Viscosity and Density Measurements on Compressed Liquid n-Tetradecane [a)]

Tânia V.M. Santos,[1] Marta F.V. Pereira,[1] Helena M.N.T. Avelino,[1,2] Fernando J. P. Caetano,[1,3] João M. N. A. Fareleira[1]

1) Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Portugal

2) Instituto Superior de Engenharia de Lisboa, Portugal

3) Universidade Aberta, Lisboa, Portugal

[a)]Article submitted to Fluid Phase Equilibria in 23 June 2017. Accepted in 28 August 2017: https://doi.org/10.1016/j.fluid.2017.08.025

AIMS:

- **Long-term:** To develop a reference correlation for the viscosity of normal tetradecane (n-C_{14}) *at* high pressures and in a wide range of temperatures.
- **Short-term** (present work):

1. To measure the **viscosity** of n-C_{14} in wide temperature and pressure ranges _ special attention to (T,p) ranges where viscosity data are scarce (or non-existent, v.g.: T<293 K).

2. To **correlate the present viscosity** data with density.

MOTIVATION

1. General economic importance of alkanes;
2. Increasing importance of paraffins (and their mixtures) for energy storage systems as PHASE CHANGE MATERIALS;
3. Lack of rigorous viscosity data for n-tetradecane, at low temperatures and moderately high pressures ($p<10$ MPa). Ranges that are relevant for the development of some sustainable processes.

SUMMARY OF THE PRESENT WORK

- New measurements of the **viscosity** of n-tetradecane (n-C_{14}) at moderately high pressures, using the vibrating wire technique.
- New measurements of the **density** of n-tetradecane using a model HP Anton Paar U-tube densimeter.
- Development of a **correlation** of viscosity with density, using a modified hard-spheres model.

Density

Experimental results obtained using an Anton Paar DMA HP model vibrating U-Tube instrument with model DMA 5000 as reading unit.

Measurements were performed along nine isotherms in the range (283 ≤*T* ≤373) K and pressures from (0.1 to 70) MPa

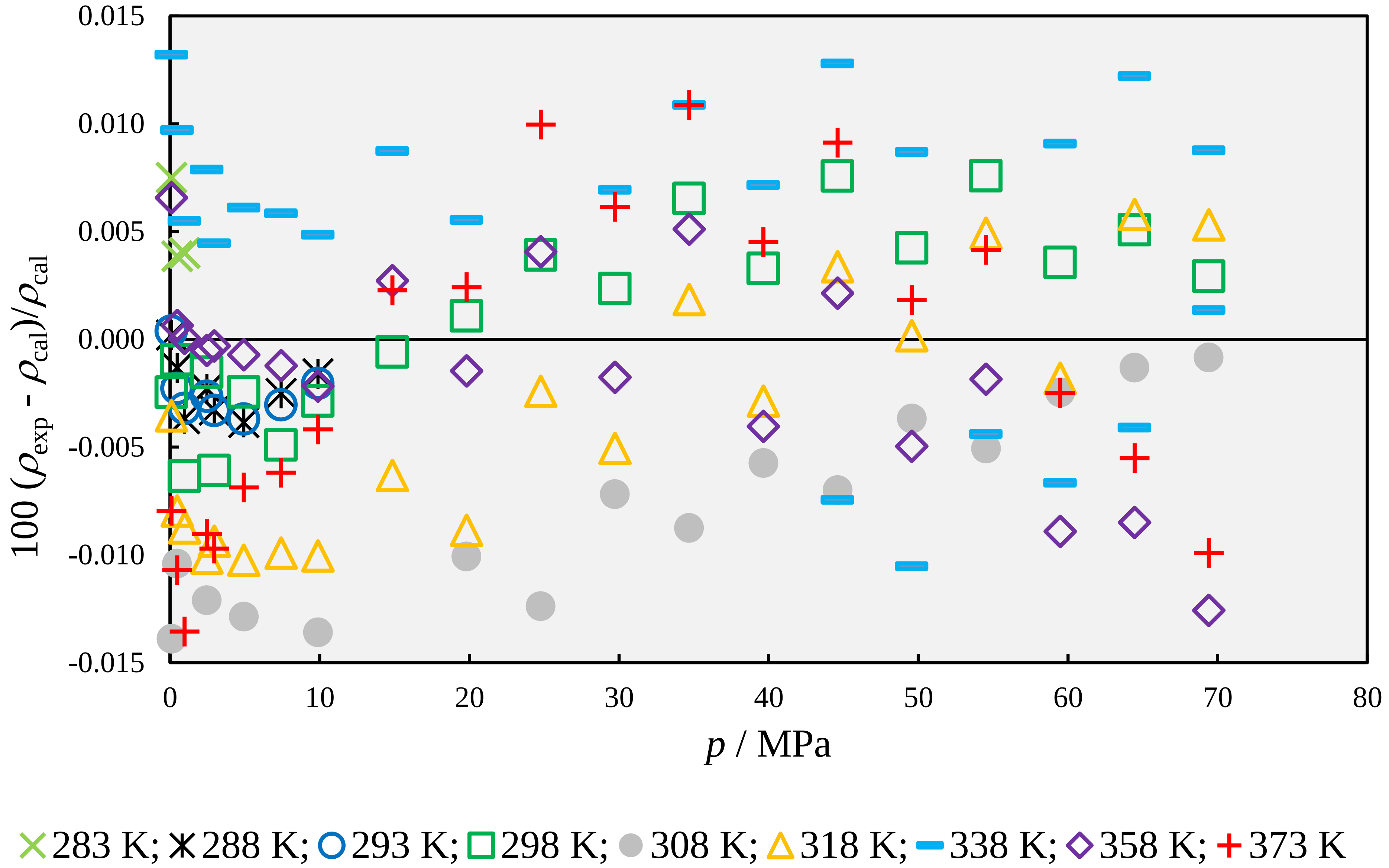
The experimental data were correlated by a modified Tait equation, proposed by

J.H. Dymond, R. Malhotra, The Tait equation: 100 years on, Int. J. Thermophys. 9 (1988) 941–951.

