viscosity results of ionic liquid samples
    - water or halides contaminations have significant effects on viscosity

Liquids Suitable to be Viscosity Standards at High Pressure

- **Moderatly High to High Viscosity:** Krytox® (DuPont patent)
  - Properties:
    - Low vapor pressure;
    - Temperature resistant;
    - Non toxic;
    - High resistance to biodegradability;
    - Chemical inert;
    - High boiling point;
    - Doesn't burn.
  - Main application: lubricants;
    - Available throughout the world
  - Liquid range: (-75 to 350) ºC;
  - Purity >99 % (up to 99.9%)

a polymer



Perfluoropolyether Oils

Krytox ® GPL	~n (average)	MW (average) / kg.mol^{-1}	~Viscosity (293 K) / mPa.s
100	5	0.96	13.3
101	6	1.18	30.4
102	10	1.72	68.4
103	13	2.28	152
104	18	3.15	342
105	28	4.73	1045
106	35	5.94	1539

Viscosity reference liquids

- **Liquids proposed as industrial references for viscosity - IUPAC with IATP**

Liquid	η(298 K) (mPa.s)	T range (K)	p range (MPa)	η range (mPa.s)	U (%)	Min Purity (%)	year
cyclopentane	**0.416**	220-310	0.1-25	0.4-1.5			
Toluene	**0.555**	213-400	0.1-250	0.2-3	0.2-3	99	2001; 2006
Squalane	**28.2**	273-473	0.1-200	0.85-954	1-5	98	2013, 2014
$[C_6mim][NTf_2]$	**69.4**	258-433	0.1	2.95-967.6			
DIDP	**88.5**	288-308	0.1	49.3-179.8			

Low Viscosity

Diesels, biodiesels, low molecular weight polymers and light oils

Moderately High Viscosity

Heavy oils and high molecular weight polymers

Viscosity reference liquids

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Dialkyl Adipates							
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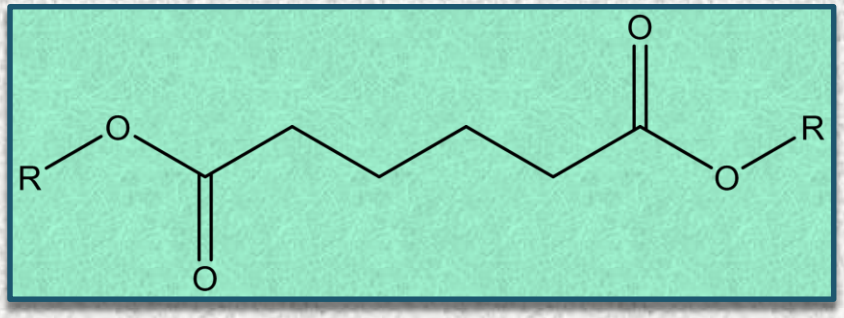
Low Viscosity

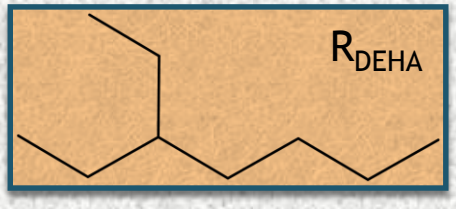
Moderately High Viscosity

Liquids Suitable to be Viscosity Standards at High Pressure

- **Low Viscosity: Dialkyl Adipates**
  - Properties:
    - low vapor pressure;
    - resistant to low and also to high temperatures;
    - "low" viscosity;
    - low toxicity;
    - high biodegradability;
    - high boiling point



  - Large application: plasticizers; solvents; lubricants; corrosion protection; pigment dispersant.
  - **Dialkyl Adipates:** Liquid range: (-30 to 200) ºC; Purity 99 %
    - **Dimethyl Adipate**
    - **Diethyl Adipate**
    - **Dipropyl Adipate**
    - **Dibutyl Adipate**
    - **Diisobutyl Adipate**
    - **Bis(2-Ethylhexyl) Adipate**



Viscosity reference liquids

- Liquids proposed as industrial references for viscosity - IUPAC with IATP

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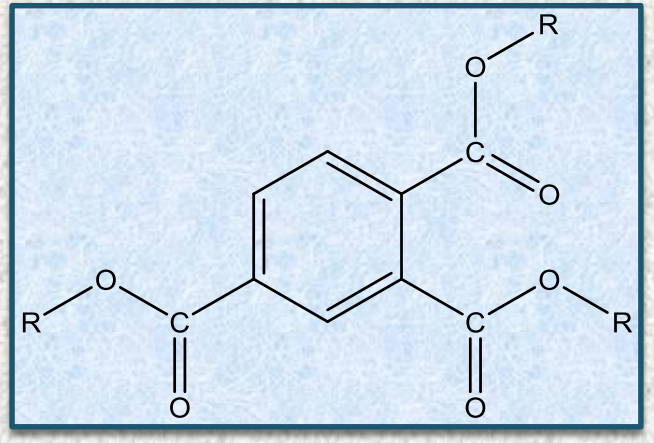
Trimillitates							

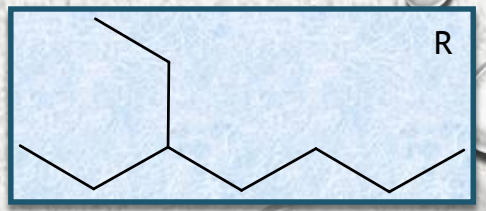
Low Viscosity

Moderately High Viscosity

Trimellitates

- adequate properties for being used as high viscosity reference liquids:
  - low vapour pressure;
  - large temperature range in the liquid state;
  - reasonably low cost
  - not classified as dangerous, according to European Directive 67/548/EEC - harmful in contact with skin, and susceptible to cause serious eye irritation
- Applications
  - plasticizers;
  - high temperature polymers;
- **Tris(2-ethylhexyl) trimellitate – TOTM**
  - Purity: 99%
  - ~ two times more viscous than DIDP;
  - one of the most used plasticizers in the polymer industry
    - makes it available throughout the world
  - Liquid range: (-50 to 414) ºC