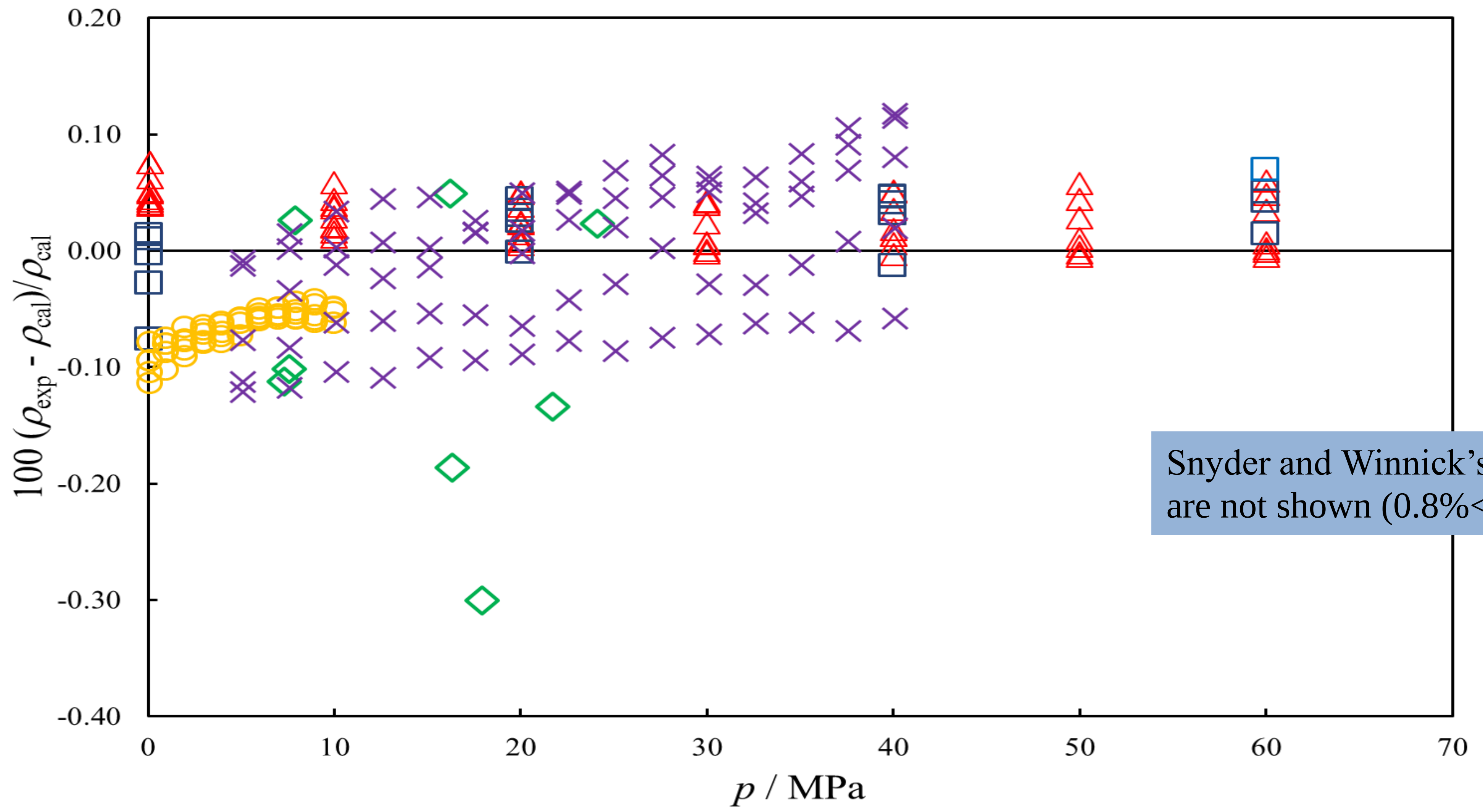
$$\rho = \rho_0 \left\{ 1 - C \ln\left[\frac{D + p}{D + p_0} \right] \right\}^{-1}$$

$$\text{with } \rho_0 = \sum_{i=0}^{2} b_i T^i$$

Deviations of the density of n-tetradecane (this work) from the correlation



Deviations of literature density data (**after 1978**) from the correlation of our results



Snyder and Winnick's, 1970 data are not shown (0.8%<dev<1%)

× Gouel; △ Valência et al.; ○ Kariznovi et al.; ◇ Gawronska et al.; □ Khasanshin et al.