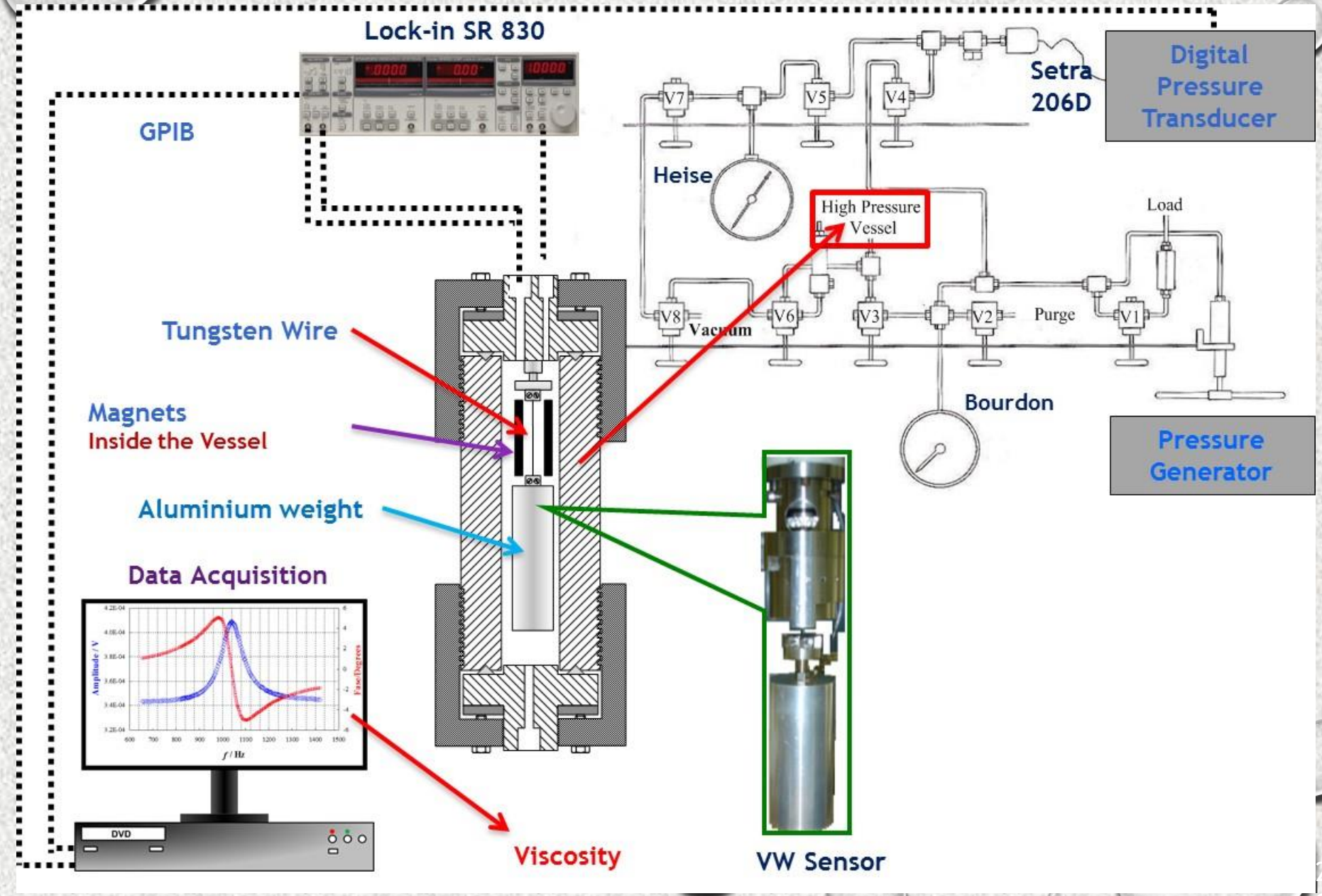




Experimental (low viscosity)

- **New viscosity measurements of DMA and DPA**
  - Vibrating wire technique
  - Range of temperatures: (303 to 358) K
  - Pressures up to 20 MPa;
  - Capillary viscosity measurements - Ubbelohde viscometer type 541 23/IIc, Schott Instruments GmbH
- **Density data measured using an Anton Paar vibrating U-tube densimeter, model DMA HP**
  - from (293 to 363) K up to 68 MPa

Vibrating-wire High Pressure Setup – Low viscosity



Experimental

- **New viscosity measurements of DBA and TOTM**
  - Vibrating wire technique
  - Range of temperatures: (303 to 373) K
  - Pressures up to 65 MPa;
  - Capillary viscosity measurements - Ubbelohde viscometer type 541 23/IIc, Schott Instruments GmbH
- **Density data measured using an Anton Paar vibrating U-tube densimeter, model DMA HP**
  - from (293 to 373) K up to 68 MPa