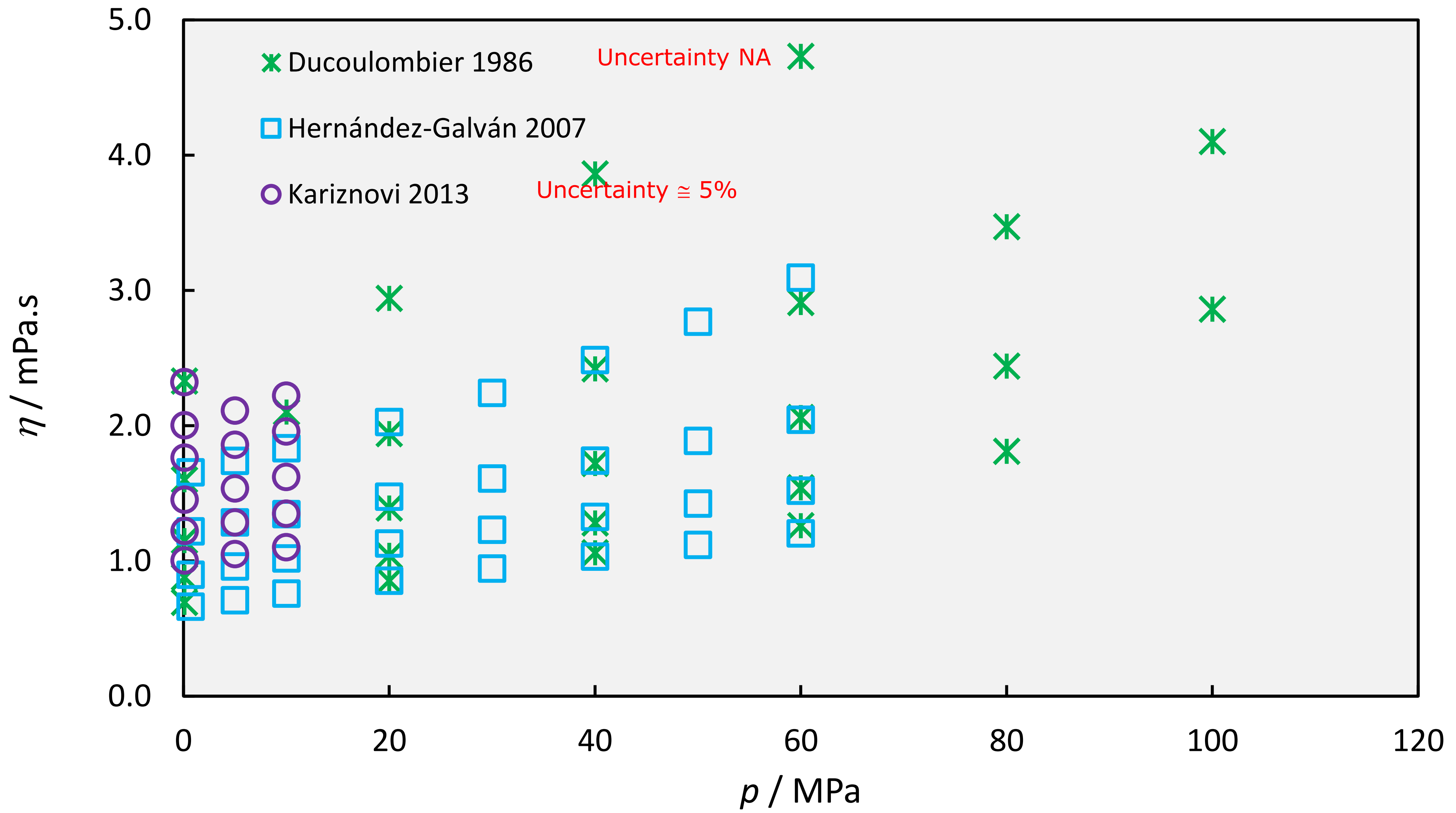
VISCOSITY

Literature viscosity data for liquid n-C_{14}

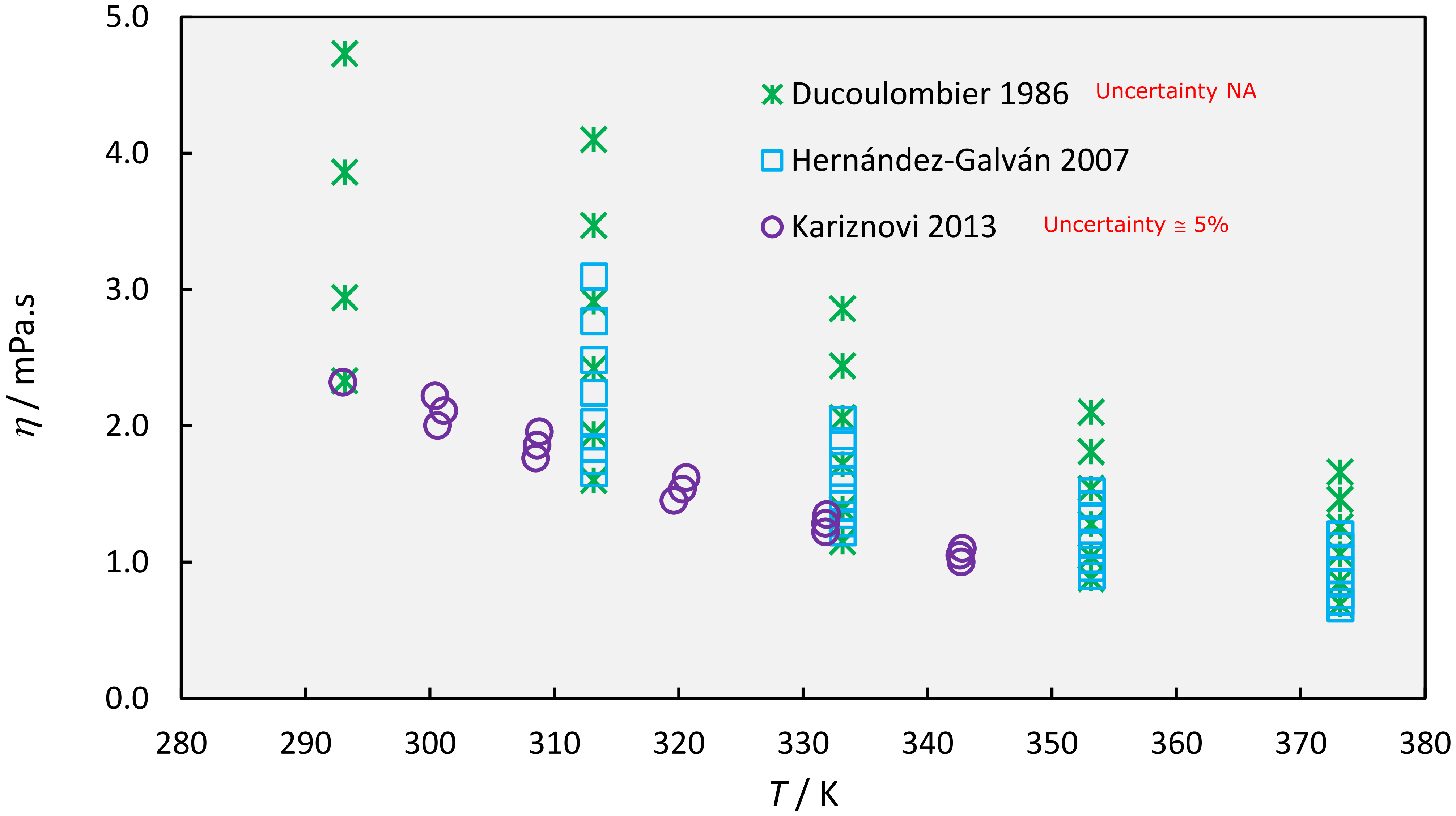
Year	First author	Temperature range/K	Pressure range/MPa	NP	Method	Purity /%	Nominal uncertainty
1986	Ducoulombier	293-373	0.1 - 100	24	falling body	NA	NA
1989	Knapstad	293-423	0.1	10	Oscillating viscometer	99	(0.33-0.56) %
2001	Franjo	298.15	0.1	1	capillary	99	$\pm 5\times10^{-4}$mm·s^{-1}
2003	Nayak	298-308	0.1	3	capillary	99	±0.001 mPa s
2007	Hernández-Galván	313-393	0.69 - 60	40	rolling-ball[a)]	99	±2.0 %
2012	Mahajan	298.15	0.1	1	capillary	99	±0.003 mPa·s[c)]
2013	Kariznovi	300-343	0.1-10	15	Cambridge Viscometer[b)]	99	5%

[a)] Kinematic Viscosity; [b)] Cambridge Viscometer Model SPC ; [c)] repeatability; NA – not available

Literature viscosity data (η *vs. p*) *for* compressed liquid n-C_{14} (up to 100 MPa)