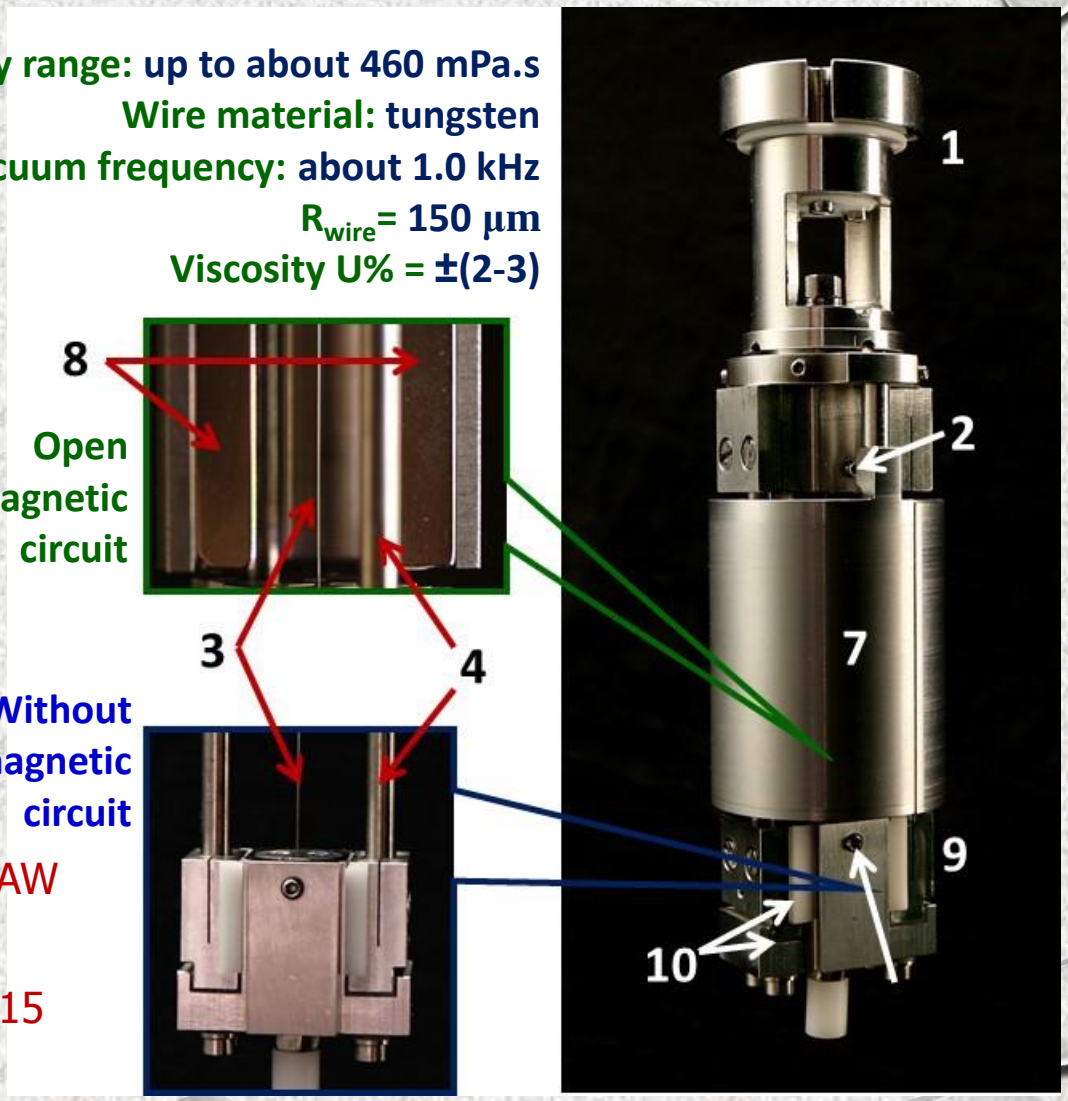
New vibrating wire sensor

- 1 - top washers;
- 2 - upper claw chucks;
- 3 - vibrating wire;
- 4 - rod spacers;
- 5 - inferior claw chucks;
- 6 - superior rod clamping;
- 7 - magnetic circuit;
- 8 - magnets;
- 9 - inferior rod clamping,
- 10 - bottom washers

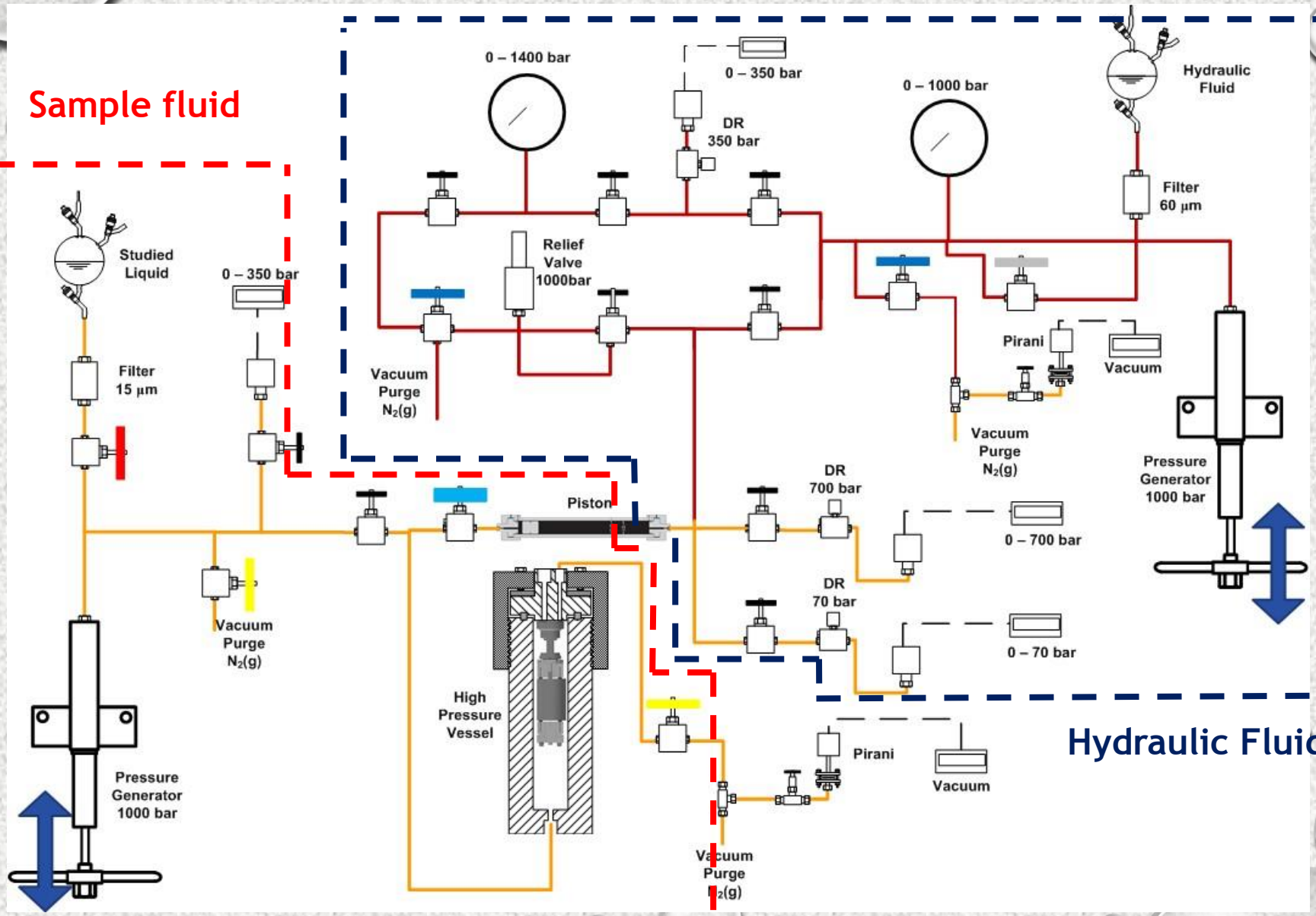
Newtonian viscosity standard (NVS) 20 AW (PTB) used to calibrate the VW sensor