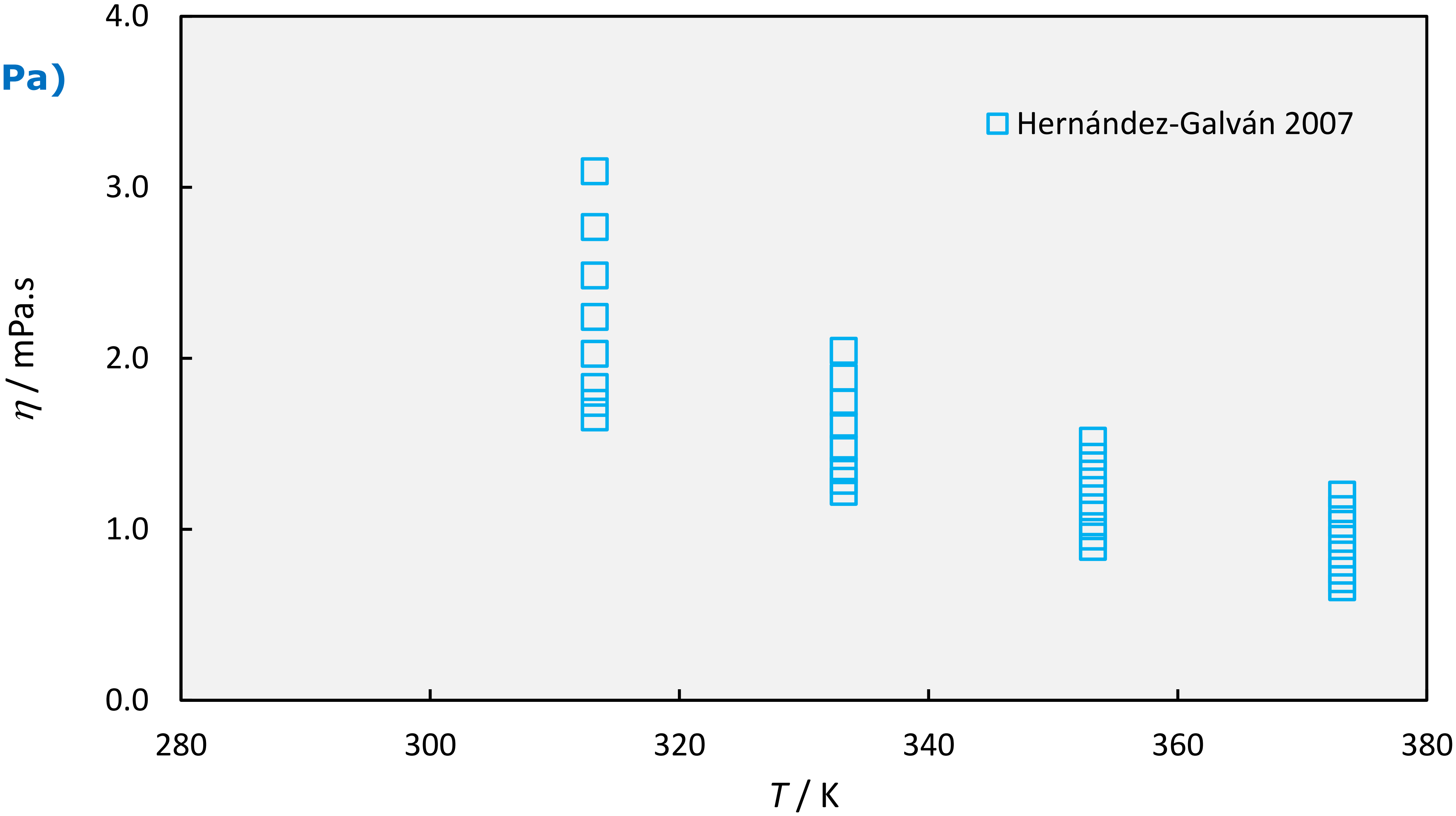


Literature viscosity (η *vs. T*) data for compressed liquid n-C_{14}



Literature viscosity data with specified uncertainty less than 5%

(p>0.1 MPa)



Viscosity:

New **measurements of the viscosity of n-tetradecane** along eight isotherms in the range ($283 \le T \le 358$) K and pressures up to 70 MPa, have been performed using the vibrating wire technique in the forced mode of operation.

Vibrating wire sensor

1 - top washers;

2 - upper claw chucks;

3 - vibrating wire;

4 - rod spacers;

5 – bottom claw chucks;

6 - upper rod clamping;

7 - magnetic circuit;

8 - magnets;

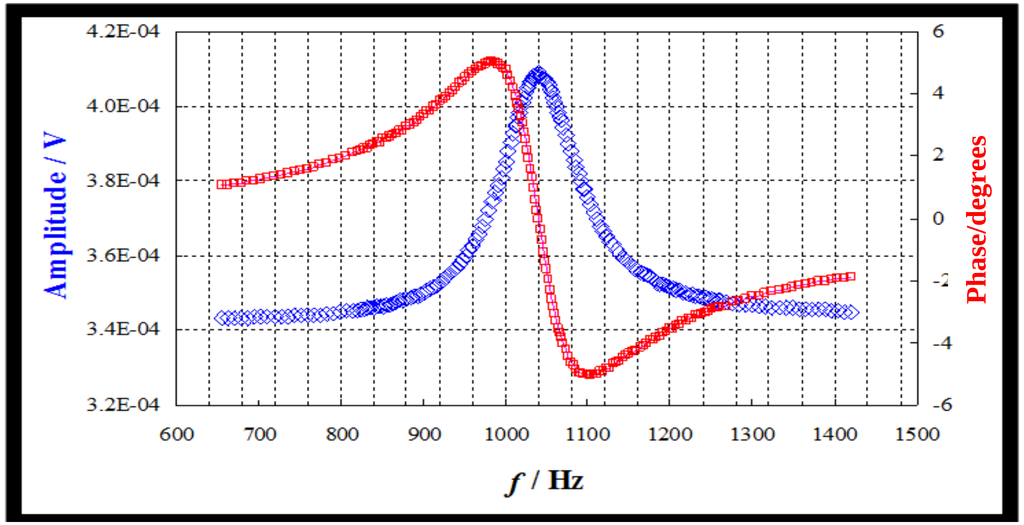
9 - lower rod clamping,

10 - bottom washers

3 - wire

8 -magnets
inside

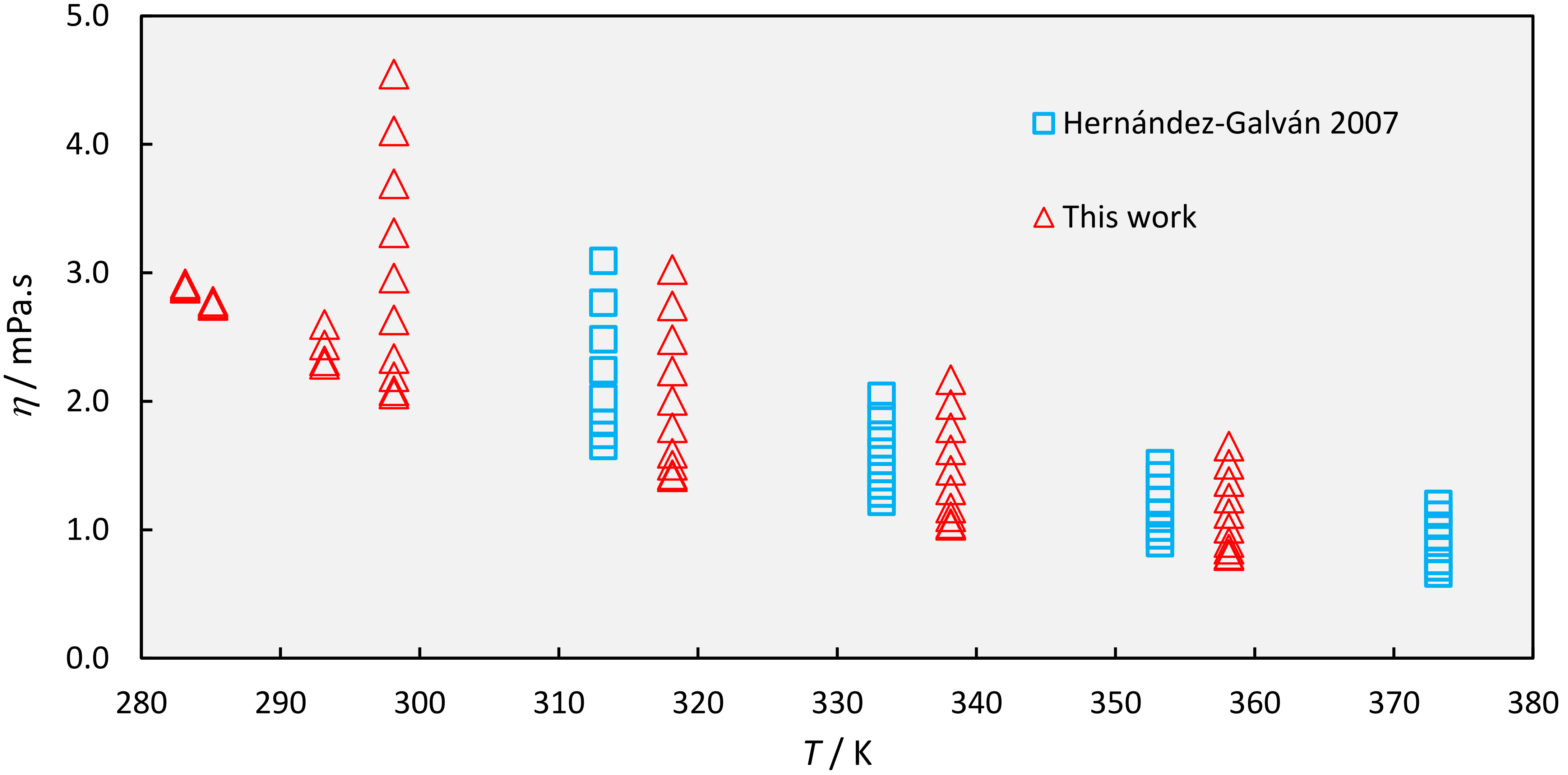
Raw data



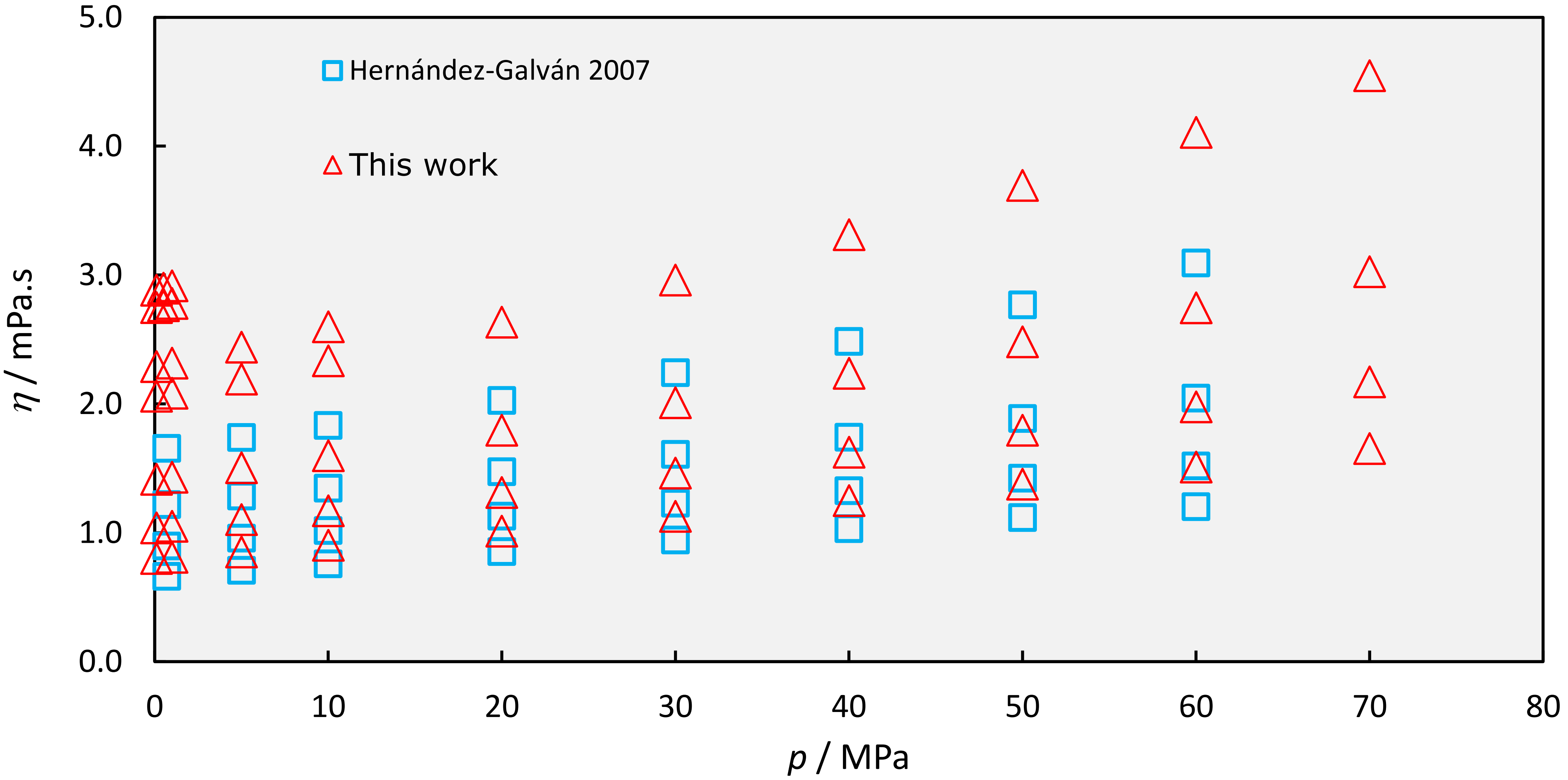
Hydrodynamic Model

Viscosity

Updated view: Viscosity (η *vs.* T) for n-C_{14} ($p \geq 0.1$ MPa) with uncertainty less than 5%