The viscosity of the NVS 20 AW, at 298.15 K is 16.02 mPa.s.

Viscosity range: up to about 460 mPa.s
Wire material: tungsten
Vacuum frequency: about 1.0 kHz
R_{wire}= 150 μm
Viscosity U% = ±(2-3)



High Pressure System Setup



(TOTM) Tris(2-ethylhexyl) trimellitate – results

Viscosity range (mPa.s)	Temperature (K)	Pressure (MPa)
9 - 460	303 -373	up to 65

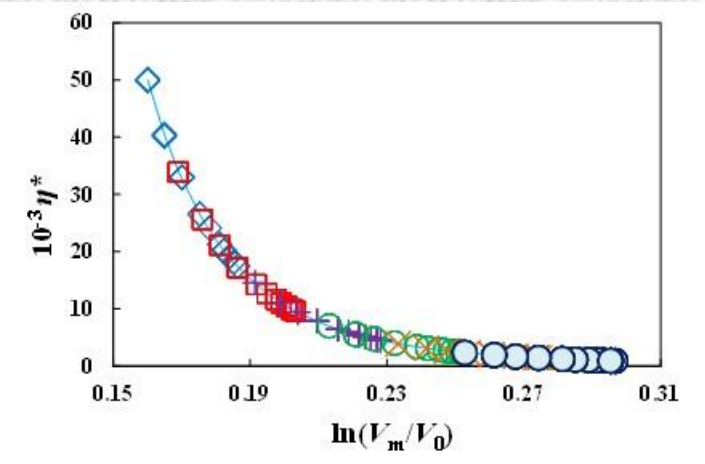
- viscosity data of TOTM were correlated with density using a semi-empirical method, a heuristic development of the kinetic theory for dense hard-sphere fluids, applied to the van der Waals model of a liquid