Updated view: Viscosity (η *vs.* p) for n-C_{14} ($p \geq 0.1$ MPa) with uncertainty less than 5%



Correlation scheme: A modified hard-spheres model of transport properties of fluids for VISCOSITY

Heuristic development[1] of the kinetic theory for dense hard-sphere fluids, applied to the van der Waals model of a liquid, proposed by Dymond.[2]

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

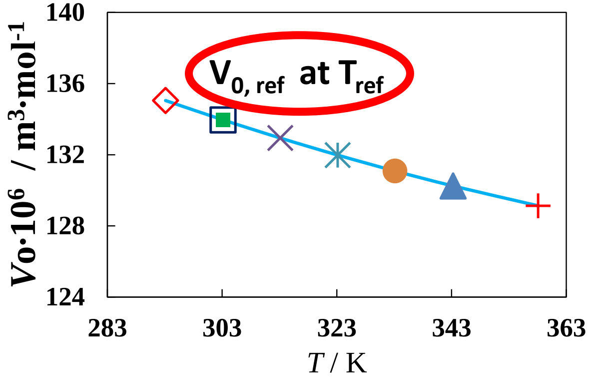
$$\eta^* = f\left(\frac{V_{\mathrm{m}}}{V_0}\right) \qquad V_0 = f(T)$$

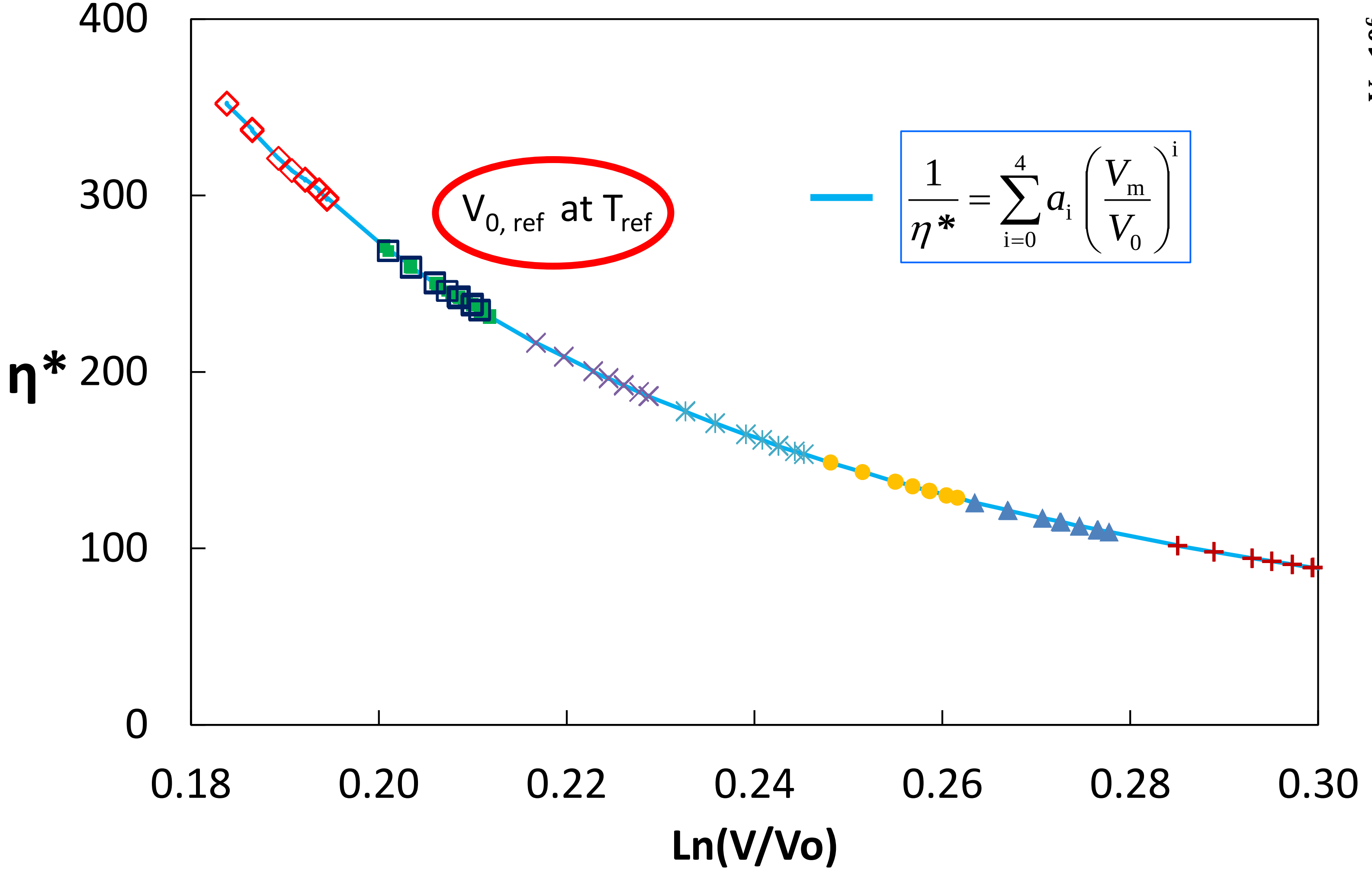
1. S.F.Y. Li, R.D. Trengove, W.A. Wakeham, M. Zalaf, *Int. J. Thermophys. 1986,* **7**, 273-284
2. Dymond, J.H., *Chem.Soc. Rev.* 1985, *14*, 317-356

Viscosity Correlation

Smooth Hard-Spheres

$$V_0(T)\times 10^6\,\left(m^3mol^{-1}\right) = V_{0,ref} + l\left(T - T_{ref}\right) + m\left(T - T_{ref}\right)^2$$