$$\eta^* = 6.035\times10^8\left(\frac{1}{MRT}\right)^{1/2}\eta\,(V_m)^{2/3}$$

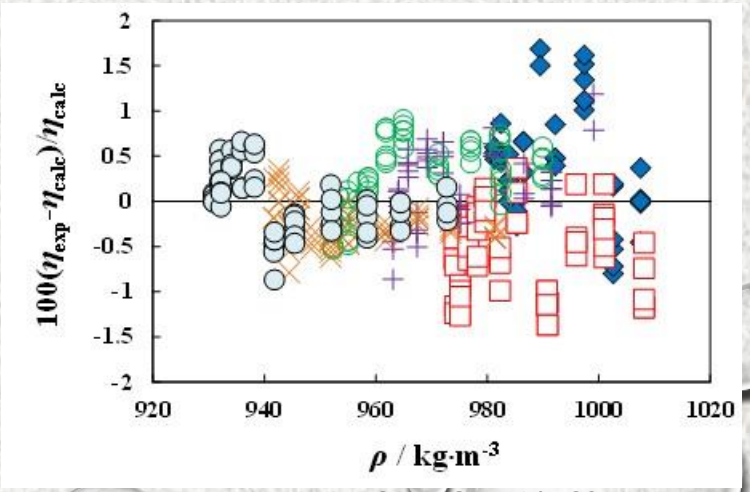
$$\frac{1}{\eta^*} = \sum_{i=0}^{4} a_i \left(\frac{V_m}{V_0}\right)^i$$

$$V_0\times10^6 / \left(\mathrm{m^3\ mol^{-1}}\right) = l + mT + nT^2$$

◆303 K □313 K +328 K ○343 K ×358 K ○373 K



Statistical parameters of correlation	
rmsd /%	0.53
bias /%	0.00
MaxDev %	+1.7



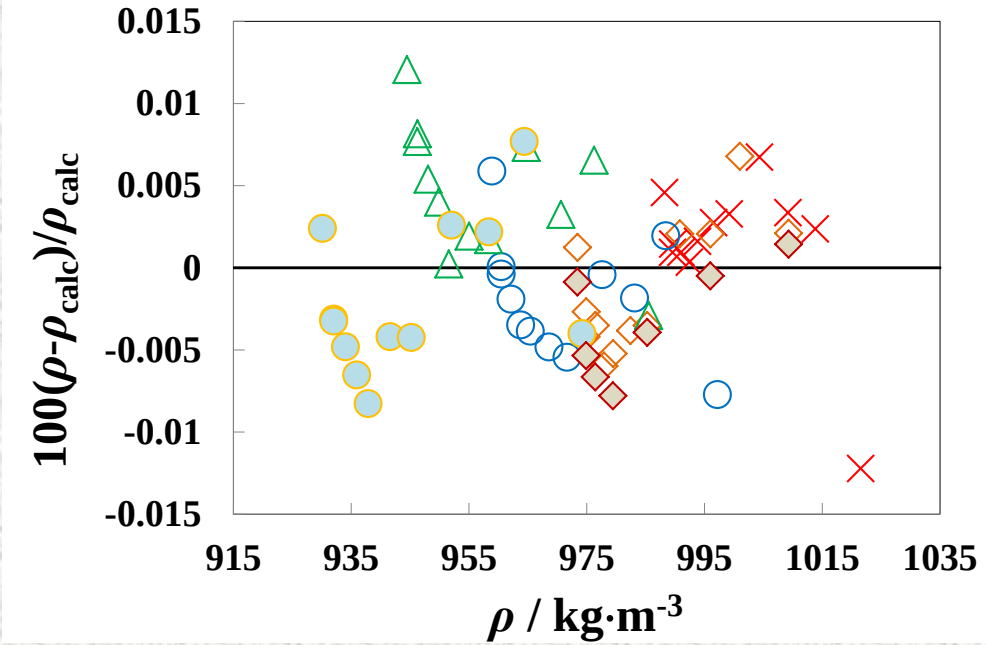
(TOTM) Tris(2-ethylhexyl) trimellitate – results

- Density

$$\rho = \rho_0 \left\{ 1 - C \ln \left[\frac{D + p}{D + p_0} \right] \right\}^{-1}$$