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

T_1

$T_{Ref}=T_0$

T_2

T_3

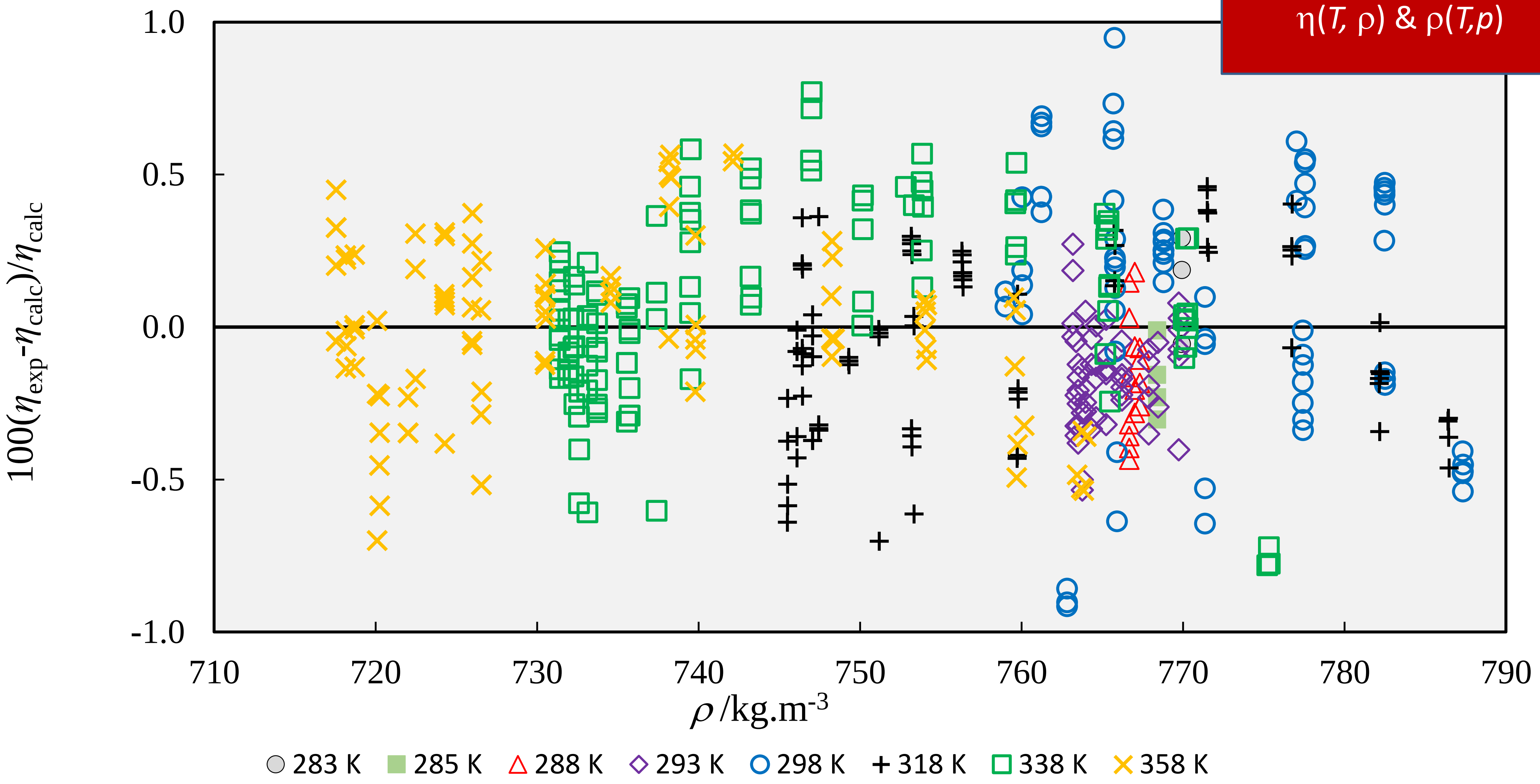
T_4

T_5

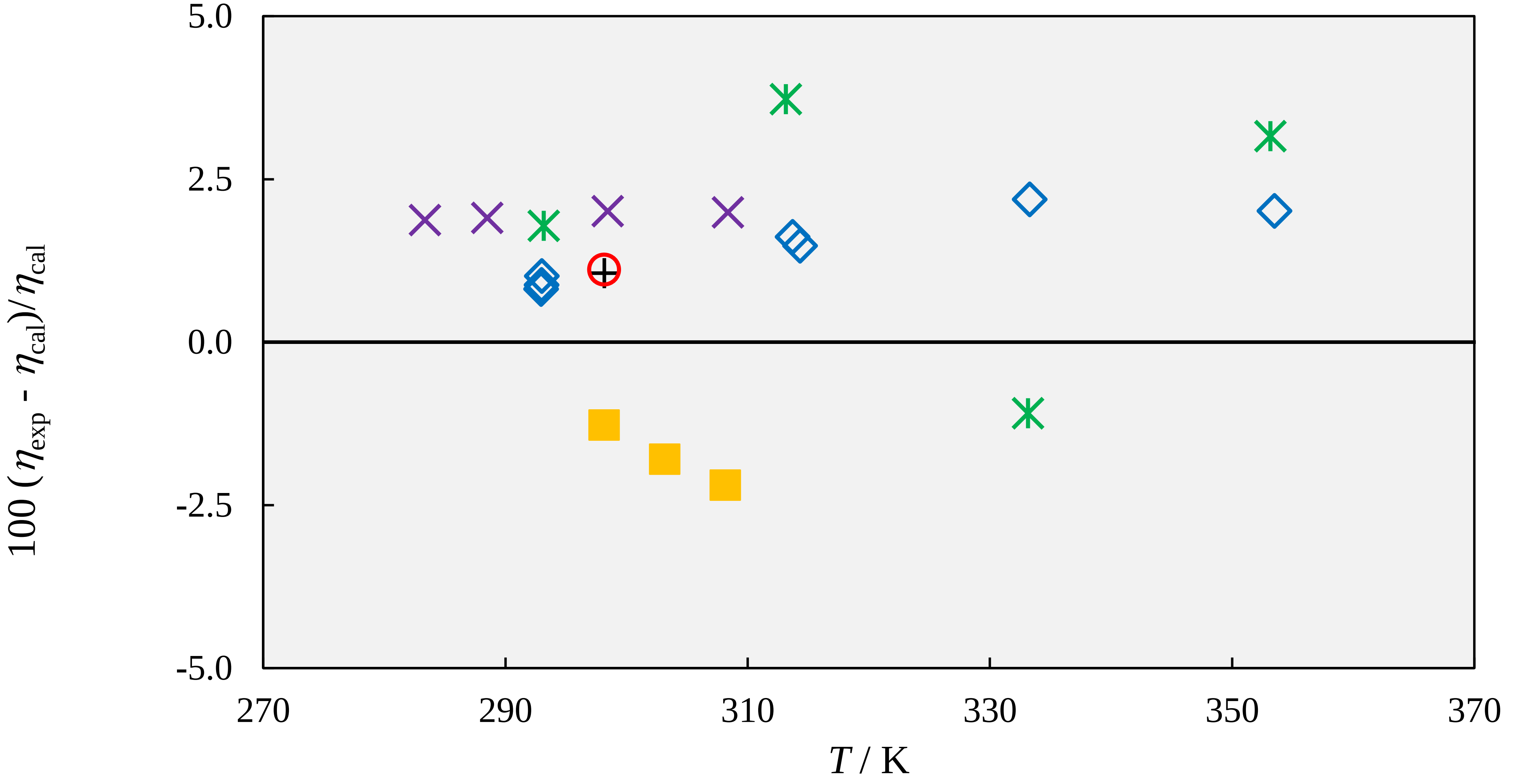
T_6

Deviations (η *vs.* ρ) for n-C_{14} ($p \geq 0.1$ MPa) obtained in the present work with the vibrating-wire technique, from the present correlation scheme

Correlations
$\eta(T, \rho)$ & $\rho(T,p)$

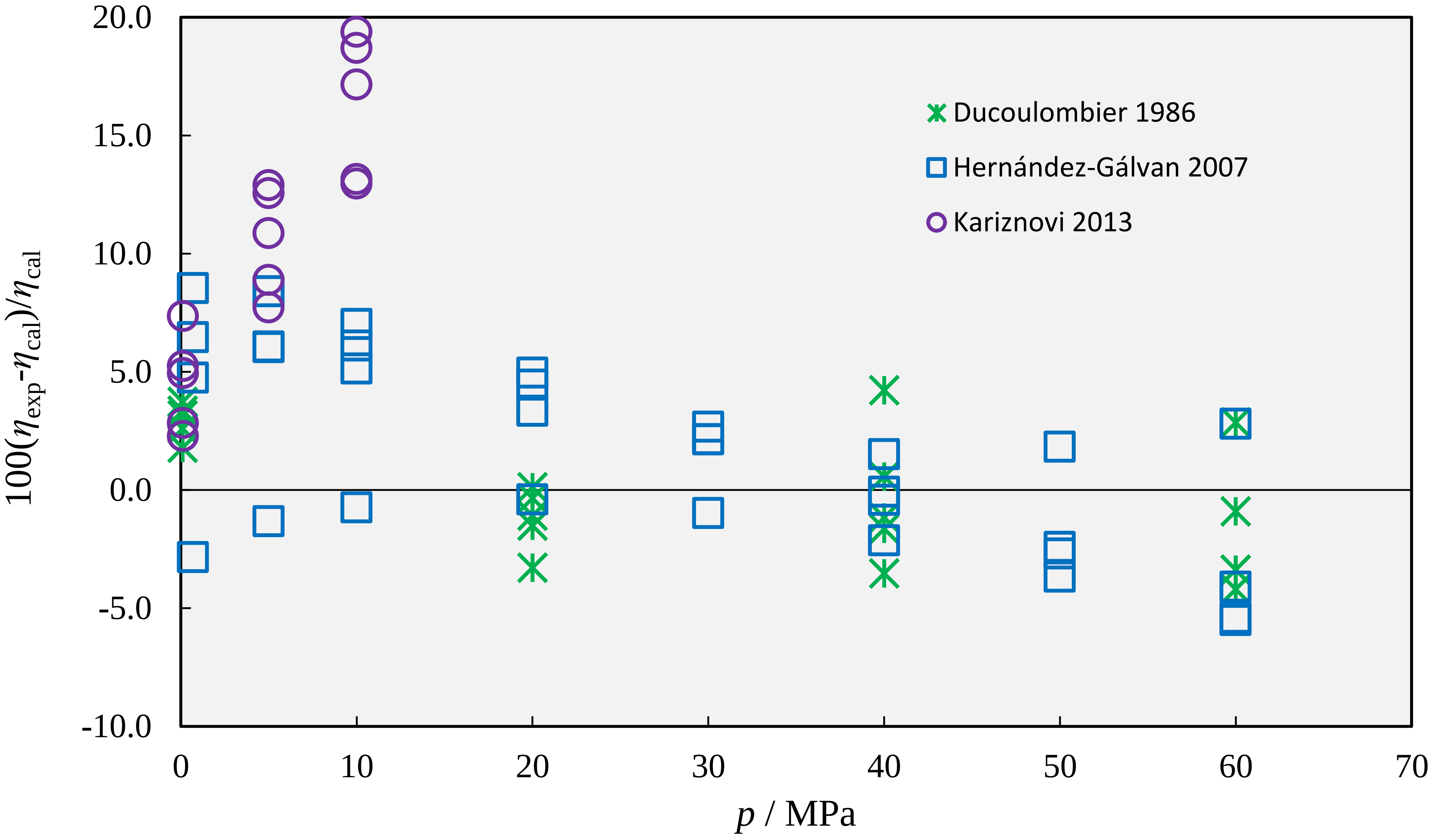


Deviations of n-C_{14} viscosity **literature data** at 0.1 MPa , from our correlation



Ducoulombier 1986; Knapstad 2002; Nayak 2003; + Franjo 2001; Mahanja 2012; This work (capillary)

Deviation of the viscosity **literature data** for n-C_{14} from our correlation as a function of pressure



Conclusions:

- This work provides **new viscosity measurements** in ranges where literature data were scarce or totally absent (**No literature data below 293 K even at 0.1 MPa!**).
- New density measurements were also performed and used to develop a provisional **viscosity correlation,** which may be used to obtain $\boldsymbol{\eta = \eta(T,p)}$ with low uncertainty in wide ranges of *T* and *p*.
- However, **large inconsistency** between literature results is observed, exceeding the nominal uncertainty of most of the available measurements, which hinders the possibility to develop **reference correlations** for the viscosity of n-tetradecane.
- A reference correlation for the **viscosity** of **n-C_{14}**, needs **new independent measurements**, using several experimental methods, covering the low temperature and intermediate pressure ranges (up to 10 MPa).

Acknowledgments:

This work was supported by the Strategic Project PEst-OE/QUI/UI0100/2013 funded by Fundação para a Ciência e a Tecnologia (FCT, Portugal).