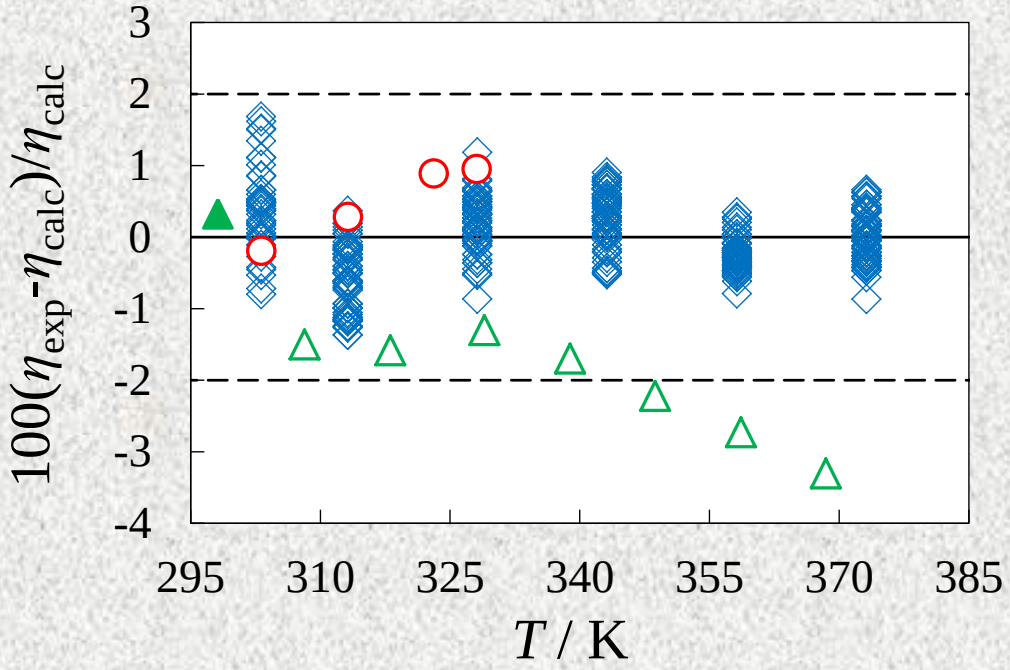
$$\rho_0 = \sum_{i=0}^{2} b_i T^i \qquad D = \sum_{i=0}^{2} d_i T^i$$

Statistical parameters of correlation	
rmsd /%	0.004
bias /%	0.000
MaxDev %	+0.012



- No literature viscosity and density data of TOTM, above atmospheric pressure, were found in literature

(TOTM) Tris(2-ethylhexyl) trimellitate – comparisons



—— **TOTM Hard Spheres Correlation**

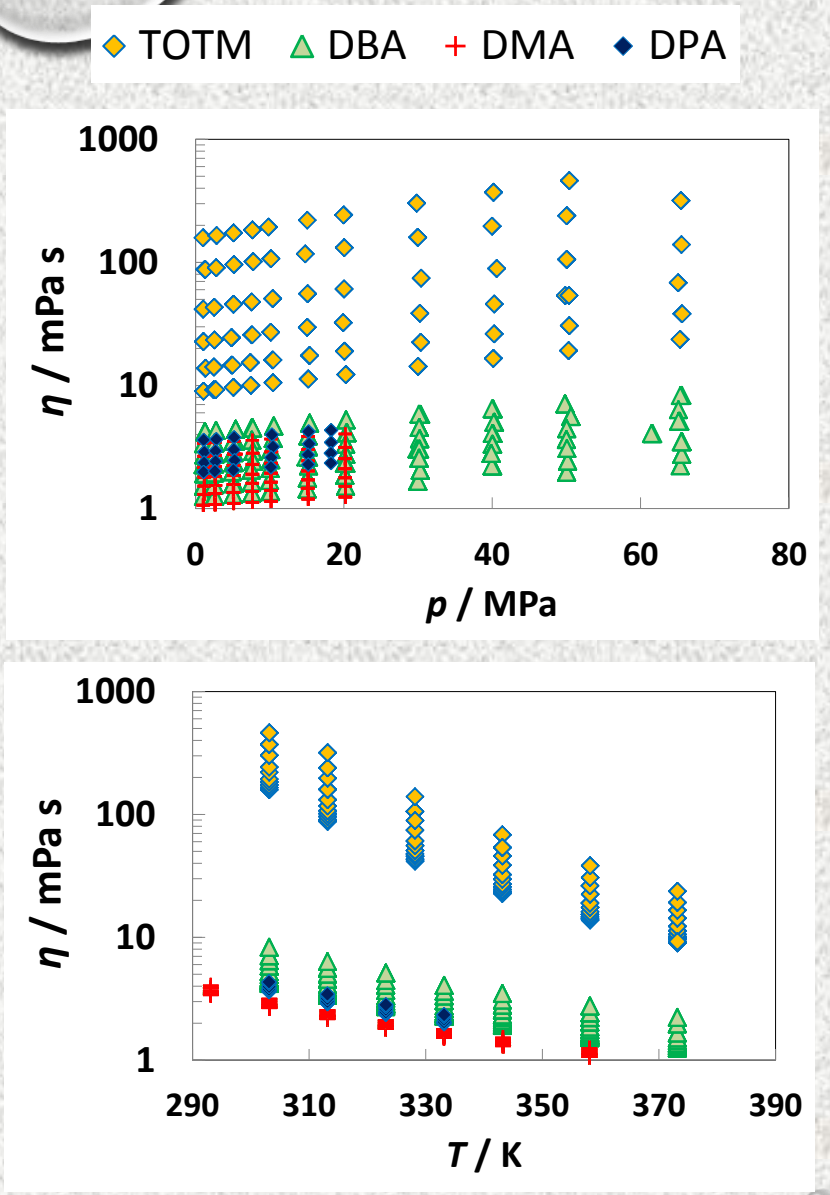
◇ **IST 2014 (*U*=±(2-3)%)**: vibrating-wire, water content - 99 to **175** ppm

○ **IST 2014 (*U*=±1.5%)**: Ubbelohde Capillary, water content - 26 to **248** ppm (TOTM VW correlation extrapolated for 0.1MPa)

△ **Lorenzi et al 1998 (*U* not reported)**: Ubbelohde Capillary (TOTM VW correlation extrapolated for 0.1MPa)

▲ **Lorenzi et al 1998 (*U* not reported)**: Ubbelohde Capillary (TOTM VW correlation extrapolated for 0.1MPa and to 298 K)

High Pressure VWire Viscosity Measurements



DMA
DPA
DBA
TOTM

p_{range}: 1 - 65 MPa
T_{range}: 293 - 373 K

η_{range}: (1.1 - 464) mPa s

Uncertainty of
±(1 to 3) %

Viscosity Reference Liquids

- Potential industrial references for viscosity (comparison with literature)

Liquid		η[(a)] (mPa s)	T range (K)	p range (MPa)	η range (mPa s)	U (%)	Min Purity (%)
Adipates	DMA	3.0	283-373	0.1-20	0.9-4	1	99
	DEA	3.1	283-373	0.1-20	0.9-4.6	1-2	99
	DPA	3.6[(b)]	303-333	0.1-18	2.0-4.3	2	99
	DBA	4.2[(b)]	303-373	0.1-65	1.3-8.3	1.5	99
	DIBA	5.3	283-373	0.1	1.3-8.6	1	99
	DEHA	11.4	291-368	0.1	2.1-14.7	--	99
Benzoates	EHB	5.6	263-248	0.1-315	1.7-286.7	2	99
Sebacates	DEHS	17.5	278-373	0.1	2.7-43	1-5.6	98
Squalane		28.2	273-473	0.1-350	0.85-954	1-5	98
Perfluoropolyether	Krytox® GPL 102	32[(c)]	311-533	0.1-246	1.2-5777	2.4	99.9
Phthalates	DEHP	57.9	273-353	0.1-371	6.2-2555	1-2	99.5
	DINP	55.3	288-368	0.1	4.5-102	--	99
	DIDP	88.5	273-373	0.1-140	5.0-845	0.3-2	99.8
Trimelitates	TOTM	213.4	298-373	0.1-65	9-464	2	99

(a) 298 K and 0.1 MPa; (b) 303 K and 0.1 MPa; (c) 311 K and 0.1 MPa;

Conclusions

- Viscosity results for tris(2-ethylhexyl) trimellitate (TOTM) were obtained
  - First viscosity measurements at pressures above atmospheric
  - using a new vibrating wire sensor
  - from (9 to 460) mPa.s, temperatures (303 to 373) K, pressures up to 65 MPa
- Comparisons:
  - Using the vibrating wire and Ubbelohde capillary, within ± 1%.
  - With available literature data (Ubbelohde capillary),
    - within ± 2% for temperatures up to 339 K
    - within ±3.3% for temperatures up to 368 K
- TOTM - plausible candidate for viscosity standard for high viscosity, at high pressures and high temperatures.
- DMA, DPA, DBA and TOTM are liquids with high interest for the industry of polymers
  - their viscosity and density data can be useful either as reference data or directly in industrial processes

Thank you